SÍNTESIS DE XEROGELES DE CARBONO INDUCIDA POR MICROONDAS.
DISEÑO DE MATERIALES POROSOS *A LA CARTA*

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ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CTAB	Hexadeciltrimetilamonio
D	Grado de dilución
DFT	Density functional theory
DOE	Design of experiments
DR	Dubinin-Radushkevich
F	Formaldehído
FTIR	Fourier transform infrared spectroscopy
MSR	Metodología de superficie de respuesta
NMP	N-metil pirrolidina
p/p^o	Presión relativa
PID	Proporcional integrativo derivativo
PVDF	Polifluoruro de vinilideno
r	radio de poro (nm)
R	Resorcinol

R/F	Ratio molar resorcinol/formaldehído
RF	Xerogel resorcinol-formaldehído
RSM	Response surface methodology
RTF	Xerogel resorcinol-tanino-formaldehído
S_{BET}	Área superficial equivalente en la ecuación BET (m^2/g)
SDBS	Dodecil benceno sulfonato de sodio
SDS	Dodecil sulfato sódico
SEM	Scanning electron microscope
S_{EXT}	Área superficial externa (m^2/g)
T	Tanino
T/F	Ratio másico tanino/formaldehído
TF	Xerogel tanino-formaldehído
TGA	Análisis termogravimétrico
V_{ads}	Volumen adsorbido (cm^3/g)
V_{DUB}	Volumen total de microporos accesibles al adsorbato en la ecuación DR aplicada en las isotermas de N2 a -196ºC (cm^3/g)
V_{macro}	Volumen de macroporos (cm^3/g)
V_{meso}	Volumen de mesoporos (cm^3/g)
ΔP	Diferencia de presión capilar (N/m^2)
θ	Ángulo de contacto sólido-líquido
Υ	Tensión superficial (N/m)

RESUMEN

Una de las principales ventajas de los xerogeles de carbono es la posibilidad de diseñar sus propiedades a medida de la aplicación donde se quieran utilizar. Esto les otorga un gran potencial comercial, por el cual, en los últimos años, se han hecho grandes esfuerzos para lograr realizar la síntesis mediante la aplicación de la tecnología microondas como método de calentamiento. La síntesis de xerogeles de carbono inducida por microondas es un método muy novedoso y, por tanto, requiere ser investigada en profundidad.

En la presente Tesis Doctoral se han estudiado las principales variables del proceso de síntesis inducida por microondas (tiempo, temperatura y volumen de mezcla) con el objetivo de determinar las condiciones óptimas de operación que permiten obtener xerogeles de carbono porosos. También se ha abordado la posibilidad de diseñar *a la carta* las propiedades de estos materiales. Esto se ha conseguido mediante el planteamiento de dos estrategias: i) variando de forma simultánea la concentración de todos los reactivos (resorcinol, formaldehído, agua y catalizador) y, ii) introduciendo agentes aditivos en las mezclas precursoras. Con el objeto de dilucidar los diferentes efectos sinérgicos que se producen entre todos los reactivos, se sintetizaron y caracterizaron más de doscientos xerogeles de carbono. Los resultados obtenidos se trataron mediante técnicas estadísticas que permitieron evaluar la interdependencia entre los reactivos y optimizar el proceso de síntesis. La variación simultánea de la concentración de los reactivos ha repercutido positivamente en el control de la formación de la estructura polimérica, ya que ha permitido obtener materiales con unas

propiedades porosas que no pueden obtenerse modificando la concentración de cada reactivo por separado.

Los xerogeles de carbono obtenidos se han utilizado como material de electrodo en baterías de ion-litio con el propósito de determinar el efecto de sus propiedades porosas sobre la capacidad electroquímica de estos dispositivos. Por otro lado, se ha apostado por la utilización de los xerogeles orgánicos como material aislante. El empleo de estos materiales presenta una gran ventaja comercial ya que se elimina la etapa de carbonización y, por tanto, se disminuyen los costes de producción. Finalmente, se ha planteado la posibilidad de sustituir uno de los reactivos principales, el resorcinol, por un compuesto más respetuoso con el medio ambiente.

ABSTRACT

One of the main advantages of carbon xerogels is the possibility of tailoring their properties in order to adapt them for the requirements of the application for which they are going to be used. This benefit gives them a high commercial value. It is for this reason that a great effort has been made in recent years to achieve the synthesis of carbon xerogels by means of microwave technology. However, the microwave-induced synthesis of carbon xerogels is a very novel method and hence it needs to be thoroughly investigated.

In this Doctoral Thesis, the main variables involved in the microwave-induced synthesis process (time, temperature and volume of the precursor solution) were studied in order to determine the optimum operating conditions for obtaining carbon xerogels with well-developed porous structures. The possibility of designing bespoke properties in these materials was also addressed by using two strategies: i) by varying simultaneously the concentration of all the reagents (resorcinol, formaldehyde, water and catalyst) and, ii) by introducing additives into the precursor solutions. In order to establish the synergistic effects produced between the reactants, over two hundred carbon xerogels were synthesized and characterized. The results obtained were processed by statistical techniques that allowed the interdependence between the reactants to be assessed and the synthesis process to be optimized. The simultaneous variations of the concentrations of reactants were found to have a positive effect on the formation of the polymeric structure. The studies led to porous materials whose properties could not have been obtained by modifying the concentration of just one reactant.

The carbon xerogels obtained were used as electrode material in lithium ion batteries in order to determine the effect of their porous properties on the electrochemical capacity of these devices. Furthermore, this PhD thesis not only evaluates the applicability of carbon xerogels, but also considers the use of organic xerogels. These materials offer an important commercial advantage in that the carbonization step is removed and thus production costs are considerably reduced. Finally, the possibility of replacing one of the main reactants, the resorcinol, by a more environmentally friendly compound was also studied.

PRÓLOGO

La presente Tesis Doctoral versa sobre la obtención de xerogeles de carbono con propiedades muy diversas, conseguidas mediante la optimización del proceso de síntesis inducida por microondas. El trabajo realizado ha dado lugar a un capítulo de libro y a nueve artículos, siete publicados y dos pendientes de aceptación, en revistas científicas con un índice de impacto relevante (véase Tabla I). La presente memoria se ha elaborado como un compendio de dichas publicaciones, recopiladas en cinco de los ocho capítulos que la conforman, tal como se muestra en el esquema de la Figura I. El contenido de cada uno de estos ocho capítulos se describe a continuación.

Figura I. Estructura de la memoria.

El Capítulo 1, *Geles de Carbono*, ofrece una visión general de los aspectos más relevantes de los geles de carbono. Se hace especial hincapié en el proceso de síntesis de los geles orgánicos, precursores de los geles de carbono, así como en el proceso de carbonización y en los posibles tratamientos secundarios que pueden llevarse a cabo. En este capítulo también se definen los distintos tipos de porosidad y se enumeran las principales propiedades que suelen presentan los geles de carbono. Seguidamente se detallan las propiedades que han de tener estos materiales para poder ser utilizados en diversos campos de aplicación, en los cuales los geles de carbono tienen un gran potencial. Finalmente, se describen los aspectos fundamentales de la utilización de métodos estadísticos para conseguir la optimización del proceso de síntesis. Al final de este primer capítulo se incluye la Publicación I que consiste en un capítulo de un libro donde se describen de forma más detallada todas las particularidades referentes a los geles de carbono.

El Capítulo 2, *Antecedentes y Objetivos*, se divide en dos secciones. En la primera se contextualiza el tema principal de esta Tesis Doctoral y se indican los motivos por los cuales se ha llevado a cabo. En la segunda sección se detallan el objetivo principal y los objetivos específicos establecidos para desarrollarla. En este segundo capítulo se pone de manifiesto que el trabajo presentado en esta memoria está basado en la síntesis de un tipo concreto de geles de carbono conocidos como xerogeles y, por tanto, en los siguientes capítulos se empleará este término para referirse a los materiales sintetizados

Los siguientes capítulos (Capítulos 3, 4, 5 y 6) conforman los cuatro grandes bloques en los que se ha dividido el trabajo realizado en esta Tesis Doctoral. En cada uno de ellos se describe brevemente el estudio realizado, se discuten los resultados más relevantes y se exponen las principales conclusiones extraídas de las publicaciones incluidas al final de la sección correspondiente de cada capítulo.

El Capítulo 3, *Optimización del Proceso de Síntesis*, muestra el efecto que tienen las variables físicas del proceso sobre las propiedades finales de los xerogeles de carbono cuando se emplea la tecnología microondas como método de calentamiento. El trabajo realizado y los resultados obtenidos se describen con detalle en la Publicación II. La conclusión más relevante de este estudio es la determinación de las condiciones óptimas de operación que, posteriormente, fueron utilizadas para llevar a cabo los estudios presentados en el Capítulo 4.

El Capítulo 4, *Diseño de las Propiedades*, se divide en dos secciones. En la primera se describe el papel que juega la concentración de cada uno de los reactivos en la reacción de polimerización y su impacto sobre las propiedades finales de los xerogeles de carbono. Al final de esta sección se incluyen las Publicaciones III, IV y V donde se detallan el trabajo realizado, los resultados obtenidos y las principales conclusiones. Estas tres publicaciones no sólo demuestran la relación directa entre la concentración de cada reactivo y las propiedades finales de los xerogeles de carbono, sino que también ponen de manifiesto la sinergia existente entre ellas. En la segunda sección del Capítulo 4 se explica el efecto que tiene, en la reacción de polimerización, la introducción de aditivos en la mezcla precursora y cómo su uso puede mejorar el diseño de las propiedades. Los detalles del trabajo realizado, los resultados obtenidos y las conclusiones del mismo se recopilan en la Publicación VI incluida al final de la sección. Todas las publicaciones que conforman el Capítulo 4 demuestran la gran versatilidad de los xerogeles de carbono debido a la posibilidad de diseñar a medida sus propiedades, obteniéndose materiales muy diversos y con un gran potencial en distintos campos de aplicación.

El Capítulo 5, *Aplicaciones*, está dividido en dos secciones. En cada una de ellas se incluye una descripción de las propiedades que deben tener los xerogeles de carbono para poder emplearlos en dos campos de aplicación con requisitos contrapuestos, como son el aislamiento térmico y las baterías de ion-litio. En cada una de estas secciones se evalúa si los materiales obtenidos en los estudios mostrados en el Capítulo 4, tanto orgánicos como carbonizados, cuyas propiedades se ajusten a nivel teórico a los requisitos de la aplicación, son adecuados como material aislante y como material de electrodo en baterías de ion-litio. Los detalles de los trabajos realizados, los resultados obtenidos y las conclusiones principales de los estudios se recopilan en las Publicación VII y VIII incluidas al final de la correspondiente sección.

El Capítulo 6, *Futuro de los Xerogeles de Carbono*, se centra en las mejoras que pueden llevarse a cabo en el proceso de síntesis de xerogeles de carbono a escala industrial. Se hace especial hincapié en la sustitución de uno de los principales monómeros, el resorcinol, por un compuesto más respetuoso con el medio ambiente. Concretamente se evalúa la posibilidad de sustituir el resorcinol por taninos, un compuesto fenólico como el resorcinol pero de origen natural. El trabajo realizado, los resultados obtenidos y las principales conclusiones se detallan en las Publicaciones IX y X incluidas al final del capítulo.

El *Capítulo 7* recoge las conclusiones generales derivadas del trabajo realizado durante la Tesis Doctoral. No obstante, cabe destacar que cada uno de los cuatro capítulos anteriores (Capítulos 3, 4, 5 y 6) presenta sus propias conclusiones generales puesto que se trata de cuatro grandes bloques con objetivos bien diferenciados.

En el *Capítulo 8* se recogen todas las referencias bibliográficas citadas a lo largo de la memoria.

Todos los experimentos realizados así como las técnicas experimentales empleadas para desarrollar el trabajo que engloba esta Tesis Doctoral se recopilan en el Anexo I. En el Anexo II se listan una serie de publicaciones que, aunque guardan una estrecha relación con el tema principal de esta memoria, no se han incluido en los capítulos principales, puesto que el proceso experimental mostrado en dichas publicaciones ha sido abordado de forma paralela a la realización del presente trabajo. Así mismo, se incluyen las contribuciones a congresos derivadas de este trabajo.

Tabla I. Publicaciones científicas que conforman la Tesis Doctoral.

Capítulo	Publicación	Título de la publicación	Factor de Impacto
Capítulo 1. Geles de Carbono	Publicación I	Rey-Raap, N., Arenillas, A. & Menéndez, J. A. (2015). Formaldehyde in the Synthesis of Resorcinol-Formaldehyde Carbon Gels. En A. Patton (Editor), Formaldehyde: Synthesis, Applications and Potential Health Effects (pp. 31-60). New York: Nova Science Publishers, Inc.	-
Capítulo 3. Optimización del proceso de síntesis	Publicación II	Rey-Raap, N., Menéndez, J. A., & Arenillas, A. (2013). Optimization of the process variables in the microwave-induced synthesis of carbon xerogels. Journal of Sol-Gel Science and Technology, 69, 488-497.	1.532
Capítulo 4. Diseño de las propiedades porosas	Publicación III	Rey-Raap, N., Menéndez, J. A., & Arenillas, A. (2014). RF xerogels with tailored porosity over the entire nanoscale. Microporous and Mesoporous Materials, 195, 266-275.	3.453
	Publicación IV	Rey-Raap, N., Arenillas, A. & Menéndez, J. A. (2016). A visual validation of the combined effect of pH and dilution on the porosity of carbon xerogels. Microporous and Mesoporous Materials, 223, 89-93.	3.453
	Publicación V	Rey-Raap, N., Menéndez, J. A., & Arenillas, A. (2014). Simultaneous adjustment of the main chemical variables to fine-tune the porosity of carbon xerogels. Carbon, 78, 490-499.	6.196
	Publicación VI	Rey-Raap, N., Rodríguez-Sánchez, S., Alonso-Buenaposada, I. D., Calvo, E. G., Menéndez, J. A., & Arenillas, A. (2015). The enhancement of porosity of carbon xerogels by using additives. Microporous and Mesoporous Materials, 217, 39-45.	3.453
Capítulo 5. Aplicaciones	Publicación VII	Rey-Raap, N., Calvo, E.G., Menéndez, J. A., & Arenillas, A. Exploring the potential of resorcinol-formaldehyde xerogels as thermal insulators.	Enviada
	Publicación VIII	Rey-Raap, N., Piedboeuf, ML. C., Arenillas, A., Menéndez, J. A., Léonard, A. F., & Job, N. A comparison of organic and aqueous inks in the preparation of lithium-ion battery electrodes based on carbon xerogels with different meso-macropore sizes.	Enviada
Capítulo 6. El futuro de los geles de carbono	Publicación IX	Rey-Raap, N., Szczurek, A., Fierro, V., Menéndez, J. A., Arenillas, A., & Celzard, A. (2015). Towards a feasible and scalable production of bio-xerogels. Journal of Colloid and Interface Science, 456, 138-144.	3.368
	Publicación X	Rey-Raap, N., Szczurek, A., Fierro, V., Menéndez, J. A., Arenillas, A., & Celzard, A. (2016). Improvements for tailoring the porosity of tannin-based carbon xerogels. Industrial Crops and Products, 82, 100-106.	2.837

CAPÍTULO 1

GELES DE CARBONO

Los avances científicos y tecnológicos producidos en las últimas décadas han causado un aumento en la demanda de nuevas tecnologías así como la realización de mejoras en las ya existentes. En muchos de los casos estas mejoras implican el desarrollo de nuevos materiales. Uno de los elementos que ha hecho posible la obtención de una nueva generación de materiales es el carbono. Aunque los materiales carbonosos de origen natural presentan unas propiedades extraordinarias que los dotan de un gran potencial para diversas aplicaciones, su contenido en impurezas y la falta de control de las propiedades presentan la necesidad de desarrollar materiales de carbono sintéticos. Estos materiales sintéticos comparten la misma estructura que los de origen natural, con la ventaja añadida de poder diseñar a medida sus propiedades químicas y porosas para que se ajusten a los requisitos de una aplicación determinada. Dentro de este grupo se encuentran los geles de carbono, materiales porosos con una estructura reticular compuesta por partículas de carbono interconectadas.

Los geles de carbono se obtienen, generalmente, mediante el tratamiento térmico de geles orgánicos. El primer gel orgánico fue obtenido por Pekala y colaboradores en 1989 mediante la aplicación de la metodología sol-gel, inspirada en el proceso de síntesis de los geles inorgánicos de sílice [Pekala 1989]. Tal como se muestra en la Figura 1.1, el método sol-gel consiste en una reacción química, donde un líquido se va condensando poco a poco pasando de tener una suspensión coloidal estable de partículas sólidas (sol) hasta formar una red porosa tridimensional compuesta por cadenas poliméricas (gel). En el caso concreto de los geles orgánicos, precursores de los geles de carbono, esta reacción sol-gel (reacción de polimerización) se produce entre un benceno hidroxilado y un aldehído en presencia de un disolvente. El gel resultante de la reacción se somete a una etapa de curado en la cual el material se endurece por el efecto simultáneo de los entrecruzamientos entre las cadenas poliméricas y la evaporación de parte del disolvente. Finalmente, el material se somete a una etapa exclusivamente de secado en la que se elimina completamente todo el disolvente remanente dentro de la estructura. El material seco obtenido (gel orgánico) puede someterse a distintos procesos térmicos con el propósito de estabilizar el material y modificar sus propiedades. En función de la condiciones del tratamiento, puede provocarse la eliminación de grupos oxigenados e hidrogenados y transformar el gel orgánico en un compuesto carbonoso: gel de carbono. Este proceso por el cual se obtiene el gel de carbono se conoce con el nombre de carbonización.

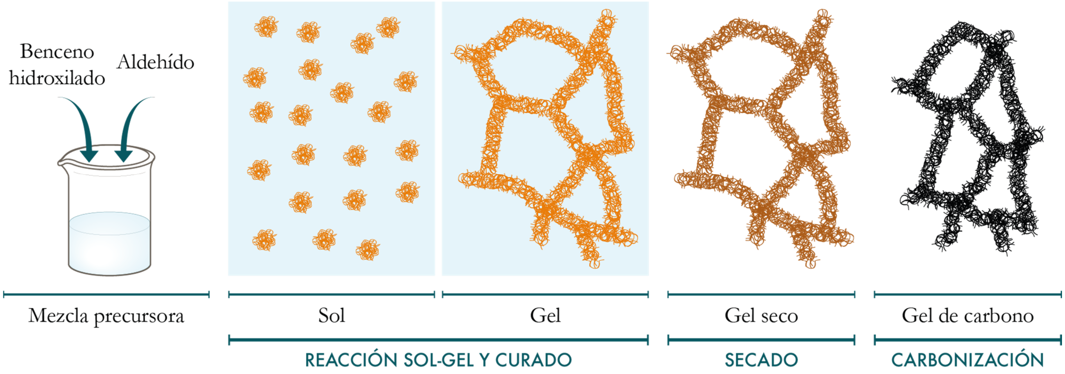


Figura 1.1. Proceso de síntesis de los geles de carbono.

Las condiciones fijadas en cada una de las etapas mostradas en la Figura 1.1 definen las propiedades químicas y porosas de los geles de carbono. No obstante, también es posible incluir en el proceso tratamientos secundarios que permiten modificar una o varias propiedades de forma individual para que se ajusten en mayor medida a los requisitos de la aplicación en la que se vayan a utilizar. La Figura 1.2 muestra de forma esquemática las etapas principales del proceso de síntesis mediante la metodología sol-gel, así como los tratamientos secundarios más utilizados. Las condiciones de todas estas etapas del proceso son de gran importancia a la hora de diseñar las propiedades de los geles de carbono, por lo que, a continuación, se detalla cada una de ellas. Así mismo, las diferentes rutas que existen para sintetizar geles de carbono y las particularidades de cada una de las etapas del proceso se detallan en la Publicación I, incluida al final del presente capítulo.

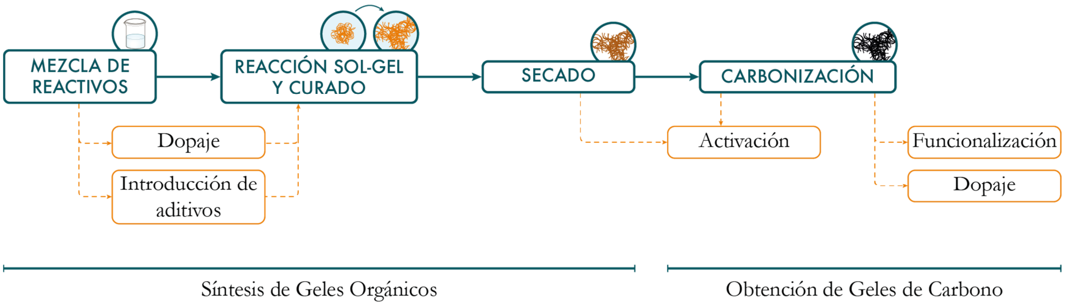


Figura 1.2. Etapas principales y secundarias del proceso de síntesis de los geles de carbono.

1.1. SÍNTESIS DE GELES ORGÁNICOS

1.1.1. REACTIVOS

La síntesis de los geles orgánicos comienza con la mezcla de los reactivos. Generalmente se utilizan dos precursores principales (un benceno hidroxilado y un aldehído), un disolvente y un cuarto compuesto que regula el pH y cataliza la reacción. De entre todos los precursores que es posible utilizar (resorcinol, fenol, cresol, taninos, melanina, formaldehído, furfural, hexametilentetramina, urea, etc.) el resorcinol y el formaldehído son los dos compuestos más empleados [Elkhatat 2011; White 2014; Allahbakhsh 2015; Rojas-Cervantes 2015]. Para que los materiales obtenidos sean porosos es necesario que la reacción entre el resorcinol y el formaldehído se lleve a cabo en presencia de un disolvente. Desde que se sintetizaron los primeros geles orgánicos han sido muchos los compuestos empleados para este fin, como el agua, el metanol, la acetona o una mezcla de ellos [Qin 2001; Kiciński 2011; Hasegawa 2012; Wickramaratne 2014]. Sin embargo, el agua es el disolvente más usado debido a que se trata de un compuesto natural y de bajo coste. Respecto al agente catalizador, aunque es posible utilizar catalizadores ácidos y básicos [Fairén-Jiménez 2006; Job 2008; Elkhatat 2011; Carrott 2012; Morales-Torres 2012; Xu 2012; Chejne 2015] la mayoría de los geles orgánicos que se encuentran en la bibliografía se obtienen empleando catalizadores básicos, generalmente carbonato sódico o hidróxido de sodio. La concentración de estos cuatro reactivos (resorcinol, formaldehído, agua y catalizador) juega un papel muy importante en las etapas de la reacción sol-gel, curado y secado y, en consecuencia, en la formación de la estructura polimérica y en las propiedades finales de los geles.

1.1.2. REACCIÓN SOL-GEL Y CURADO

La forma más habitual de sintetizar los geles orgánicos consiste en la reacción de polimerización entre el resorcinol (R) y el formaldehído (F), utilizando agua como disolvente y un catalizador básico como promotor de la reacción [Elkhatat 2011; Haghgoo 2012; Xu 2012; Schwan 2013; Taylor 2014; Kakunuri 2015]. Esta reacción de polimerización consta de dos etapas principales: reacción de adición (Figura 1.3) y reacción de condensación (Figura 1.4).

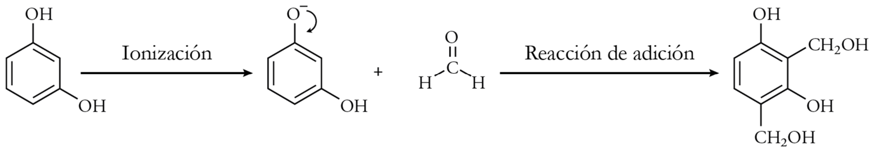


Figura 1.3. Esquema de la reacción de adición entre el resorcinol y el formaldehído.

El resorcinol es un compuesto bencílico con dos grupos hidroxilo en las posiciones 1 y 3 que permite la adición del formaldehído en las posiciones 2, 4 y 6 [Al-Muhtaseb 2003; Job 2008]. En presencia de un catalizador básico, se produce la ionización del resorcinol mediante la abstracción de los hidrógenos hidroxílicos, dando lugar a aniones de resorcinol (Figura 1.3). Estos aniones son más reactivos que el propio resorcinol, lo que favorece la adición de formaldehído formando derivados hidroximetílicos, tal como se muestra en la Figura 1.3 [Matos 2006; Allahbakhsh 2015]. Estos derivados hidroximetílicos son los monómeros necesarios para que ocurra la polimerización. Simultáneamente a la reacción de adición, ocurre la reacción de condensación, en la cual los derivados hidroximetílicos pierden grupos OH para formar un catión bencilo (Figura 1.4) [Rojas-Cervantes 2015]. Este catión reacciona con un anillo de benceno de otra molécula uniendo los anillos mediante puentes de metileno y éter, tal como se muestra en la Figura 1.4 [Almazán-Almazán 2011; Schwan 2013], dando lugar a la formación de partículas poliméricas (sol), conocidas como nódulos. Los nódulos se agregan y se entrecruzan entre sí mediante cadenas poliméricas hasta formar una red porosa tridimensional en un medio líquido (Figura 1.4).

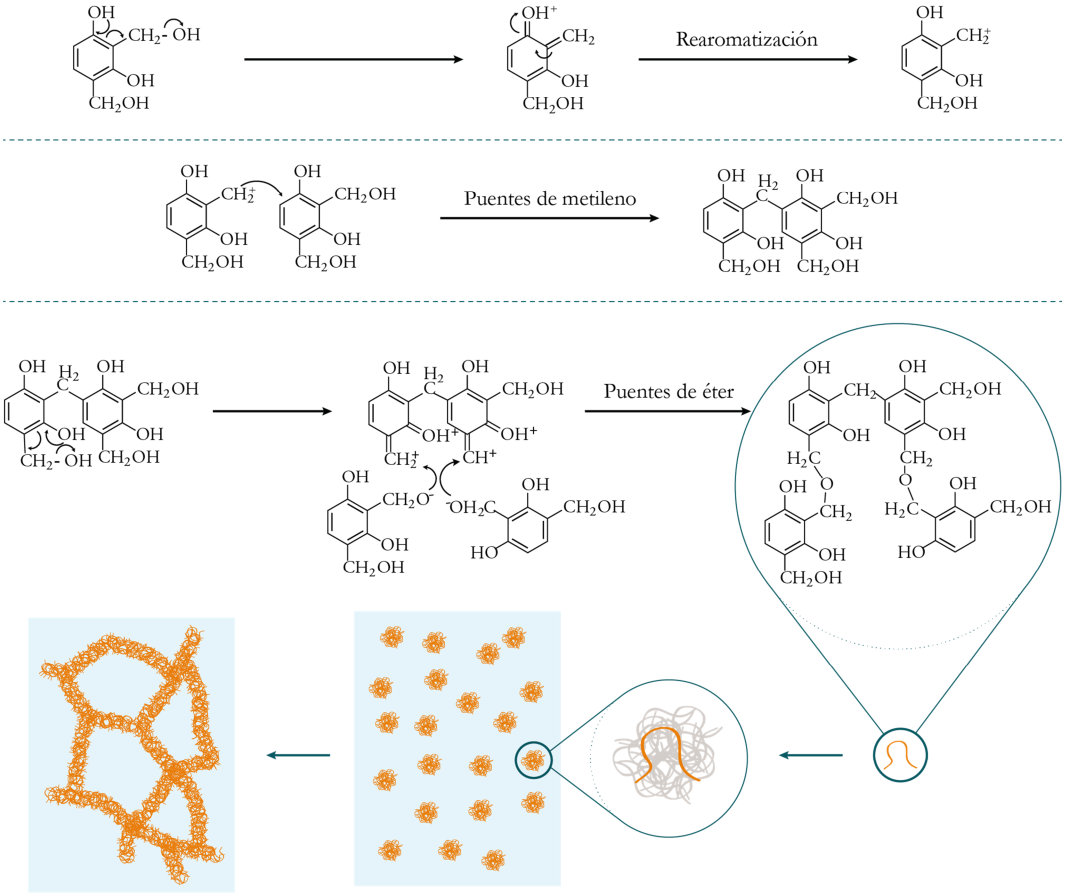


Figura 1.4. Esquema de la reacción de condensación entre el resorcinol y el formaldehído.

La aparición de los nódulos disminuye la fluidez de la mezcla precursora. El tiempo necesario desde que comienza la reacción hasta que la disolución pierde fluidez, es decir, hasta que se forma el gel, se conoce como tiempo de gelificación, mientras que el momento exacto en el que se obtiene el gel se denomina punto de gelificación [Juárez-Pérez 2010]. Tras alcanzar este punto de gelificación, la estructura sólida inmersa en el líquido continúa su evolución. Esta etapa se llama curado y, en ella, los grupos hidroxilo que no habían reaccionado continúan con la reacción de polimerización aumentando los entrecruzamientos entre los nódulos [Moreno-Castilla 2005]. Durante la etapa de curado también se produce la evaporación de parte del disolvente, causando una ligera contracción espontánea de la estructura.

La formación de los nódulos, su crecimiento y el entrecruzamiento entre las cadenas poliméricas dependen de la concentración de cada uno de los reactivos utilizados. En función de los valores fijados para estas variables la estructura presenta una forma determinada. La forma de la estructura polimérica es de gran importancia ya que de ella dependen las propiedades finales de los materiales y, por tanto, su adaptación a los requisitos de una aplicación concreta.

1.1.3. SECADO

Los geles orgánicos obtenidos tras la reacción sol-gel y el curado deben secarse para eliminar completamente el disolvente embebido en su estructura. Principalmente, existen tres métodos: el secado bajo condiciones supercríticas, el secado criogénico y el secado bajo condiciones subcríticas [Al-Muhtaseb 2003; Job 2005; Elkhatat 2011]. En función del tipo de secado empleado, el material obtenido se conoce como aerogel, criogel o xerogel, respectivamente (Figura 1.5). Aunque los tres métodos de secado dan lugar a materiales con propiedades muy similares, el secado bajo condiciones sub-críticas produce materiales con menor porosidad que el secado bajo condiciones supercríticas y el secado criogénico [Liang 2000; Job 2005]. Sin embargo, el secado bajo condiciones sub-críticas es un proceso mucho más sencillo, rápido y económico y, por tanto, aplicable a escala industrial.

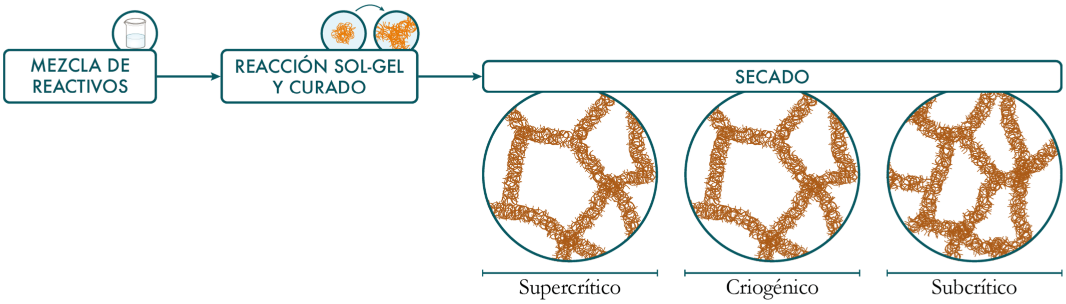
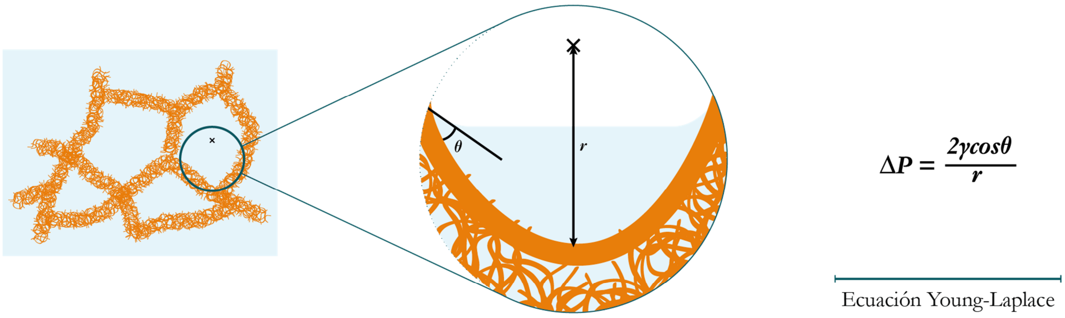


Figura 1.5. Tipo de geles orgánicos en función del método de secado aplicado.

No obstante, hay que tener en cuenta que durante el secado bajo condiciones sub-críticas se crea una interfase líquido-vapor en la superficie interna del material, de modo que cuando el disolvente se evapora se generan elevadas tensiones superficiales, debidas a las fuerzas de capilaridad, que pueden provocar el colapso parcial o total de la estructura [White 2014; Allahbakhsh 2015; Rojas-Cervantes 2015]. En base a la ecuación de Young-Laplace mostrada en la Figura 1.6 y considerando que los poros son esféricos, puede deducirse que el grado de colapso depende de la energía superficial específica, del ángulo de contacto entre la estructura porosa y el disolvente y del tamaño de los poros [Amrei 2015].



$$\Delta P = \frac{2\gamma\cos\theta}{r}$$

Ecuación Young-Laplace

Figura 1.6. Fuerzas de capilaridad en sólidos porosos.

En el caso concreto de los geles orgánicos, los dos primeros términos de la ecuación de la Figura 1.6 se mantiene prácticamente constantes, por lo que el grado de colapso depende principalmente del tamaño de los poros de la muestra, es decir, de la forma de la estructura polimérica.

1.1.4. MÉTODOS DE CALENTAMIENTO

La reacción de polimerización entre el resorcinol y el formaldehído es una reacción espontánea pero lenta, por lo que para promover el inicio de la reacción sol-gel y completar las etapas de curado y secado en un intervalo de tiempo corto es necesario someter la mezcla precursora a un proceso de calentamiento. El proceso más utilizado consiste en su calentamiento en un horno eléctrico a una temperatura no superior a 100ºC para evitar el hervor de la mezcla precursora. Este método requiere varios días, generalmente 72 horas, para completar la reacción sol-gel y el curado [Pekala 1989; Job 2006a; Mirzaeian 2009b]. Además, a este tiempo se le ha de añadir el tiempo necesario para completar la etapa de secado, que depende en gran medida del método empleado. La utilización de hornos eléctricos en las tres etapas principales del proceso de síntesis (reacción sol-gel, curado y secado) supone un gran coste de producción debido a los elevados consumos energéticos y los largos tiempos requeridos para producir el gel orgánico [Rojas-Cervantes 2015].

Con el objetivo de obtener materiales más competitivos, algunos estudios plantean la utilización de otras fuentes de calor más rápidas y económicas como la emisión de ultrasonidos o la radiación microondas [Tonanon 2006; Menéndez 2010; Elkhatat 2011]. De entre ambas técnicas, el calentamiento con microondas es la tecnología que se presenta hoy en día como la más eficaz y económica, ya que permite producir xerogeles orgánicos con propiedades porosas similares a los obtenidos de forma convencional pero con una reducción del tiempo de síntesis del 90% [Calvo 2011]. Como ejemplo de ello, desde 2014 la empresa Xerolutions S.L. emplea la tecnología microondas en la síntesis a gran escala de geles orgánicos, de un modo sencillo y rápido, obteniendo materiales muy competitivos y de alto valor añadido.

1.2. CARBONIZACIÓN

La carbonización, proceso a partir del cual se obtienen los geles de carbono, consiste en poner el gel orgánico en contacto con un gas inerte dentro de un horno tubular a alta temperatura. El gas inerte usado en la mayoría de los casos es nitrógeno, helio o argón [Mirzaeian 2009a; Wu 2012]. El flujo de este gas es constante y moderado, acorde a la cantidad de muestra y al tamaño del horno tubular. Generalmente, se utilizan temperaturas entre 600 y 1000ºC con rampas de calentamiento lentas para evitar grandes tensiones en la estructura, provocadas por la eliminación de los gases producidos en el interior del material [Al-Muhtaseb 2003; Wiener 2006; Girgis 2011]. Los parámetros con mayor impacto sobre las propiedades finales de los geles de carbono son la naturaleza y el flujo del gas, la temperatura del proceso, el tiempo de residencia y la granulometría de la muestra [Kiciński 2011; Moreno 2013].

El principal objetivo del proceso de carbonización es la obtención de geles de carbono térmicamente estables. No obstante, en un gran número de casos este proceso también se lleva a cabo con el propósito de aumentar el área superficial de los materiales [Lin 2000]. Durante el proceso se produce la rotura de enlaces carbono-oxígeno a bajas temperaturas y de enlaces carbono-hidrógeno a altas temperaturas [Lin 1997; Maldonado-Hódar 1999; Fairén-Jiménez 2006]. Estas roturas provocan el reordenamiento de las moléculas formándose material de carbono estable. Por otro lado, las reacciones producidas durante el proceso generan gases (materia volátil) que, al eliminarse, producen grietas en el interior de los nódulos [Allahbakhsh 2015]. Este fenómeno se da en todos los procesos de carbonización de modo que el gel de carbono siempre presenta mayor área superficial que su correspondiente precursor, es decir, el gel orgánico.

1.3. TRATAMIENTOS SECUNDARIOS

Como se ha comentado anteriormente, es posible llevar a cabo tratamientos determinados para modificar una o varias propiedades de forma aislada y mejorar las propiedades obtenidas tras la síntesis y/o la carbonización para que se ajusten de manera más precisa a los requisitos de una aplicación. Existen tratamientos enfocados a modificar las propiedades porosas y procesos para modificar las propiedades químicas.

1.3.1. MODIFICACIÓN DE LAS PROPIEDADES POROSAS

1.3.1.1. ACTIVACIÓN

El proceso de carbonización no solo convierte los geles orgánicos en geles de carbono sino que además, incrementa el área superficial obteniéndose, por lo general, valores de alrededor de 600-700 m^2/g [Moreno 2013]. Sin embargo, determinadas aplicaciones, como algunos sistemas de almacenamiento de energía [Fang 2005; Inagaki 2010], requieren áreas más elevadas por lo que es necesario aplicar otro tipo de tratamiento térmico. El proceso de activación permite aumentar el área superficial hasta incluso alcanzar 2000-3000 m^2/g [Calvo 2013b]. Así mismo, durante la activación, también se consigue incrementar el volumen de poros estrechos creado durante la síntesis del gel orgánico y/o el proceso de carbonización [Conceição 2009; Chejne 2015].

Hay dos tipos principales de activación: química y física. La activación química consiste en poner el gel orgánico o de carbono en contacto con un agente activante (ácido fosfórico, cloruro de cinc, carbonatos alcalinos, hidróxidos alcalinos, etc.) a temperaturas entre 400 y 800ºC [Zubizarreta 2008; Zubizarreta 2009b; Lee 2012; Calvo 2013a]. Tras este tratamiento térmico, el material debe lavarse para eliminar el agente químico residual y los posibles productos inorgánicos generados en la reacción. La activación física es el método más utilizado y consiste en poner el material en contacto con un gas (vapor de agua o dióxido de carbono) a temperaturas entre 700 y 1000ºC [Lin 2000; Fang 2005; Contreras 2010]. Los geles de carbono obtenidos mediante este tratamiento térmico presentan propiedades porosas distintas a las obtenidas mediante la activación química. Por tanto, en función de la aplicación donde se vaya a utilizar el material, se empleará un proceso de activación u otro.

1.3.1.2. INTRODUCCIÓN DE ADITIVOS

La formación de la estructura polimérica y, en consecuencia, las propiedades porosas de los geles de carbono, pueden modificarse mediante la alteración de la reacción de polimerización. Esto se consigue introduciendo compuestos orgánicos en la mezcla precursora. Los más habituales son los surfactantes (iónicos y no iónicos) [Wu 2006; Bruno 2010a; Szczurek 2014; Haghgoo 2015]. Los surfactantes iónicos (catiónico y aniónicos) forman micelas dejando la parte hidrófila en contacto con la mezcla precursora. En el caso de los surfactantes catiónicos las cabezas hidrófilas están cargadas positivamente, mientras que en los surfactantes aniónicos están cargadas negativamente. Las cargas positivas de los surfactantes catiónicos generan fuerzas de atracción entre las micelas y los aniones de resorcinol provocando que la estructura polimérica se forme más cerca de la micela. Por el contrario, las cargas negativas de los surfactantes aniónicos generan fuerzas de repulsión, haciendo que la estructura se forme alejada de la micela [Matos 2006; Maldonado-Hódar 2013b]. Los surfactantes no iónicos consisten generalmente en cadenas poliméricas lineales que pueden interaccionar con la estructura del gel orgánico, creando nuevos enlaces y, por ende, modificándola [Tonanon 2003]. Por tanto, la adición de surfactantes puede ser un tratamiento clave en el diseño de las propiedades porosas de los geles de carbono. La selección del tipo y de la concentración de surfactante depende de las propiedades porosas finales que requiera el gel de carbono.

1.3.2. MODIFICACIÓN DE LAS PROPIEDADES QUÍMICAS

Como se ha comentado anteriormente, la formación de la estructura polimérica depende de las condiciones seleccionadas en las principales etapas del proceso de síntesis y de si se emplea la activación o la adición de surfactantes como tratamientos secundarios. En función de esta estructura el material obtenido presenta unas propiedades porosas determinadas. Sin embargo, la porosidad no es el único factor que se ha de considerar a la hora de diseñar las propiedades de los geles de carbono debido a que las propiedades químicas también juegan un papel muy importante en un gran número de aplicaciones. La modificación de las propiedades químicas se consigue generalmente mediante procesos de funcionalización y/o dopaje.

1.3.2.1. FUNCIONALIZACIÓN

El principal objetivo de la funcionalización es la introducción de heteroátomos, principalmente oxígeno y nitrógeno, en la superficie de los geles de carbono [Inagaki 2010]. El término funcionalización no es muy común en el campo de la síntesis de geles de carbono, llamándose oxidación cuando se introducen grupos funcionales oxigenados y dopaje cuando se introducen grupos funcionales nitrogenados. El proceso de oxidación puede realizarse con gases oxidantes (ozono, oxígeno, óxido nitroso, óxido nítrico, dióxido de carbono, etc.) o con disoluciones acuosas oxidantes (hipoclorito de sodio, peróxido de hidrógeno, peroxidisulfato de amonio, ácido nítrico, etc.) [Alegre 2011]. El proceso de incorporación de grupos nitrogenados puede realizarse con diversos compuestos como amoniaco, amonio o borato de amonio [Kang 2008; Moreno-Castilla 2012; Rojas-Cervantes 2015]. El grado de funcionalización y la naturaleza de los grupos funcionales dependen de la reactividad del agente oxidante o dopante, la naturaleza del material carbonoso y la temperatura y el tiempo de tratamiento [Xin 2015]. El incremento en el número de grupos funcionales favorece el posterior anclaje de las partículas metálicas (propiedad de gran interés en soportes catalíticos [Kiciński 2014; Xin 2015] y, en algunos casos, mejora la hidrofilicidad (propiedad necesaria en algunos adsorbentes) [Kiciński 2014; Xin 2015]. En los últimos años también se ha estudiado la posibilidad de incorporar otro tipo de heteroátomos como el azufre, el flúor o el boro, ya que mejoran las prestaciones de los geles de carbono en determinadas aplicaciones como en algunos procesos catalíticos o en sistemas de almacenamiento de energía [Inagaki 2010; Kiciński 2014].

1.3.2.2. DOPAJE

El principal objetivo del proceso de dopaje es la introducción de agentes metálicos (Ni, B, P, Cu, Ca, Co, Mn, etc.) en la estructura del gel, ya sea orgánico o carbonizado [Moreno-Castilla 2005; Marques 2011; Nagy 2014]. Los métodos de dopaje más habituales son la impregnación en exceso de solución, la impregnación húmeda incipiente, la adsorción de iones, el intercambio iónico y la mezcla física [Moreno-Castilla 2005; Carrott 2010; Alegre 2011; Maldonado-Hódar 2013b]. El grado de dispersión depende del método seleccionado, del agente dopante utilizado y de la estructura del gel de carbono. La introducción de agentes metálicos es un factor de gran importancia en el almacenamiento de hidrógeno y en sistemas electroquímicos y catalíticos [Maldonado-Hódar 1999; Lee 2012; Celorrio 2014]. Cabe destacar que los agentes dopantes también pueden añadirse en la mezcla precursora, paso previo al proceso de síntesis de los geles orgánicos [Moreno-Castilla 2005; Sánchez-Polo 2008; Nagy 2014]. En este caso, hay que tener en cuenta que el proceso de dopaje también influye en la formación de la estructura polimérica y, por tanto, no solo se modifican las propiedades químicas sino también las propiedades porosas.

1.4. PROPIEDADES

Los geles de carbono han despertado un gran interés en las últimas décadas debido a que sus propiedades pueden ser diseñadas a medida de una aplicación concreta. Esto se consigue mediante la selección adecuada de la condiciones del proceso de síntesis, carbonización y tratamientos secundarios que permiten controlar la formación de la estructura. Como se ha comentado anteriormente, en las etapas de la reacción sol-gel y curado puede controlarse la formación de los nódulos, su crecimiento y el entrecruzamiento entre las cadenas poliméricas mediante la selección adecuada de la concentración de los reactivos utilizados. En la etapa de secado puede controlarse el grado de contracción de la estructura formada, especialmente desde el punto de vista de los huecos entre nódulos, mientras que mediante la modificación de las condiciones del proceso de carbonización puede controlarse la estructura interna de los nódulos. Por tanto, en función de las condiciones fijadas en cada etapa, la estructura presenta una forma determinada. La forma de la estructura polimérica es de gran importancia ya que de ella dependen las propiedades finales de los geles de carbono.

La estructura de los geles de carbono es una estructura polimérica porosa, es decir, presenta huecos (poros) entre los nódulos. Los poros se distinguen entre [Sing 1985]:

- Microporos: huecos dentro de los nódulos con una anchura inferior a 2 nm.

- Mesoporos: huecos entre nódulos con una anchura entre 2 y 50 nm.

- Macroporos: huecos entre nódulos con una anchura superior a 50 nm.

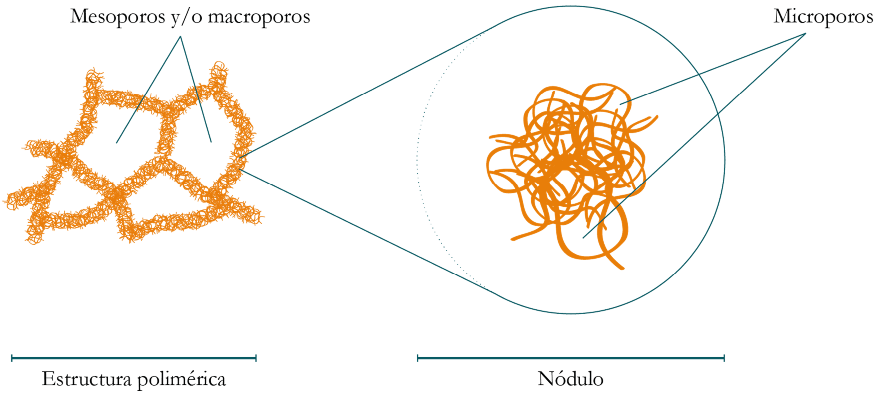


Figura 1.7. Estructura polimérica de los geles de carbono.

En función de la forma de la estructura, los geles de carbono presentan distintas propiedades tales como área superficial (100-1200 m^2/g), porosidad (60-90%), volumen de poro (0.1-3 cm^3/g), tamaño de poro (desde 1nm a pocos milímetros), densidad aparente (0.1-1.0 g/cm3), conductividad eléctrica (5-100 S/cm), conductividad térmica (30-70 mW/m·K), pureza (80-99 % en peso de carbono), etc. La adecuada combinación de estas propiedades hace de los geles de carbono candidatos con un gran potencial para ser empleados en diversas aplicaciones.

1.5. APLICACIONES POTENCIALES

La gran versatilidad de los geles de carbono ha hecho de ellos unos materiales con un gran potencial en un amplio rango de aplicaciones como sistemas de adsorción, aislamiento térmico, dispositivos de almacenamiento de gases y energía y soporte de catalizadores. Las propiedades de los geles de carbono son cruciales para poder utilizarlos en cada una de estas aplicaciones, por lo que a continuación se destacan los requisitos más relevantes que han de tener para poder ser empleados en cada una de ellas.

1.5.1. ADSORCIÓN

La utilización de geles de carbono como adsorbentes para la eliminación de contaminantes es una aplicación ampliamente estudiada [Fairén-Jiménez 2007; Wu 2007; Veksha 2009; Wu 2012; Wang 2015a]. El hecho de poder diseñar su estructura porosa junto a su elevada resistencia mecánica y la posibilidad de sintetizarlos en forma de monolitos y/o esferas hace que los geles de carbono sean unos candidatos idóneos en este tipo de proceso [Fairén-Jiménez 2007]. Las propiedades del material carbonoso dependen, en gran medida, del tipo de elemento contaminante. Es decir, el tamaño de los poros ha de ser tal que permita la introducción del compuesto a eliminar [Veksha 2009; Wang 2015a; Xin 2015]. Por otro lado, la distribución del tamaño de los poros, es decir, la forma de la estructura polimérica, ha de permitir la desorción del compuesto para poder recuperar el material carbonoso y re-utilizarlo [Wu 2007]. Otra característica fundamental que han de tener los geles de carbono para utilizarlos como adsorbentes es una elevada resistencia mecánica que permita emplearlos en columnas de lecho móvil o en dispositivos con vibraciones [Fairén-Jiménez 2007]. Las propiedades químicas también son de gran importancia, ya que los geles deben tener la química superficial más indicada para interaccionar apropiadamente con las moléculas a adsorber [Veksha 2009; Xin 2015].

1.5.2. AISLAMIENTO TÉRMICO

La capacidad de un material de aislar térmicamente viene dada por su conductividad térmica, que depende de los tres mecanismos de transmisión de calor: conducción, convección y radiación [Cuce 2014]. En el caso de los materiales porosos, como lo son los geles, la conducción es el mecanismo de mayor importancia. Al tener porosidad, la contribución de la conducción a la conductividad térmica total depende de la transmisión de calor a través de la estructura sólida y de los poros, generalmente llenos de aire [Feng 2011; Bi 2012]. La contribución a través de la estructura sólida puede minimizarse utilizando materiales con elevada porosidad y baja densidad, mientras que una reducción en el tamaño de los poros disminuye la contribución a través del fluido, aire, que ocupa los poros [Wiener 2009; Feng 2011; Guo 2015; Zhang 2015]. Por tanto, un diseño adecuado de las propiedades de los geles puede hacer de ellos unos buenos candidatos como aislantes térmicos.

1.5.3. ALMACENAMIENTO DE ENERGÍA

El estudio del uso de los geles de carbono como electrodos en sistemas electroquímicos, principalmente supercondensadores y baterías, ha aumentado considerablemente en los últimos años debido a la importancia que han adquirido estos dispositivos en el campo del almacenamiento de energía. No obstante, los requisitos que han de tener los geles de carbono para poder utilizarse como material electrodo, en un sistema u otro, difieren considerablemente.

- **Supercondensadores:** los geles de carbono utilizados como material electrodo en supercondesadores han de presentar elevada conductividad eléctrica [Li 2008; Kiciński 2014]. Por otro lado, el área superficial del material carbonoso, en la que se produce la adsorción de los iones, debe ser lo más alta posible para conseguir elevadas capacidades electroquímicas [Li 2008; Calvo 2013a]. Además de presentar elevada microporosidad para asegurar la acumulación de carga, los geles de carbono han de presentar una estructura porosa con poros suficientemente abiertos para que se produzca la correcta humectación por parte del electrolito y se facilite el transporte iónico [Zhang 2009; Inagaki 2010]. Generalmente, estos procesos se consiguen diseñando materiales carbonosos con tamaños de poro inferiores a 15 nm [Zhang 2009; Calvo 2013b]. La química superficial también es un aspecto de gran relevancia ya que tiene un efecto directo en las reacciones que se producen. En este sentido, la introducción de heteroátomos puede aumentar la capacidad de estos dispositivos a través de las reacciones redox [Liang 2000; Kiciński 2014]. No obstante, la aparición de estas reacciones puede disminuir el rendimiento a largo plazo debido a que se disminuye su durabilidad [Moreno-Castilla 2012].

- **Baterías ion-litio:** el material carbonoso más utilizado como material electrodo en estos dispositivos es el grafito. No obstante, en los últimos años ha aumentado el número de estudios donde se utilizan materiales carbonosos porosos desordenados, consiguiendo capacidades electroquímicas superiores a las obtenidas con el grafito [Roberts 2014; Sun 2014; Miranda 2015; Wang 2015b]. De estos estudios se deduce que los geles de carbono podrían utilizarse como material electrodo en baterías ion-litio. La introducción de heteroátomos como el oxígeno o el flúor, así como el dopaje con estaño o cobalto, entre otros, puede aumentar el rendimiento de estos dispositivos [Kiciński 2014]. No obstante, todavía no se ha esclarecido de forma precisa y evidente qué propiedades porosas han de tener los geles de carbono para que las baterías ion-litio posean elevada capacidad electroquímica.

1.5.4. ALMACENAMIENTO DE GASES

El almacenamiento de hidrógeno es uno de los campos donde la aplicación de los geles de carbono tiene un gran interés. La adsorción de hidrógeno se lleva a cabo en los microporos estrechos, por lo que es requisito indispensable que los geles de carbono presenten poros con un tamaño que no exceda 1 nm [Zubizarreta 2009a; Kiciński 2014]. Esto se debe a que los poros estrechos aumentan la energía de interacción entre la superficie del carbón y el hidrógeno. También es necesario disponer de un elevado volumen de poros para aumentar la capacidad de adsorción [Zubizarreta 2010; Xin 2015]. Otro aspecto a tener en cuenta es que los geles de carbono pueden doparse durante el propio proceso de síntesis con metales de transición que ayudan a mejorar la interacción entre la superficie del material y el hidrógeno [Saha 2009; Yang 2011; Chen 2014]. Cabe destacar que la modificación del tamaño de los poros también permite utilizar los geles de carbono para el almacenamiento de otro tipo de gases como metano o dióxido de carbono [Kiciński 2014].

1.5.5. SOPORTE DE CATALIZADORES

Los geles de carbono también se emplean como soporte de catalizadores en diversos procesos catalíticos. En esta aplicación es fundamental que el gel de carbono se dope con compuestos metálicos (fase activa) [Maldonado-Hòdar 2000; Xin 2015; Zhai 2015]. Los procesos de dopaje modifican la estructura porosa, por lo que ésta depende de la naturaleza del agente dopante [Maldonado-Hódar 2013a]. En general, es necesario que el material carbonoso posea una elevada mesoporosidad y, preferiblemente, con poros anchos. Esto permite que el metal se pueda alojar correctamente y se disponga de espacio para la adsorción y desorción de los reactivos y productos [Xin 2015; Zhai 2015]. Por otro lado, el área superficial también ha de ser elevada para permitir mejorar la dispersión de la fase activa [De 2015]. La modificación de la química superficial, especialmente desde el punto de vista de la presencia de grupos oxigenados y nitrogenados, puede mejorar tanto la actividad catalítica como la durabilidad de los catalizadores [Moreno-Castilla 2005; Samant 2005; Xin 2015; Zhai 2015]. Un ejemplo del uso de geles de carbono como soporte de catalizadores que ha despertado un gran interés en las últimas décadas es el campo de las pilas de combustible, donde el dopaje de los geles de carbono también se utiliza como estrategia para aumentar la conductividad eléctrica, factor que carece de importancia en otras reacciones catalíticas [Alegre 2011].

1.6. ESTADÍSTICA APLICADA AL PROCESO DE SÍNTESIS

Como se ha mencionado a la largo del presente capítulo, existe un gran número de variables que influyen en las propiedades finales de los geles de carbono. El efecto de cada una de estas variables no puede considerarse de forma aislada ya que cada una de ellas puede modificar el efecto de las otras. Por este motivo la optimización del proceso de síntesis requiere la aplicación de técnicas estadísticas que permiten evaluar de forma global el efecto de cada una de las variables del proceso y la sinergia existente entre ellas. Dentro del campo de la estadística existe una estrategia experimental de gran utilidad para la optimización de procesos conocida como Metodología de Superficie de Respuesta (MSR o *Response Surface Methodology, RSM*). Esta metodología engloba tres fases básicas (Figura 1.8): i) diseño de experimentos, ii) aplicación del modelo y iii) técnicas de optimización.

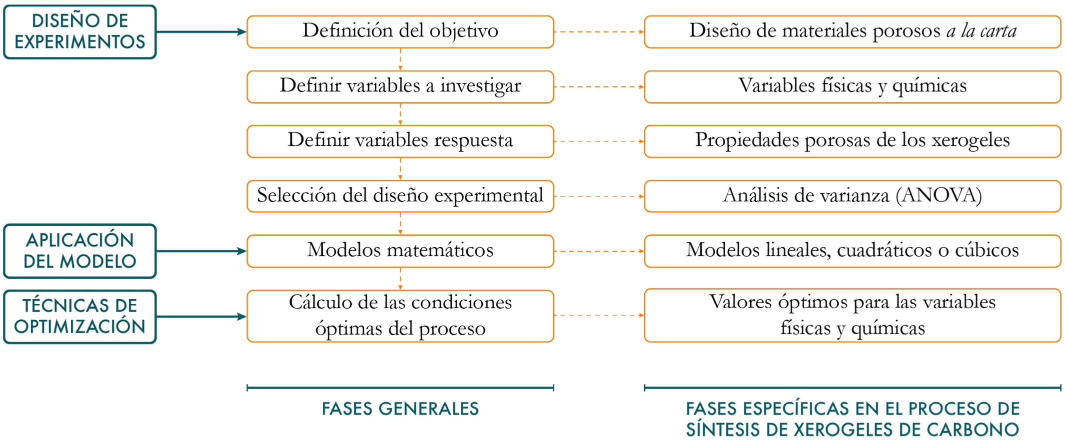


Figura 1.8. Esquema de la Metodología de Superficie de Respuesta aplicada a procesos.

Una buena estrategia de optimización de un proceso requiere la realización de un apropiado Diseño de Experimentos *(Design Of Experiments, DOE*) antes de comenzar a cambiar de forma aleatoria las variables que modifican dicho proceso. Para ello, es preciso establecer el objetivo y las variables que se quieren investigar y las variables que se utilizarán como respuesta. En función del número de variables establecidas, se determina el número de experimentos necesarios. Tras la realización de los experimentos se aplica un análisis de varianza (*Analysis of Variance, ANOVA*) a cada una de las variables respuestas en función del modelo estadístico que mejor se ajuste a los resultados experimentales obtenidos. De los muchos resultados que se obtienen del ANOVA, uno de los parámetros clave es la probabilidad de aceptar o rechazar la hipótesis nula. Este parámetro se conoce como p-value y determina la significación de cada uno de las variables por separado y la de la sinergia que puede haber entre ellas. Si el valor de p-value es inferior a 0.05 entonces la variable es significativa, mientras que si el valor es superior a 0.05 la variable investigada no se considera significativa. El modelo estadístico seleccionado, generalmente lineal, cuadrático o cúbico, debe representar los resultados experimentales de la forma más precisa posible ya que de él depende la posterior optimización del proceso. El modelo estadístico obtenido permite determinar las condiciones del proceso que se deben utilizar para obtener geles de carbono con unas propiedades determinadas. Así mismo, también es posible predecir qué propiedades tendrá un material sintetizado bajo determinadas condiciones de síntesis. Finalmente, cabe destacar que la utilización de métodos estadísticos no solo permite evaluar las condiciones operativas del proceso sino que, además, permite obtener conclusiones fiables a partir de muestras reducidas sin necesidad de analizar poblaciones de datos completas.

PUBLICACIÓN I

FORMALDEHYDE IN THE SYNTHESIS OF RESORCINOL-FORMALDEHYDE CARBON GELS

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Chapter 2

FORMALDEHYDE IN THE SYNTHESIS OF RESORCINOL-FORMALDEHYDE CARBON GELS

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ABSTRACT

Carbon gels are porous materials obtained from the polymerization of resorcinol with formaldehyde in the presence of a solvent. In this reaction, formaldehyde is the reagent responsible for the crosslinking that takes place during the polymerization and, hence, it plays an important role in determining the final porous structure of these materials.

This chapter goes deeply into the way in which formaldehyde modifies the final porous properties of carbon gels and how its influence is affected by other variables involved in the synthesis process. In general terms, an increase in the concentration of formaldehyde shifts the chemical equilibrium towards the products, thereby increasing the reaction rate. This implies that clusters are formed and grow faster. On the other hand, an excess of formaldehyde also leads to more interconnections between clusters, resulting in a materials with highly branched structures. However, the effect of formaldehyde may be modified by the effect of other reagents. For example, an increase in the amount of solvent hinders the crosslinkages produced during the reaction. Similarly, the initial pH of the precursor solution also influences the effect of formaldehyde, since acidic conditions favour the addition of formaldehyde among the resorcinol anions. The use of surfactants also affects the normal course of the sol-gel reaction. Commonly, these additives are either ionic or non-ionic and, depending on their chemical load, their effect on the formation of the porous structure will be different. Generally, anionic surfactants create repulsive forces between resorcinol anions while cationic surfactants generate attractive forces. Depending on the method of preparation of the precursor solution, non-ionic surfactants are either incorporated into the structure of the gel or remain as micelles, leaving voids when the surfactant is removed.

Generally, the formaldehyde used in the synthesis of carbon gels (37 wt. % in water) is stabilized by methanol. The role of the methanol is to prevent the polymerization of formaldehyde by forming hemiacetal groups. The concentration of methanol in the solution depends largely on the manufacturer and is usually set between 0.6 and 15 wt.%.

This variation in the concentration of methanol also affects the influence of formaldehyde on the polymerization reaction of carbon gels since the formaldehyde needs to be in its free form in order to react with resorcinol. Solutions that contain low concentrations of methanol contain larger amounts of free formaldehyde molecules and therefore, materials with greater porosity are obtained.

CARBON GELS: SYNTHESIS AND APPLICATIONS

Inspired by the synthesis of inorganic silica gels, whose method of preparation and properties have made them highly versatile materials suitable for multiple industrial applications [1], Pekala and co-workers produced the first organic gel by applying the sol-gel methodology in 1989 [2]. This methodology consists in provoking a chemical reaction in which a liquid condenses gradually from a stable suspension of colloidal solid particles (sol) to create a tridimensional porous network formed by polymeric chains in a liquid medium (gel). In the case of organic gels, from which carbon gels are obtained, the sol-gel reaction occurs between hydroxylated benzenes and aldehydes in the presence of a solvent [2-7]. The gel resulting from this reaction goes through a curing stage, in which the material becomes harder due to the simultaneous occurrence of crosslinkages between polymeric chains and the partial evaporation of the solvent [1, 8, 9]. Because the removal of the solvent is not completed during curing, a drying stage is needed in order to completely eliminate the solvent embedded inside the polymeric structure [1, 10]. The dried gel is then stabilized by means of thermal treatments in which oxygenated and hydrogenated groups are removed, resulting in a carbonaceous material known as carbon gel [9, 11].

Figure 1 shows the main stages involved in the synthesis of carbon gels by means of the sol-gel method: the sol-gel reaction and curing, drying and carbonization. Each of these steps plays an important role in determining the final properties of the resultant materials and therefore, each one is reviewed below in more detail.

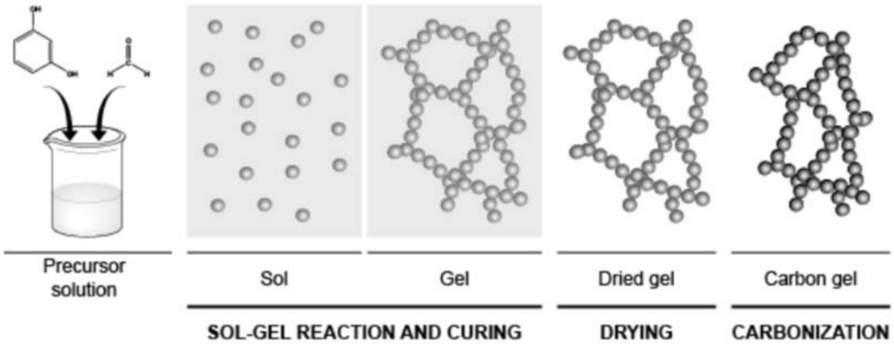

Figure 1. Main stages involved in the synthesis process of carbon gels.

Sol-Gel Reaction and Curing

The synthesis of carbon gels begins with the preparation of an aqueous solution containing hydroxylated benzene, aldehyde and solvent and, when necessary, a fourth compound, known as catalyst, which regulates the pH and catalyzes the reaction [9]. The nature and concentration of these reagents, the pH of the precursor solution, the incorporation of additives and the heating method all play a key role in the synthesis of organic gels, i.e., in the sol-gel reaction and curing stages [12].

The choice of a suitable reagent for synthesizing organic gels is essential for the sol-gel reaction to take place. Several precursors can be employed to develop carbon gels, as is shown in Figure 2. Phenol [4, 5, 13-15], cresol [6, 16-18], cellulose [19] or tannins [20-22] have been used as the hydroxylated benzene, though resorcinol is probably the most commonly used for the synthesis of carbon gel [2, 8, 9, 23, 24]. For aldehydes, formaldehyde is the most widely employed reagent because of its importance for the development of the polymer structure [25]. However, some studies have also resorted to furfural [3, 26-28] or hexamethylenetetramine (HMTA) [5, 29].

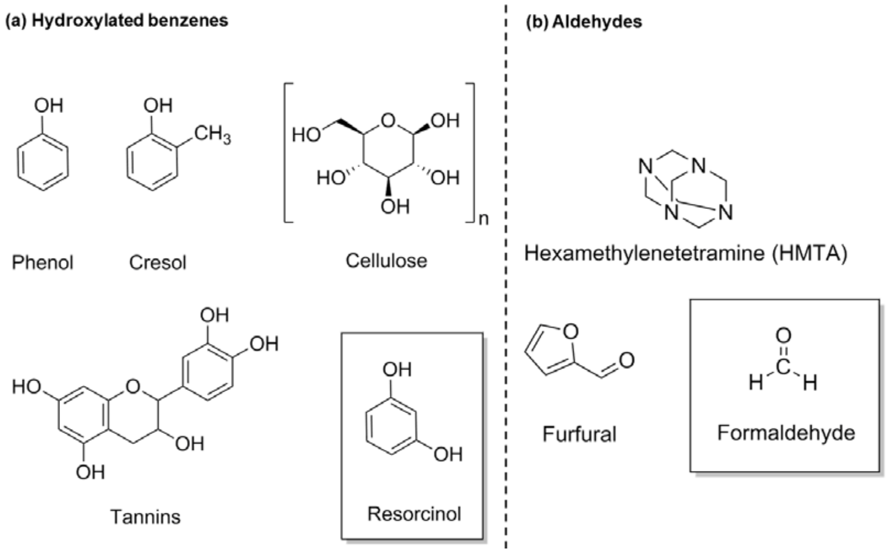

Figure 2. The most common reagents used for the synthesis of carbon gels as hydroxylated benzene (a) and as aldehyde (b).

The reaction medium is also an important factor in the synthesis of carbon gels. Several solvents are available including deionized water [23, 24, 30, 31], acetone [32], methanol [33-35] or ethanol [36]. Each of these compounds has a different surface tension and therefore, their behavior during the curing and drying stages will result in different pore structures. Although water exhibits the highest surface tension value giving rise to a further collapse of the polymeric structure when the solvent evaporates, it is the least expensive reaction medium and therefore, the most preferred for synthesizing carbon gels. The nature of the catalyst may also influence the sol-gel reaction because of their different capacities of polarization [37].

Catalysts can be acidic such as perchloric acid [38, 39], nitric acid [40], citric acid [41] and acetic acid [42] or basic such as alkali carbonates [7, 30, 43-47] or sodium hydroxide [13, 31, 36, 48-51]. However, basic catalysts are the most frequently used [9, 52].

Of all the possible reagents available, the most commonly employed for synthesizing carbon gels are resorcinol and formaldehyde [2, 12, 23, 24, 31, 53, 54]. Hence, from now on, all references regarding the precursors of carbon gels will assume the involvement of these two reagents.

It is important to emphasize that the type of reagent is not the only important factor in the synthesis of carbon gels. The concentration of the reagents also has a strong influence on the final properties of these materials [9, 10, 23, 52, 55]. These concentrations are related to the molar ratio between the resorcinol and the formaldehyde [23, 25, 55, 56], the pH of the precursor solution [2, 7, 10, 24, 37, 44, 52, 57] and the dilution ratio [10, 23, 37, 44, 48, 57-59].

The effect of the molar ratio between the resorcinol and the formaldehyde is determined by the amount of formaldehyde. This reagent is responsible for the crosslinking between clusters that takes place during the sol-gel reaction and curing stage [25]. By a way of introduction it may be said that a high concentration of formaldehyde could result in materials with greater porosity by choosing suitable synthesis conditions [55]. The influence of the pH of the precursor solution on the final properties of the carbon gels has been one of the most widely studied variables and its value depends on the amount of catalyst added [2, 7, 23, 37, 44, 52, 57, 60]. An increase in the pH value favours the addition of formaldehyde, leading to the formation of highly branched aggregates and, in turn, to smaller and more interconnected clusters [7, 23, 37, 44, 52, 57, 60]. The dilution ratio, commonly defined as the molar ratio between the total solvent and reagent, can modify the behavior of the formaldehyde in the sol-gel reaction. The effects of varying the degree of dilution are diverse and depend largely on the conditions chosen for the preparation of the precursor solutions and on the methods employed for the synthesis and drying stages. Generally speaking an increase in the amount of water will results in a structure with a few weakly branched clusters [48]. The mechanical strength of these materials is low, and therefore, during the drying stage they will undergo further contraction, leading to materials with a smaller pore volume [7, 23, 48, 57, 58].

Although modifying the concentration of the reagent is the most common way to change the pore structure of carbon gels, the addition of additives can also affect the normal course of the sol-gel reaction, by altering the formation of the polymeric structure [61]. The additives most commonly used in the synthesis of carbon gels are surfactants [61, 62]. In general, it may be said that there are three fundamental types of surfactant: anionic, cationic and non-ionic [61-65]. The nature and concentration of each surfactant alters the behavior of formaldehyde in the sol-gel reaction and, in turn, the final shape of the porous structure [61, 62].

Once the reagents involved in the sol-gel process have been selected and mixed in the appropriate proportions, the precursor solution of the carbon gel is subjected to a heating process in order to initiate the sol-gel reaction, which will yield a stable organic wet gel. The process most frequently used to carry out the sol-gel reaction and curing involves heating the precursor solutions in a conventional electric furnace at a temperature not exceeding 100 ºC [2, 6, 7, 31, 66]. The synthesis of organic wet gel by means of conventional heating requires several days to produce the final material, resulting in a less cost-competitive material than activated carbon, which is the one preferred for most applications because of its low production cost [31, 53]. Hence, the implantation of the synthesis of carbon gels at industrial scale entails reducing the cost of the manufacturing process, in order to produce more competitive materials than activated carbons. Researchers in this field are directing their effort towards the development of faster and cheaper heating methods such as ultrasonic and microwave radiation [26, 31, 47].

Ultrasonic radiation has been found to be a helpful strategy for increasing reaction rates and product yields and for shortening the reaction time required [67]. However, so far this heating method has only been used for the gelation of the material, the curing and drying stages being performed in a conventional furnace [67].

Microwave radiation as a heating method for the synthesis of carbon gels was applied for the first time in 2006 [68]. Initially, the application of microwave heating for the synthesis of carbon gels was directed at some specific stage of the synthesis process, e.g., the gelation and curing stages which were then followed by drying in an electrical oven [69] or just the drying stage [53, 68]. In all cases, the organic gels obtained exhibited a well-developed porous structure and both time and costs were greatly reduced. Nowadays, microwave heating is used to carry out all three stages of the production process (the sol-gel reaction, curing and drying), resulting in porous materials with similar properties to those obtained by conventional methods [31]. Thus, it can be said that microwave radiation is as a cost-effective technology that allows the synthesis of organic gels on a large scale via a simple and rapid procedure, yielding very competitive and high value-added materials.

Drying

Whatever the heating method used for synthesizing organic gels, the material obtained must be dried so that the solvent embedded in the polymeric structure can be completely removed. To eliminate the solvent, not only is it necessary take into account the type of solvent added but also the solution in which the formaldehyde is dissolved. Generally, the formaldehyde employed to synthesize carbon gels (37 wt. % in water) is stabilized by methanol. The role of the methanol is to prevent the polymerization of the formaldehyde by forming hemiacetal groups, which are molecules of stabilized formaldehyde [35]. The concentration of methanol in the solution depends largely on the manufacturer and, depending on this concentration and on the drying method used, the surface tension at the liquid-vapor interface can be altered and consequently, different degree of shrinkage can occur. Accordingly, not only are the nature and concentration of the reagent key factors in the synthesis of carbon gels but also the method of solvent removal [59].

Three different types of drying method can be found in the literature, supercritical drying, freeze-drying and subcritical drying, each of which is carried out under different process conditions, as shown in Figure 3.

The most widely used drying method for the synthesis of organic gels is supercritical drying [13, 28, 37, 47, 70]. In this method the solvent is replaced by CO_2 which is subsequently disposed of in a process carried out at high pressure [28, 37, 70]. The main problem with this method is that if water is used as solvent it must be replace by an organic solvent prior to its replacement by CO_2, due to the solubility of CO_2 in water [71]. Alternatively, the CO_2 replacement step can be eliminated by directly removing the organic solvent at high pressure and high temperature [72]. However, in this case the structure undergoes further collapse, leading to materials with less porosity [72]. The gels obtained by applying this drying method are known as aerogels and their properties make them very promising materials for a wide range of applications. Notwithstanding, it is a laborious, time-consuming and expensive method and, therefore, difficult to carry out at an industrial scale [24].

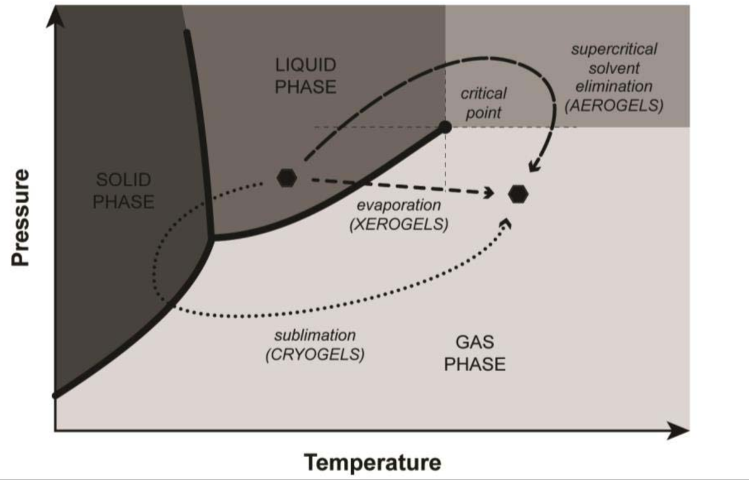

Figure 3. Scheme of the different drying conditions used in the synthesis of organic gels.

Cryogenic drying involves freezing the solvent that is embedded in the polymeric structure and its subsequent removal by sublimation [59]. If water is used as solvent, it must be replaced by an organic solvent in order to prevent the formation of megalopores [30, 59] and changes in the density of the gel after freezing [59]. The materials obtained by this drying technique are known as cryogels and generally exhibit a high mesoporosity [59]. Although it is somewhat cheaper than the supercritical drying method, the need to use organic solvents or to have the water replaced by an organic solvent entails an increase in time and costs, making the process unfeasible at industrial scale.

The third drying method, which results in materials called xerogels, is based on the direct evaporation of the solvent [59, 70] and hence, the drying temperature will greatly depends on the type of reagent used as solvent. However, unlike the other two drying methods, the subcritical conditions lead to the formation of a liquid-vapor interface and, when the solvent evaporates high surface tensions emerge that may cause the collapse of the polymeric structure [10, 24, 54, 59, 70].

Nevertheless, although shrinkage occurs during drying, several studies have reported that carbon xerogels with a well-developed porous structure can be obtained if appropriate process conditions are chosen [7, 24, 31, 53]. Furthermore, it is the cheapest, easiest and fastest method of drying and therefore, economically viable at industrial scale [36]. Hence, carbon xerogels with similar characteristics to those of aerogels and cryogels can be obtained but by via of a more competitive method.

Carbonization

Once dried organic gels have been obtained, carbonization must be applied in order to produce the carbon gels. The main aims of this process are first to stabilize the material and, secondly to increase the micropore volume and surface area and also to widen the narrow pores created during the process of synthesis [7, 8, 36, 73].

Carbonization, the most commonly used thermal treatment, involves heating the sample in a non-reactive atmosphere [1]. Time, temperature and the nature and flow rate of the carrier gas are the parameters that have the greatest effect on the final properties of the carbon gel [11, 73-75]. Temperatures between 600 and 1000 ºC are generally used with slow heating ramps to prevent excessive shrinkage of the structure, as a result of the removal of the gases produced inside the material [73, 75]. Nitrogen, helium or argon are used as carrier gas and constant and moderate flows are selected according to the amount of sample and the size of the tube furnace.

Several authors have reported that the carbonization process involves the breaking up of C-O bonds at low temperatures and the breaking up of C-H bonds at high ones [76, 77]. The breakage of bonds leads to the rearrangement of molecules and more stable structure [58]. Furthermore, according to some published works [78], the walls separating individual micropores break, resulting in the enlargement of narrow micropores [78]. On the other hand, the condensation produced during the carbonization process causes a slight shrinkage of the polymeric structure and, consequently, the size of the pores decreases [60]. Both phenomena contribute to an increase in the microporosity during carbonization.

It is well known that some applications require materials with a high amount of microporosity, which cannot be achieved by carbonization alone. Consequently, another thermal treatment known as activation need to be applied to organic gels in order to increase the microporosity of these materials [46, 78]. The activation process can be carried out either during or after carbonization, resulting in materials with different properties. The temperature and time of activation, the activating agents and precursors are some of the variables that need to be optimized in order to obtain well-developed activated carbons [75, 78]. Basically, there are two types of activation methods: physical activation and chemical activation [78]. Physical activation is the most widely used method. With this thermal treatment, the material is heated under a reactive gas flow. Gases such as air, steam or CO_2 or a combination of them are generally used [75]. Chemical activation involves mixing the sample with an activating agent and then increasing the temperature. This method requires a subsequent washing step to remove the unreacted chemical agent and any possible residual products from the reaction [46]. Examples of the activating agents used are phosphoric acid, zinc chloride, alkali metal carbonates and alkali hydroxides [12, 46, 79]

Applications

Carbon gels are very versatile materials whose polymeric structure can be designed to fit the requirements of a specific application by selecting the appropriate process conditions. Bearing in mind the shape of the polymeric structure of carbon gels, the porosity of these materials can be defined as: i) voids within polymeric clusters with a width of less than 2 nm known as micropores and [10], ii) voids between polymeric clusters, which are called mesopores when their width is in the 2-50 nm range and macropores when the size of voids are wider than 50 nm [10]. A schematic representation of the porous structure of RF xerogels is shown in Figure 4.

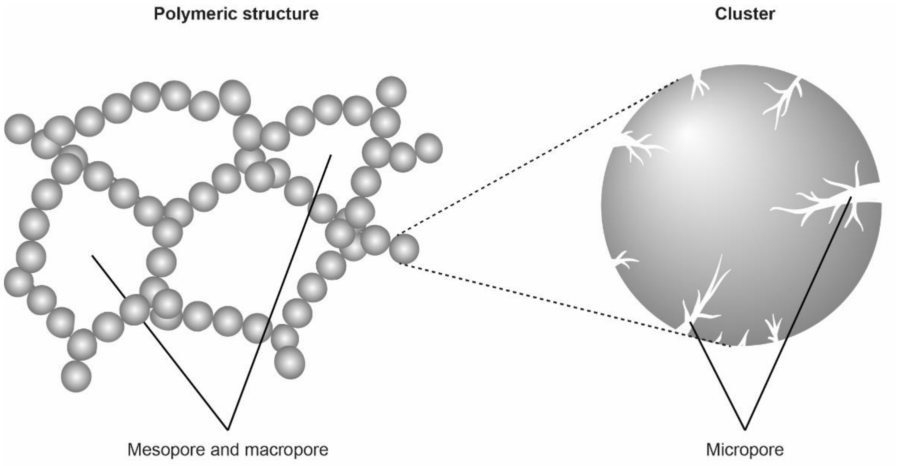

Figure 4. Schematic representation of the porous structure of carbon gels.

Depending on the shape of the porous structure formed, carbon gels will differ in surface area, volume and pore size, density, electrical and thermal conductivity, chemical composition, etc. The right combination of these properties makes carbon gels perfect candidates for various applications such as adsorption [11, 23, 52], hydrogen storage [28, 80], electrode material for supercapacitors [51, 81-84] or lithium batteries [85, 86], catalyst support [10, 23], etc.

In dynamic adsorption processes, diffusion limitations can be minimized by choosing a carbon gel with pores large enough to overcome mass transfer limitations [87]. A high hydrogen storage capacity can be achieved by using carbon gels with a highly developed microporosity and an appropriate micropore size distribution [80]. When carbon gels are to be used as electrode material, in addition to microporosity, mesopores are required in order to facilitate a good electrolyte diffusion [69, 81, 82]. In the case of catalyst supports carbon gels need to have a porous structure that allows an adequate support and dispersion of the metal particles added in the catalytic reactions [10]. Accordingly, the porous and chemical properties of the carbonaceous material should be designed with a view to the type of metal that is going to be used and the type of reaction in which it is going to be employed.

ROLE OF FORMALDEHYDE IN THE SYNTHESIS OF CARBON XEROGELS

Controlling the porous structure of resorcinol-formaldehyde (RF) xerogels is essential for tailoring the properties of these materials to fit the requirements of a specific application. As mentioned in the previous section, there are many variables that need to be controlled for tailoring the final properties. These variables are related to the conditions selected in each stage of the production process: sol-gel reaction and curing, drying and carbonization. Although all of these stages are key factors for designing the final porous properties of carbon gels, this section will focus principally on the synthesis of organic gels (sol-gel reaction, curing and drying), since this is where formaldehyde, the main protagonist of this chapter, plays an important role.

Formaldehyde is the most widely used aldehyde for performing the sol-gel reaction in order to obtain RF xerogels [55]. Most of the published studies on the synthesis of RF gels have employed the stoichiometric molar ratio between the resorcinol and the formaldehyde (i.e., an R/F molar ratio value of 0.5) [7, 8, 11, 24, 39, 46, 48, 53, 59, 78]. However, some studies report that it is possible to modify the concentration of formaldehyde altering the sol-gel reaction and as a consequence the porous structure of the gels [23, 25, 55, 58].

The role of the formaldehyde in the formation of the porous structure can be explained by the polymerization reaction between resorcinol and formaldehyde. According to several published works [2, 7, 52] the polymerization reaction involves two main stages: i) an addition reaction in which hydroxymethyl derivatives of resorcinol are formed and, ii) a condensation reaction in which the hydroxymethyl derivatives are linked by methylene and ether bonds.

All the steps involved in the polymerization reaction between the resorcinol and formaldehyde are illustrated in Figure 5. First, resorcinol anions are formed due to the abstraction of hydroxyl hydrogen, as shown is Figure 5a [2, 88]. Resorcinol is a trifunctional benzyl compound with two hydroxyl groups in positions 1 and 3 which allows the addition of formaldehyde in positions 2, 4 and 6 [10]. This feature along with the fact that resorcinol anions, formed at the beginning of the addition reaction, are more reactive than resorcinol itself, leads to the addition of formaldehyde [10]. Primarily, the addition of formaldehyde occurs via the formation of hydroxymethyl derivatives (Figure 5b), which are the monomers necessary for polymerization to occur [10, 44].

During the addition reaction condensation also takes place. The hydroxymethyl derivatives lose OH^- groups to form benzyl-type cations, as shown in Figure 5c [61]. Each cation reacts with the benzene ring of another molecule linking themselves to each other by forming methylene and ether bonds as illustrated in Figure 5d and Figure 5e, respectively [2, 10, 44, 60, 66, 89]. As the reaction proceeds the number of bonds between the rings increases, to form the polymer backbone, which leads to cross-linked polymer clusters. These clusters aggregate and crosslink with each other to complete the sol-gel reaction and curing steps [9, 10, 25], resulting in a three-dimensional interconnected porous structure (Figure 5f). Therefore, from this reaction mechanism, it can be seen that formaldehyde is the factor responsible for the formation of clusters and crosslinkages during the polymerization reaction.

According to Feng et al. [58], an increase in the concentration of formaldehyde, i.e., a decrease in the R/F molar ratio, shifts the chemical equilibrium toward the products. This suggests that the clusters will form and grow faster, allowing the reaction medium to last longer during the nucleation stage. The fact that clusters have more time to grow gives rise to the formation of a small number of large clusters. However, an excess of formaldehyde not only accelerates the formation and growth of clusters but also creates more interconnections between them, leading to a highly branched structure of high mechanical strength [2, 58]. A small number of large clusters gives rise to a low vapor-liquid interface causing small surface tensions to appear during drying. This phenomenon together with the high mechanical strength just mentioned, prevents the collapse of the structure, resulting in materials with a low degree of shrinkage and a low density, as shown in Figure 6 [58].

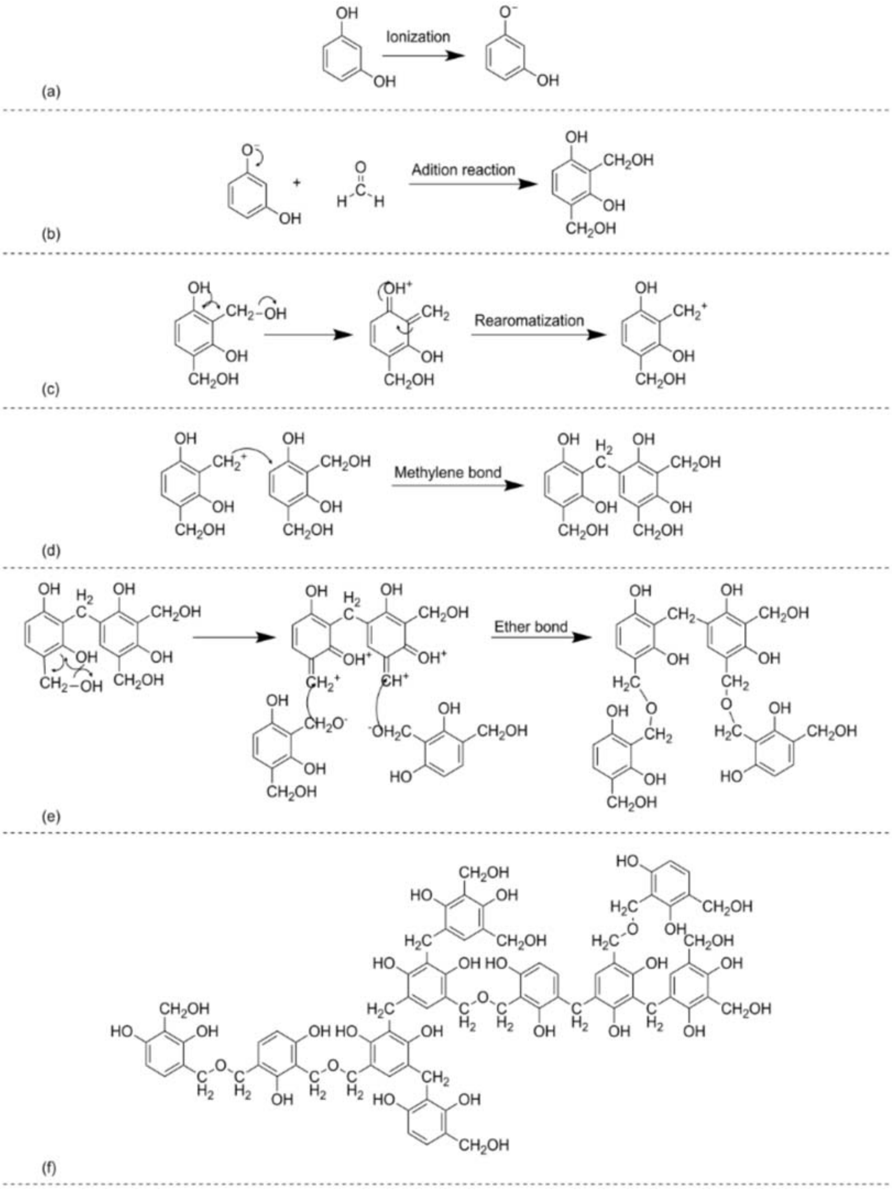

Figure 5. Mechanism of the polymerization reaction between resorcinol and formaldehyde.

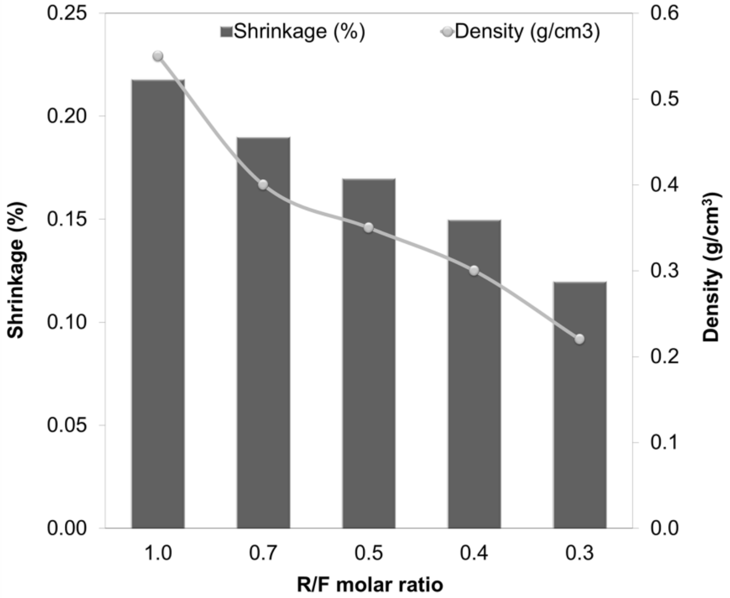

Figure 6. Percentage of shrinkage and density of carbon aerogels as a function of the R/F molar ratio. Adapted from reference [58].

On the other hand, an insufficient amount of formaldehyde (i.e., when the R/F molar ratio value is above the stoichiometric value) leads to the formation of small clusters and a weakly branched structure [25]. Small clusters give rise to a high vapor-liquid interface and as a consequence, considerable surface tensions during drying, especially when direct evaporative drying is applied. As the slightly branched structure is not able to counteract the surface tension the material shrinks, leading to the maximum compaction of the porous structure, which ends when the clusters come into contact. The compaction of the polymeric structure when the concentration of formaldehyde decreases results in a highly dense material (Figure 6).

In the literature dealing with the variation of the amount of formaldehyde to be added for the synthesis of RF gels, maximum and minimum R/F molar ratio values are proposed for obtaining well-developed porous structures. Some published works quote a value of 0.7 as the maximum limit [23, 25]. The use of concentrations of formaldehyde for below the stoichiometric value (i.e., R/F molar ratio values above 0.7) results in some cases in non-porous materials [23, 25], whilst in other cases such low values could prevent the precursor solution from reaching the gelation point [55]. However, there is considerable controversy as to the minimum R/F molar ratio value that can be used for the synthesis of RF gels. Some authors have stated that this value needs to be above 0.4 [23, 25], while other authors have reported the synthesis of well-developed porous RF gels using R/F molar ratio value of below 0.4 [39, 55, 56]. These differences are due to the fact that the formation, growth and crosslinking of the clusters not only depend on the concentration of formaldehyde and resorcinol but also on the concentration of the other reagents used to prepare the precursor solution: i.e., water and the catalyst [55]. The concentrations of these compounds are reported in the literature to be related to the dilution ratio [10, 23, 37, 44, 48, 57-59] and the pH of the precursor solution [2, 7, 10, 24, 37, 44, 52, 57], respectively.

pH of the Precursor Solutions

The pH of the precursor solution is given by the concentration of the catalyst [59]. In fact, in many of the studies that can be found in the literature the pH is defined by the R/C parameter which is the molar ratio between the resorcinol and the catalyst [8]. For any given concentration of resorcinol, the higher the concentration of the catalyst, the lower the value of the R/C ratio.

Initially, the precursor solution comprising resorcinol, formaldehyde and water has a pH value of about 3-4 [48]. Base catalyst can be added until maximum pH value is obtained. However, many studies that have dealt with the dependence of porosity on the initial pH have reported that precursor solutions with a pH value above 7 are hardly able to produce porous material [7, 48]. Consequently, most studies only consider a pH variation value of 3-7 as viable [48].

The effect of the pH of the precursor solution on the final properties of the RF xerogel has been one of the most studied variables [7, 9, 41]. Several works published in the literature have reported that both the volume and the size of the voids between the clusters are modified by the pH of the precursor solution whereas the micropore volume is unaffected [7]. Figure 7 shows the volumes of micropores, mesopores and macropores of carbon xerogels. As can be seen, the microporosity is independent of the R/C ratio and depends exclusively on the carbonization process [46]. It can also be appreciated from Figure 7 that the size and volume of the voids between the clusters (mesoporosity and macroporosity) depends largely on the R/C ratio of the precursor solution [46]. Thus, by means of small variations in the pH value, RF xerogels can be obtained corresponding to micro-macroporous materials, micro-mesoporous materials and even microporous materials.

The effect of the pH on the porosity of RF xerogels can be explained taking into account the polymerization reaction between resorcinol and formaldehyde shown in Figure 5. It can be seen from Figure 5a that the reaction starts with the abstraction of the hydroxyl hydrogen from the resorcinol. The addition of catalyst promotes the abstraction of hydroxyl hydrogens and in turn, the formation of resorcinol anions [7]. Therefore, increasing the concentration of catalyst (i.e., raising the pH value or lowering the R/C ratio) causes an increase in the number of resorcinol anions to which the formaldehyde is added [7]. As the number of resorcinol anions increases, the addition reaction proceeds faster. Thus, the addition reaction is favored by increasing the pH, resulting in the formation of a large number of small clusters [7, 25, 52], as shown in Figure 8. On the other hand, the addition of low concentrations of catalyst (i.e., low pH values or a high R/C ratio) leads to the formation of a small number of resorcinol anions [41]. As the number of resorcinol anions available decreases the addition of formaldehyde takes place more slowly than when more catalyst is added [8, 41, 52]. Several works suggest that in this case, it is not the addition reaction that is favored but the condensation reaction, as a results of which the reaction medium lasts longer during the nucleation step [7, 41]. Consequently, the number of clusters is small but of a large size (Figure 8).

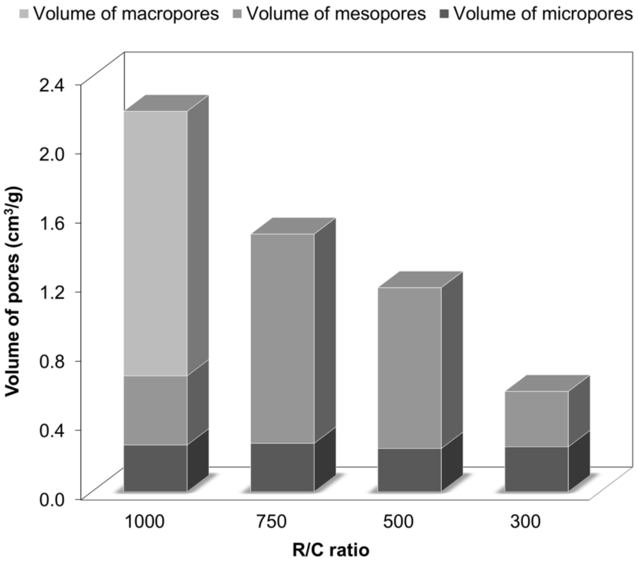

Figure 7. Volume of micropores, mesopores and macropores of carbon RF xerogels synthesized from precursor solutions with different pH values. Adapted from reference [46].

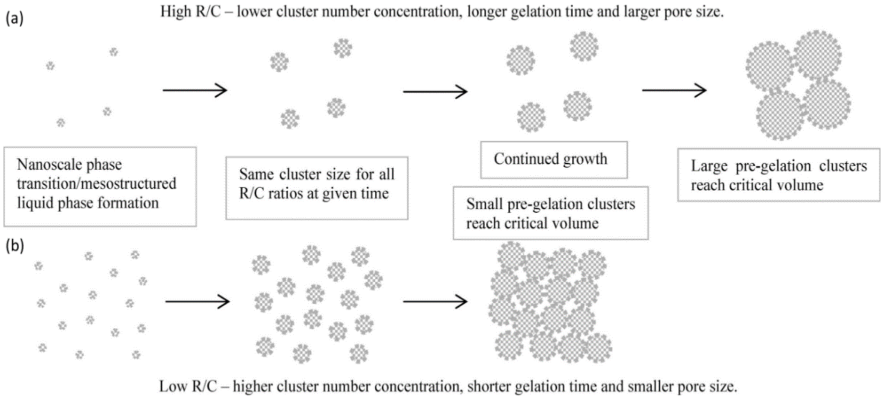

Figure 8. Schematic representation of cluster formation and growth process of resorcinol-formaldehyde gels synthesized from precursor solutions with low pH values (a) and high pH values (b). Reproduced with permission from reference [52].

Samples synthesized from precursor solutions with high pH values give rise to a greater number of clusters of small size, resulting in a more compact structure [23]. Some authors have observed that compaction of the polymeric structure occurs during the shrinkage that takes place when the material is dried [8]. During drying, porous structures formed by a large number of small clusters exhibit a high vapor-liquid interface, leading to the appearance of strong surface tensions and capillary forces [8]. Most of the formaldehyde in the precursor solution has been used in the addition reaction (i.e., in the formation of clusters) leaving less formaldehyde available for the formation of crosslinkages between the clusters. Hence, a weakly branched structure is formed. The mechanical strength of this structure is not able to counteract the surface tension produced during drying, causing the material to shrink until all the clusters are touching each other. The voids remaining between the clusters are small and therefore, materials synthesized with high pH values have a small pore size, as shown in Figure 9.

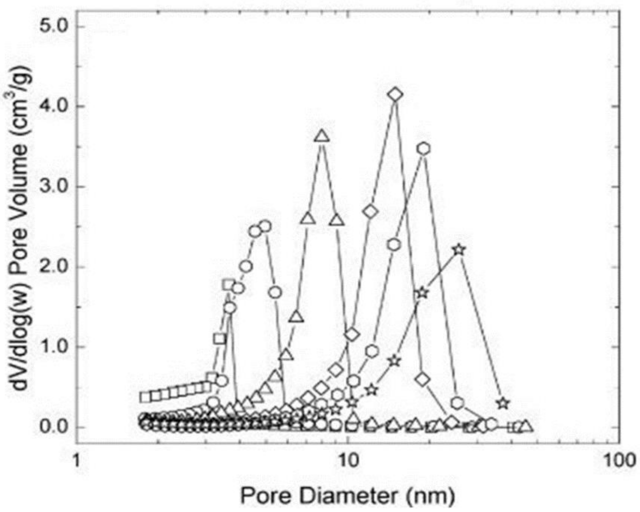

Figure 9. Pore size distribution of RF xerogels synthesized using precursor solutions with R/C ratios of (□) 100, (○) 200, (Δ) 300, (◊) 400, (⬠) 500, and (☆) 600. Reproduced with permission from reference [52].

Dilution Ratio

The dilution ratio (D) is a parameter that is directly related to the amount of solvent that is added to the precursor solution. Most studies dealing with the synthesis of RF xerogels define the dilution ratio as the molar ratio between the total solvent and reactants [7, 48]. Total solvent refers to the water and methanol contained in the formaldehyde and the deionized water that is added, whilst the term reactant refers to the resorcinol and pure formaldehyde [48]. Some studies also include the moles of catalyst in the term reactant [30, 59]. The dilution ratio has also been defined as the molar ratio between resorcinol and water [89], while other authors defined this variable as the solid content of the precursor solution, usually in terms of weight percentage [90].

Based on the most commonly used definition of dilution ratio, a remarkable number of published studies on RF gels employ a dilution ratio value of 5.7 [7, 12, 31, 53, 78, 87]. Nevertheless, it is also possible to find publications that deal with the effect of varying the total amount of solvent [23, 30, 48, 59]. The influence of the dilution ratio is somewhat controversial probably due to differences in the method of synthesis and drying used by each author. Some authors have reported that the degree of dilution does not affect the porous properties of RF aerogel synthesized by means of conventional electric furnaces [59], while other authors have found significant differences in the porous structure of RF xerogels synthesized by means of microwave heating [48]. With microwave heating the sol-gel reaction takes place much faster so that the solvent does not have enough time to evaporate and much of it remains embedded within the structure. This influences the behaviour of the formaldehyde during the polymerization reaction and drying, modifying the porous structure of the carbon xerogels. Figure 10 shows the volume of micropores, mesopores and macropores of organic RF xerogels synthesized by microwave heating. As can be seen, the micropore volume of the RF xerogels is independent of the dilution ratio, while mesoporosity and macroporosity are significantly modified when this variable is adjusted [23].

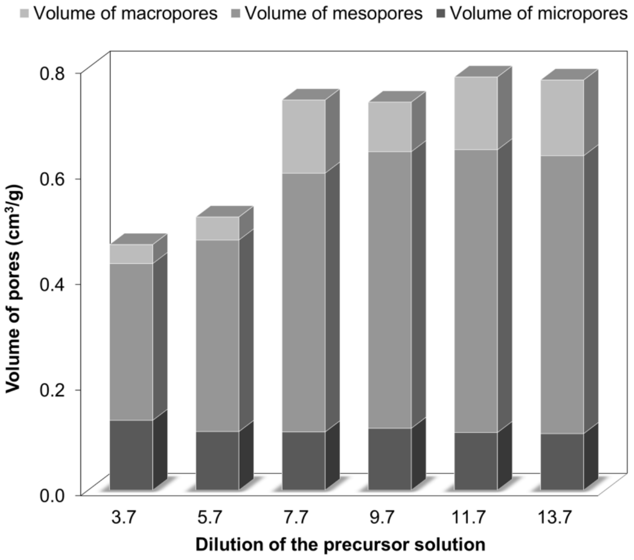

Figure 10. Volume of micropores, mesopores and macropores of organic RF xerogels synthesized by microwave heating from precursor solutions with a pH of 6.5 and different dilution ratio values.

As previously mentioned, the mesoporosity and macroporosity of RF xerogels depend on the number and size of the clusters formed during the sol-gel reaction and curing steps and on the shrinkage that occurs during drying. Therefore, the effect of the dilution ratio on the porosity of RF xerogels can be explained by the polymerization reaction between resorcinol and formaldehyde illustrated in Figure 5. According to the definition of the dilution ratio (D) given above and for the same initial volume of precursor solution, low values of D involve high concentrations of resorcinol and formaldehyde (RF). The higher the concentration of resorcinol, the greater will be the number of resorcinol anions generated, which will favour the addition of formaldehyde [55]. SEM images of samples synthesized from RF precursor solutions with different dilution ratios are shown in Figure 11. As can be seen, a decrease in the dilution ratio gives rise to the formation of a large number of small clusters. These results are in good agreement with those of a recent published work dealing with the variation of the dilution ratio [90], whose authors also reported that an increase in the speed of the addition reaction had resulted in the formation of a large number of small clusters [90].

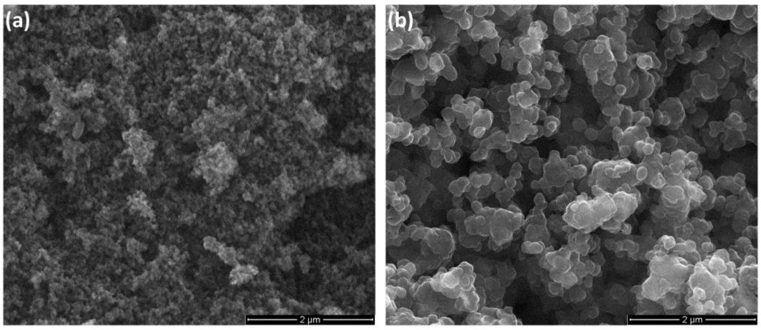

Figure 11. SEM images of carbon xerogels synthesized from RF precursor solutions with a pH value of 5.8 and low (a) and high (b) dilution ratio values.

Increasing D values (i.e., decreasing RF content) lead to the formation of a small number of resorcinol anions. As the number of resorcinol anions decreases, the addition of formaldehyde takes place more slowly, favoring the condensation reaction and resulting in a small number of large clusters [48]. Porous structures with large clusters have a low vapor-liquid interface, which leads to small surface tensions during the drying process. Furthermore, according to some published studies [89], low concentrations of resorcinol and formaldehyde (i.e., high D) result in poorly branched clusters. This phenomenon along with the low degree of shrinkage that occurs during drying leads to less dense materials, as shown in Figure 12.

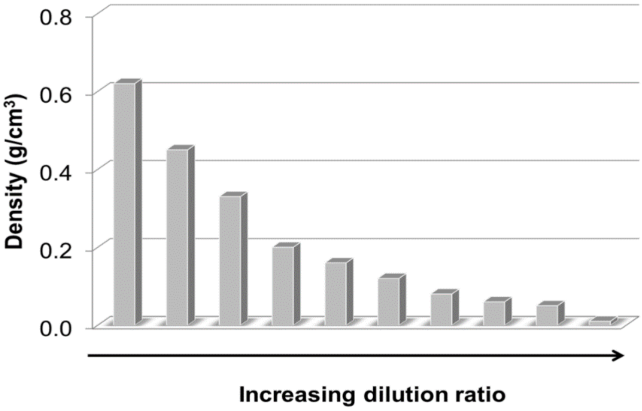

Figure 12. Evolution of the density of resorcinol-formaldehyde organic aerogel with the modification of the dilution ratio. Adapted from reference [91].

Influence of pH and Dilution Ratio on the Behavior of Formaldehyde

From the evidence presented so far it is clear that each one of the variables related to the concentrations of the reactants (R/F molar ratio, pH and dilution ratio) has some influence on the mechanism of the sol-gel reaction. Hence, these three variables are key factors in the design of the porous properties of RF gels as they can be adjusted in order to control the number and size of the clusters formed and, consequently, the number and size of the voids between them, i.e., mesoporosity and macroporosity of the materials. However, it is important to note that the effect of each of these variables may be modified by the effect of the others. In support of this idea, Rey-Raap et al. graphically showed all the combinations of pH-D from which RF xerogels could be synthesized by means of microwave heating [48]. These authors reported that when the dilution ratio was too high (i.e., the amount of RF was too low) only a few small clusters were formed [48]. This phenomenon and the fact that a large amount of water increased the distance between the clusters prevented the solution from reaching the gelation point. Accordingly, controlled synthesis of RF xerogels was only achieved in the pH range of 3.0-7.0 when the dilution ratio was fixed at below 14. Within this range, porous materials with very different properties were obtained due to the combined effect of the pH and D on the addition of formaldehyde. Figures 13a and 13b present contour plot showing the effect of the pH and dilution ratio on the volume of mesopores and macropores of RF xerogels, respectively.

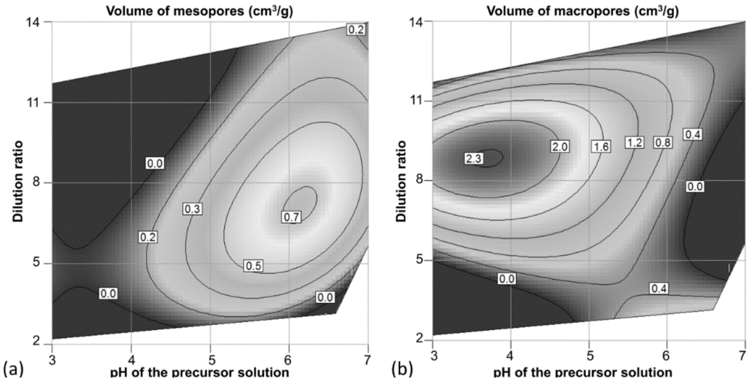

Figure 13. Contour plots showing the effect of the pH and dilution ratio on the mesoporosity (a) and macroporosity (b) of RF xerogels. Reproduced with permission from reference [48].

As can be seen in Figure 13 the samples with a pH above 5.5 are exclusively mesoporous while the sample synthesized from a precursor solution with a pH below 5.5 gives rise to macroporous materials. However, for any given pH, the highest mesoporosity and macroporosity which can be obtained for each sample is dependent on the dilution ratio used. From Figure 13, it can be concluded that within the range of mesoporosity (i.e., pH values above 5.5) the maximum pore volume is obtained by fixing the dilution ratio between 6 and 8, and in the case of macroporous samples between 8 and 10. However, as already mentioned, formaldehyde favours the condensation reaction that leads to the formation of a small number of large clusters. Some authors state that, within the range of maximum mesoporosity shown in Figure 13a, the volume of mesopores can be increased even more by lowering the R/F molar ratio size [55]. Figure 14 shows the volume of micropores and mesopores of organic RF aerogels [23]. As can be seen, the microporosity of the carbon gels is independent of the R/F molar ratio while mesoporosity depends largely on the amount of formaldehyde added.

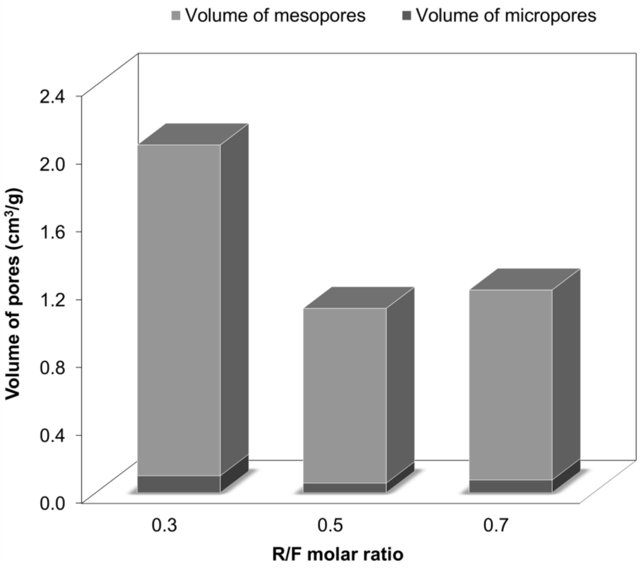

Figure 14. Evolution of the volume of mesopores of organic RF xerogels with a decrease in the R/F molar ratio from 0.5 (a) to 0.3 (b). Adapted from reference [23].

However, a recent published work reported that variations in the R/F molar ratio may also produce a significant change in the volume of micropores depending on the dilution ratio and pH values selected when preparing the precursor solutions. As pointed out before, the catalyst favors the addition reaction, which leads to the formation of a large number of small clusters interconnected by long necks. At the same time, a decrease in the dilution ratio results in an increase in the amount of resorcinol and formaldehyde used, which leads to a highly branched structure. Nonetheless, the results reported in this study demonstrated that the effect of these two chemical variables disappeared during the carbonization process, leaving the R/F molar ratio as the only significant chemical variable [55]. The authors postulated that an increase in the concentration of formaldehyde, i.e., a decrease in the R/F molar ratio, led to the formation of highly branched clusters. Consequently, carbon xerogels synthesized from precursor solutions with a higher concentration of formaldehyde displayed a greater number of highly branched clusters of larger size and so, larger micropore volumes were achieved. Furthermore, they also emphasized that there was the possibility that after the sol-gel reaction and curing steps, over-loaded and unreacted formaldehyde still remained among the clusters. The unreacted formaldehyde was eliminated during drying due to the low boiling point of formaldehyde. In this case, the place occupied by the formaldehyde molecules would become micropores resulting in higher micropore volumes.

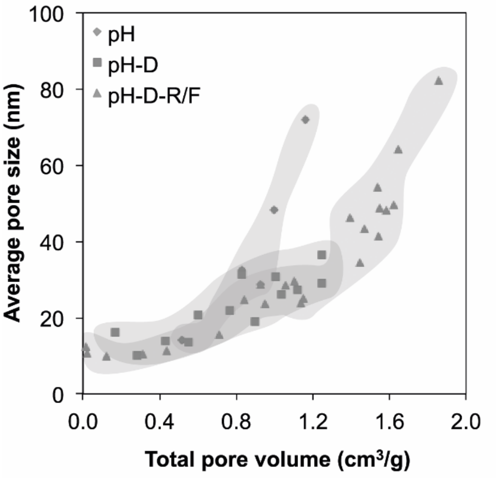

Figure 15. Improvement of the control of porosity of carbon xerogels achieved by the simultaneous modification of the molar ratio of resorcinol and formaldehyde, the pH and the dilution ratio. Reproduced by permission from reference [55].

There is no doubt that by modifying the R/F molar ratio, pH and D simultaneously it is possible to obtain a much wider range of materials than if only one variable is altered. Rey-Raap et al. reported the total pore volume versus the average pore size, as shown in Figure 15. In this figure three regions are highlighted. Each region indicates the materials synthesized from precursor solutions in which: i) different pH values were used while the dilution ratio and the R/F molar ratio were fixed at the most commonly used values in the literature, i.e., 5.7 and 0.5, respectively, ii) the pH and the dilution ratio were simultaneously modified while the R/F molar ratio was fixed at 0.5 and iii) the three chemical variables were simultaneously modified. As can be seen from Figure 15, the simultaneous adjustment of the R/F molar ratio, pH and dilution ratio yields average pore sizes within the range required for most applications where carbon gels are used (0- 200 nm), but with an increase in pore volume of 40% and also a much better control of the porous properties of the carbon xerogels.

Addition of Surfactants

The sol-gel reaction can be altered by adding additive agents such as surfactants, as these compounds can have a marked influence on the behavior of formaldehyde in the polymerization reaction [61, 62]. The most widely used classification for surfactants is based on the mode of dissociation of its molecules in solution. Accordingly, three groups can be distinguished: cationic, anionic and non-ionic surfactants.

The behavior of ionic surfactants (cationic and anionic) in the synthesis of RF gels has been studied by several research groups. Of all the possible cation surfactants, probably the most commonly used for synthesizing RF gels is hexadecyltrimethylammonium bromide (CTAB) [64, 76, 92, 93], whereas as anionic surfactant sodium derivatives, such as sodium docedilsulfate (SDS) [61] or sodium dodecylbenzenesulfonate (SDBS) [62, 63, 76, 94] are used. These surfactants form micelles in solution leaving their hydrophilic heads in contact with the precursor solution of the gel. The hydrophilic heads of cation surfactants are positively charged while the anionic surfactants have negative hydrophilic heads.

According to the polymeric reaction between resorcinol and formaldehyde, Matos et al. schematically show the effect of the cationic surfactant on the sol-gel reaction [61]. They postulate that the positive heads of the micelles interact electrostatically with resorcinol anions formed during the addition reaction, so that the addition of formaldehyde takes place close to the micellar surface, as shown in Figure 16.

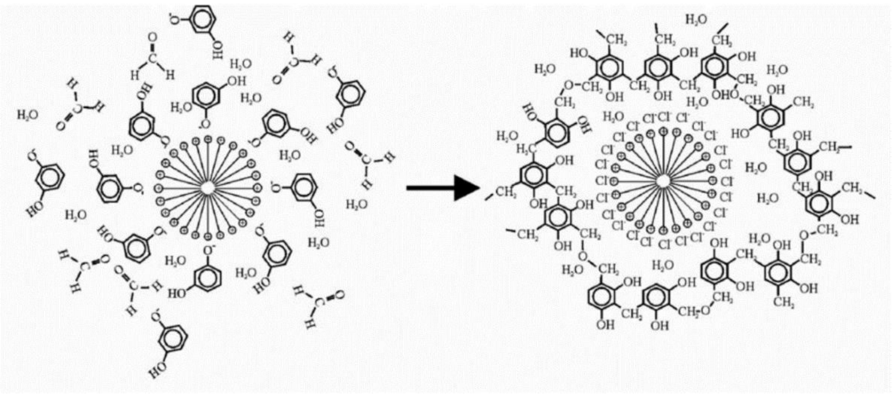

Figure 16. Scheme of the effect of the cationic surfactant on the polymeric structure of RF xerogels. Reproduced by permission from reference [61].

The effect of the cationic surfactant on the sol-gel reaction proposed by Matos et al. is in good agreement with the results of other authors [64]. Wu et al. showed that the use of cationic surfactant results in the formation of smaller clusters. Due to the effect of the surfactant, resorcinol anions are closer together, causing the addition of formaldehyde to proceed faster and, therefore, small clusters are formed. Furthermore, these authors indicated that an increase in the concentration of surfactant leads to greater shrinkage during drying, probably due to the higher surface tensions generated by small clusters. Accordingly, samples synthesized with a large amount of surfactant display a denser structure, as can be appreciated in Figure 17 which shows SEM images of samples synthesized with 5 wt. % and 8 wt. % of cationic surfactant, respectively [64]. In short, the use of a cationic surfactant results in less-mesoporous and more highly microporous materials. These porous properties make these materials suitable candidates for use as adsorbents, microporous membranes, porous electrolytes and catalyst supports [95].

On the other hand, the negative heads of anionic surfactants create electrostatic repulsion between resorcinol anions and the micellar surface, so that the polymeric structure is formed far away from the micelle, as shown in Figure 18 [61].

The repulsive forces between the resorcinol anions and surfactant cause the alienation of the resorcinol anions from the micelles. The addition of formaldehyde proceeds more slowly due to the large distances between the resorcinol anions, resulting in a structure with larger clusters, as shown in Figure 19 [63]. It can be seen from this figure that the use of anionic surfactant in the synthesis of RF gels leads to less compact structures with larger pore sizes.

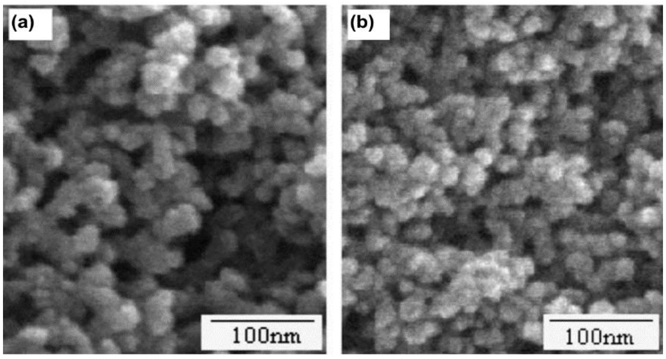

Figure 17. SEM images of organic RF gels synthesized from RF precursor solutions with 5 wt. % (a) and 8 wt. % (b) of cationic surfactant. Reproduced with permission from reference [64].

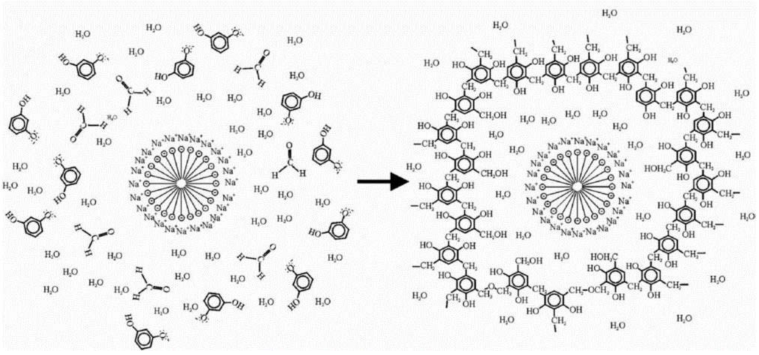

Figure 18. Scheme of the effect of anionic surfactant on the polymeric structure of RF xerogels. Reproduced by permission from reference [61].

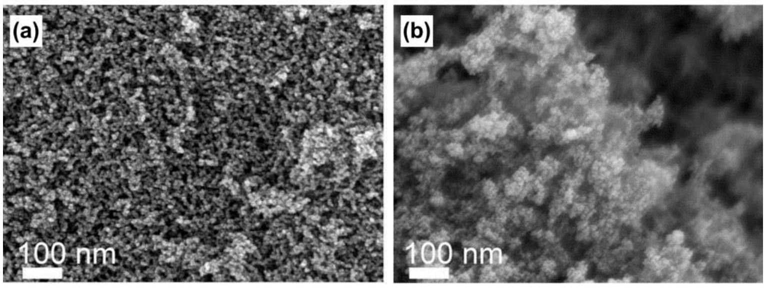

Figure 19. SEM images of carbon gels synthesized from RF precursor solutions with 0 wt. % (a) and 4 wt. % (b) of anionic surfactant. Reproduced by permission from reference [63].

The behavior of non-ionic surfactants in the synthesis of RF gels has also been widely studied. The commercial surfactants known as Span and Pluronic are the non-ionic surfactants most frequently found in the literature [54, 65, 76, 96]. However, it is worth noting that the effect that non-ionic surfactants have on the formation of the polymer structure is somewhat controversial due to differences in the method of preparation of the precursor solution used in each study. The most common method of preparation is based on emulsions [54, 61, 65, 76, 96]. First, the resorcinol-formaldehyde precursor solution is prepared. After gelation has taken place the surfactant is added. This step is followed by the curing and drying stages. Most of these studies indicate that the addition of a non-ionic surfactant has no significant effect on the sol-gel reaction between resorcinol and formaldehyde and therefore, does not alter the final properties of RF gels [61]. However, research work involving the dissolution of the surfactant in a solution of resorcinol prior to the addition of formaldehyde can also be found in the literature. Formaldehyde is then added to the resulting mixture and finally the sol-gel reaction, curing and drying stages are carried out [62, 95]. By using this method of preparation, Jirglovà et al. found that during the sol-gel reaction Span 80 may be linked to the RF structure through aliphatic C=C bonds or OH groups [62]. Consequently, they obtained more polymerized structures, resulting in more compact materials with low pore sizes. The properties of such materials make them highly suitable for use as molecular sieves.

Methanol As a Stabilizer of Formaldehyde

Formaldehyde is commercialized in solution due to its high propensity to polymerize. This propensity is the reason why formaldehyde, commonly used for the synthesis of RF gels (37 wt. % in water), is stabilized by methanol. The role of the methanol is to prevent the polymerization of formaldehyde by forming hemiacetal groups. The oxygen of the carbonyl group from formaldehyde is protonated under acidic conditions, yielding the formation of hemiformal, as shown in reaction A in Figure 20 [35]. The hemiformal formed is unstable and the equilibrium of the reaction shifts to favor the reactant. However, a sufficient amount of methanol allows the reaction to continue and form hemiacetals, as shown in the reaction B of Figure 20, which are, unlike hemiformal, more stable compounds [35]. Therefore, an increase in the concentration of methanol results in the formation of more hemiacetals, leaving less formaldehyde available to participate in the sol-gel reaction.

The concentration of methanol in the solution depends largely on the manufacturer. Table 1 shows concentrations of methanol ranging from 0.6 and 15 wt. % found in solutions of formaldehyde provided by different manufacturer.

Although there are a large number of studies in the literature that deal with the synthesis of RF gels (in which formaldehyde solutions stabilized with methanol are used), very few focus on the stabilizing effect of methanol. On the basis of the reaction mechanism shown in Figure 20, it can be said that the acidity of the medium clearly affects the stabilizing function of methanol. As seen throughout this chapter, the acidity of the medium is determined by the concentration of the catalyst. Low concentrations of catalyst (i.e., low pH values) not only result in the formation of fewer resorcinol anions but also promote the formation of hemiacetals. Therefore, not only are fewer resorcinol anions formed but also a lower amount of formaldehyde is available, leading to the formation of smaller clusters [33, 34]. Polymeric structures with small clusters give rise to small voids between clusters and; hence, samples which are macroporous at low pH values become mesoporous materials when the amount of methanol is increased, as shown in Figure 21.

Accordingly, materials with different porous properties can be obtained by using formaldehyde solutions provided by different manufacturers. However, the effects of the addition of methanol can be offset by an appropriate adjustment of other chemical variables such as the molar ratio between resorcinol and formaldehyde, the dilution ratio or the pH value of the precursor solution.

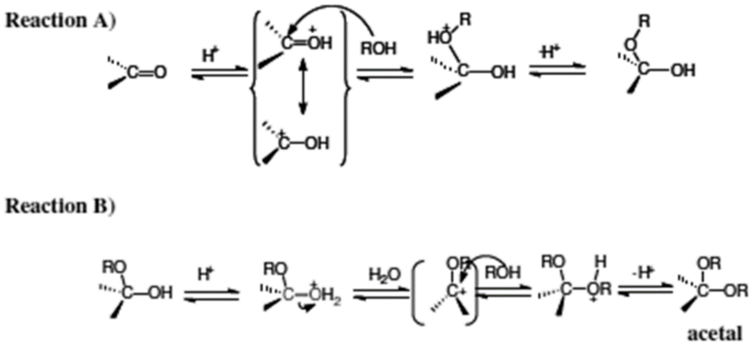

Figure 20. Stabilization mechanism of formaldehyde via the formation of hemiformal (a) and hemiacetals (b). Reproduced with permission from reference [35].

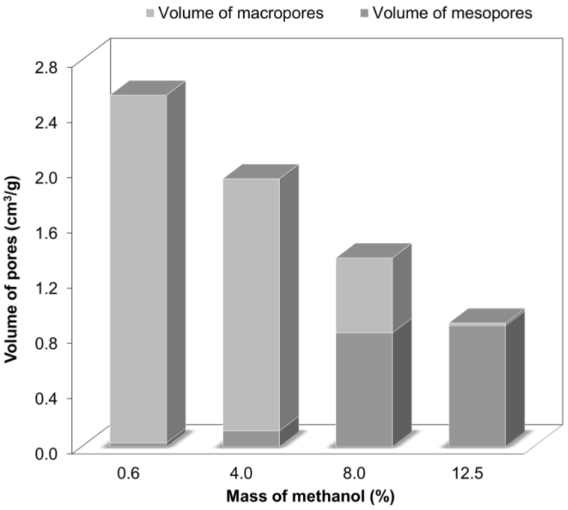

Figure 21. Volume of mesopores and macropores of organic RF xerogels synthesized by microwave heating from precursor solutions with different concentrations of methanol.

Table 1. Concentrations of methanol in solutions of formaldehyde provided by different manufacturers

Brand	Concentration of methanol (% wt.)
Fernández Rapado	≤ 1.3
Panreac	9 - 14
Solvech	9 - 15
Merck Chemicals	10
Oxidal	10 - 15
Sigma-aldrich	10 - 15
Spi-Chem	Non specified

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CAPÍTULO 2

ANTECEDENTES Y OBJETIVOS

Los geles de carbono son materiales con un gran potencial comercial debido a la posibilidad de diseñar sus propiedades a medida de una aplicación concreta. Sin embargo, el proceso de síntesis más utilizado, que consiste en el calentamiento de la mezcla precursora en un horno eléctrico, requiere de varios días para obtener el material, lo que dificulta enormemente su aplicabilidad industrial. En 2011, el grupo de investigación Microondas y Carbones para Aplicaciones Tecnológicas (MCAT, *www.incar.csic.es/mcat*) del Instituto Nacional del Carbón (INCAR-CSIC), donde se ha llevado a cabo la presente Tesis Doctoral, consiguió resolver este inconveniente mediante la aplicación de la tecnología microondas como método de calentamiento. Mediante este proceso se consiguió reducir en un 90% el tiempo necesario para sintetizar el material, pudiéndose llevar a cabo a escala industrial. No obstante, se trata de un método novedoso y, por tanto, es necesario optimizar el proceso. Por este motivo, el **primer objetivo** de este trabajo consistió en optimizar el proceso de síntesis inducida por microondas, prestando mayor atención al efecto que produce la utilización de este nuevo método de calentamiento en la etapa de reacción sol-gel y curado (Figura 2.1). Tal como se detalla en el Capítulo 3, para alcanzar este primer objetivo fue necesario determinar las condiciones del proceso más apropiadas mediante la evaluación del efecto de las variables físicas (tiempo y temperatura de síntesis y volumen de mezcla precursora por unidad de energía consumida) sobre las propiedades de los xerogeles de carbono.

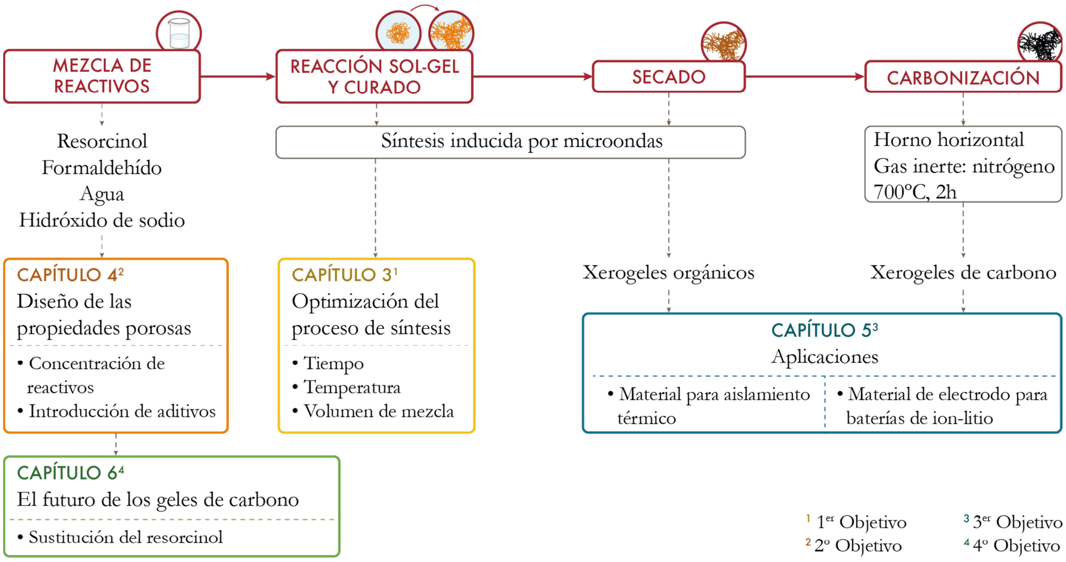

Figura 2.1. Planteamiento y objetivos de la Tesis Doctoral.

El calentamiento con microondas en la síntesis de geles de carbono no solo se aplica en la etapa de reacción sol-gel y curado sino también en la etapa de secado (Figura 2.1). La utilización de un horno microondas en esta última etapa, implica el empleo de condiciones de secado subcríticas. Por tanto, mediante la tecnología microondas se obtienen los llamados xerogeles orgánicos, que posteriormente pueden carbonizarse para obtener xerogeles de carbono. El proceso de carbonización se lleva a cabo para estabilizar térmicamente el material y modificar la microporosidad, pero el resto de las propiedades porosas (densidad, tamaño y volumen de poros, porosidad, etc.) depende fundamentalmente del proceso de síntesis del gel orgánico. Como se detalla en el Capítulo 1, algunas de las técnicas que pueden emplearse para diseñar estas propiedades porosas consisten en variar la naturaleza y la concentración de los reactivos utilizados y/o incorporar aditivos en la mezcla precursora. Con el propósito de evaluar el efecto de la concentración de los reactivos, el trabajo expuesto a lo largo de la presente memoria considera la naturaleza de los precursores como una variable constante, utilizando en la síntesis de todos los materiales los siguientes reactivos: resorcinol, formaldehído, agua e hidróxido de sodio. Por tanto, el **segundo objetivo** establecido se basó en el diseño de las propiedades porosas y estructurales de los xerogeles orgánicos resorcinol-formaldehído (RF) mediante la modificación de la concentración de los reactivos y la incorporación de aditivos en la mezcla precursora (Figura 2.1). El desarrollo de este segundo objetivo se detalla en el Capítulo 4. En la mayoría de los estudios mostrados en dicho capítulo, los xerogeles orgánicos RF se carbonizaron empleando siempre las mismas condiciones de operación (Figura 2.1). Dado que, como se ha mencionado anteriormente, la carbonización modifica la microporosidad pero no produce cambios en la meso-macroporosidad de los xerogeles orgánicos, puede considerarse que los efectos de las variables estudiadas en el Capítulo 4, sobre las propiedades porosas de los xerogeles orgánicos RF, se mantienen en sus correspondientes xerogeles carbonizados. Por lo que de ahora en adelante todas las consideraciones mostradas en la presente Tesis Doctoral se harán sobre la síntesis inducida por microondas de xerogeles de carbono, aunque a nivel práctico la tecnología microondas se utilice exclusivamente para obtener los xerogeles orgánicos RF.

Llegados a este punto es preciso destacar que, aunque es en la síntesis de los geles orgánicos donde realmente se controla la formación de la estructura polimérica, y por ende, las propiedades finales; más del 85% de los estudios de las últimas dos décadas están enfocados al estudio de los geles de carbono (Figura 2.2), mientras que solo el 15% versan sobre los geles orgánicos sin carbonizar. Esto se debe probablemente a que más del 50% de los estudios tratan sobre el empleo de materiales carbonosos en distintos campos de aplicación. Es cierto que algunas de las aplicaciones listadas en el Capítulo 1 requieren materiales carbonosos con elevada microporosidad y, por tanto, se deben utilizar geles de carbono. Sin embargo, existen otras aplicaciones en las cuales la idoneidad de los geles de carbono se basa en su estructura porosa y, sobretodo, en la posibilidad de poder diseñarla a medida. Para cumplir con estos requisitos no es necesario utilizar un material carbonizado, por lo que se podrían utilizar los xerogeles orgánicos. La posibilidad de utilizar los xerogeles orgánicos supone una gran ventaja comercial ya que se elimina la carbonización, una de las etapas más costosas del proceso de síntesis, disminuyendo los costes de la producción del material y, por tanto, incrementando su competitividad en el mercado frente a otros productos. Por este motivo, el **tercer objetivo** planteado en esta Tesis Doctoral fue la evaluación del potencial, no solo de los xerogeles de carbono, sino también de los xerogeles orgánicos. Por tanto, para alcanzar este tercer objetivo, se evaluó la adecuación de los xerogeles orgánicos resorcinol-formaldehído con diferentes propiedades como material para aislamiento térmico y la adecuación de los xerogeles de carbono como material de electrodo para baterías de ion-litio.

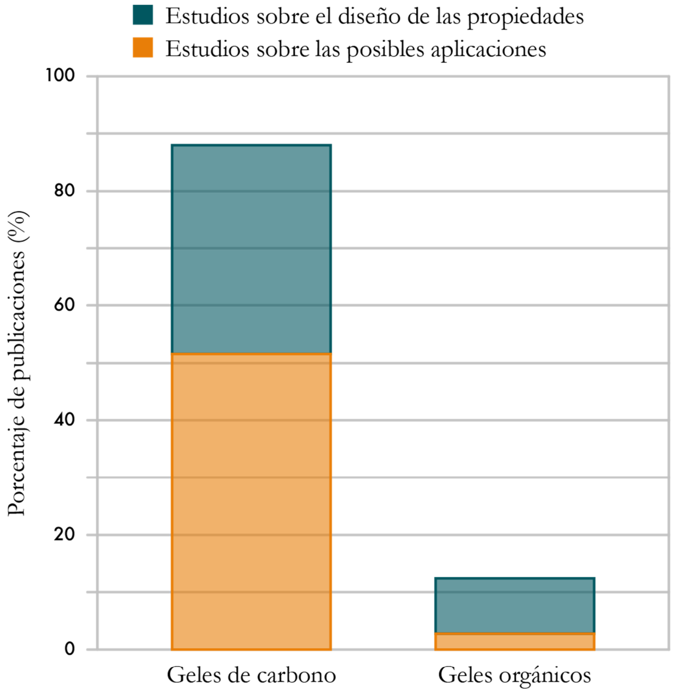

Figura 2.2. Porcentaje de estudios sobre geles de carbono y geles orgánicos publicados entre 1995 y 2015. Fuente: Scopus.

Estos tres primeros objetivos, cuyos estudios se detallan en los Capítulos 3, 4 y 5 de la presente memoria (Figura 2.1) abarcan el objetivo principal de esta Tesis Doctoral, que surge de la necesidad de optimizar el proceso de síntesis inducida por microondas de xerogeles de carbono, con el propósito de poder diseñar materiales porosos cuyas propiedades se ajusten a los requisitos demandados en distintos campos de aplicación. Todos los estudios realizados se llevaron a cabo a escala de laboratorio, no obstante, en todo momento se consideró la posibilidad de llevarlos a cabo a escala industrial. Y es aquí donde tiene cabida el último objetivo planteado para este trabajo. En los procesos industriales siempre es conveniente plantear nuevas perspectivas de futuro, tanto desde un punto de vista económico como medio ambiental, para poder obtener un producto más competitivo. En el caso concreto de los geles de carbono, un aspecto a tener en cuenta son los reactivos principales utilizados para preparar el gel orgánico, el resorcinol y el formaldehído, ya que son compuestos químicos de elevado coste económico y dañinos tanto para el ser humano como para el medio ambiente. Por tanto, el **cuarto objetivo** fijado fue discernir si el monómero principal de mayor coste, el resorcinol, podría ser sustituido por otro compuesto más respetuoso con el medio ambiente y, en la medida de lo posible, más económico; cuando se emplea la tecnología microondas como método de calentamiento.

CAPÍTULO 3

OPTIMIZACIÓN DEL PROCESO DE SÍNTESIS

3.1. CALENTAMIENTO CON MICROONDAS

El proceso de síntesis utilizado a lo largo de la presente Tesis Doctoral consiste en calentar mediante microondas la mezcla precursora a partir de la cual se obtienen los xerogeles orgánicos resorcinol-formaldehído (RF). El calor proporcionado por la radiación microondas se transfiere al material dieléctrico mediante dos mecanismos: rotación dipolar y conducción iónica [Jones 2002; Menéndez 2010]. Estos mecanismos permiten que la energía se disipe uniformemente dentro del material, proporcionando una distribución de temperatura uniforme (Figura 3.1a). Los mecanismos de aporte de calor mediante microondas tienen como resultado un calentamiento localizado que se produce de forma instantánea, de modo que la velocidad de calentamiento es muy superior a la del método convencional, mediante el cual la transmisión de calor se produce por conducción desde la superficie hasta el interior del material (Figura 3.1b).

La uniformidad de la distribución de la temperatura junto al aumento en la velocidad de calentamiento son dos de los factores por los que la tecnología microondas se emplea como método de calentamiento en muchos procesos industriales [Bermúdez 2015; Singh 2015]. Sin embargo, su uso en el campo de la síntesis de xerogeles RF es novedoso y, por tanto, es necesario evaluar qué variables juegan un papel importante en el proceso y qué efecto tienen sobre las propiedades de estos materiales.

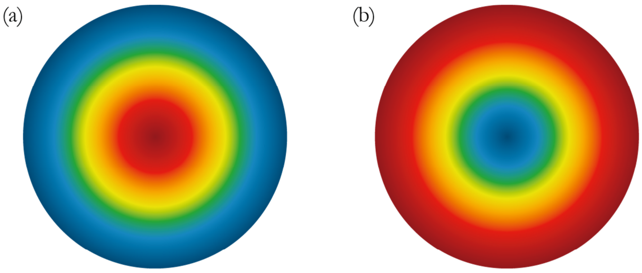

Figura 3.1. Distribución de la temperatura en el interior de materiales calentados mediante radiación microondas (a) y calentamiento convencional (b).

El dispositivo experimental utilizado en la síntesis de los xerogeles RF se muestra en la Figura 3.2a y Figura 3.2b. Se trata de un horno microondas multimodo que opera a una frecuencia de 2450 MHz y en cuyo interior se introduce un recipiente de vidrio, transparente a la radiación microondas, que contiene la mezcla precursora. El volumen del recipiente depende de la cantidad de material que se quiera sintetizar (Figura 3.2c).

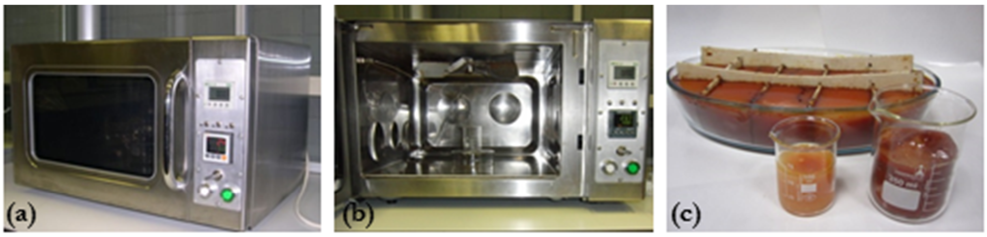

Figura 3.2. Dispositivo microondas (a) y recipientes de vidrio (b) utilizados en la síntesis de xerogeles orgánicos resorcinol-formaldehído.

El horno microondas consta de tres componentes que permiten controlar el proceso de síntesis: i) un termopar que mide la temperatura del material durante la reacción, ii) un controlador tipo PID que regula la temperatura y iii) un contador de energía eléctrica que permite llevar a cabo un seguimiento del consumo energético durante todo el proceso. Cabe destacar que, aunque estos tres componentes son fundamentales para controlar el proceso, la utilidad del contador de energía eléctrica se considera de especial interés. Se trata de un medidor de potencia conectado al horno microondas que registra y almacena el consumo energético en función del tiempo. El consumo energético necesario para mantener la temperatura del proceso, es decir, la cantidad de energía registrada, varía en función de las propiedades dieléctricas del material que se calienta. En el caso concreto de los geles orgánicos, las propiedades dieléctricas de la mezcla precursora cambian según avanza la reacción de polimerización, ya que esta mezcla pasa del estado líquido al estado sólido (método sol-gel). De este modo, puede cuantificarse el tiempo que requiere cada una de las etapas del proceso de síntesis.

3.2. VARIABLES FÍSICAS

El primer paso para conseguir la correcta optimización del proceso de síntesis inducida por microondas de xerogeles resorcinol-formaldehído (RF) es determinar la temperatura y el tiempo mínimos para que se produzca la reacción sol-gel y el curado de forma apropiada, es decir, para que se desarrolle la estructura porosa. Así mismo, se debe tener en cuenta que la cantidad de energía microondas absorbida por un material depende de varios factores tales como su orientación con respecto a las ondas, sus propiedades térmicas y dieléctricas y el tamaño de la muestra. En el caso concreto de los xerogeles RF puede considerarse que los dos primeros factores se mantienen constantes, ya que los materiales sintetizados a lo largo del presente trabajo son similares en cuanto a composición química y presentan una evolución parecida durante el proceso de síntesis. No obstante, es necesario evaluar el efecto de la relación del volumen de muestra por unidad de energía. El estudio de estas tres variables (temperatura y tiempo de síntesis, y volumen de muestra), llamadas variables físicas, no solo es de gran importancia para optimizar el proceso sino que también pueden tener una repercusión relevante en la reacción de polimerización y, por tanto, en las propiedades finales de los materiales. Por este motivo, la modificación de las variables físicas ha sido objeto de estudio durante la realización de esta Tesis Doctoral.

Objetivos

Los objetivos planteados para llevar a cabo dicho estudio fueron los siguientes:

- ✓ Evaluar el efecto de las variables físicas sobre las propiedades porosas de los xerogeles de carbono obtenidos a partir de xerogeles resorcinol-formaldehído sintetizados mediante calentamiento con microondas.

- ✓ Obtener las condiciones óptimas a escala de laboratorio que permitan obtener xerogeles de carbono porosos.

- ✓ Demostrar la posibilidad de transferir la tecnología microondas aplicada a la síntesis de xerogeles resorcinol-formaldehído a escala industrial.

Selección del rango de estudio

El estudio de las variables físicas consistió en evaluar el efecto sobre la porosidad de los xerogeles de carbono al utilizar dos temperaturas (75 y 85ºC), tres tiempos de síntesis (2000, 6000 y 10000 segundos) y tres volúmenes de mezcla precursora (30, 200 y 3000 ml). La selección del rango de estudio de las variables físicas se realizó considerando los siguientes aspectos:

- ➢ Selección de la temperatura de síntesis: el método convencional utilizado para sintetizar xerogeles resorcinol-formaldehído consiste en introducir la mezcla precursora en un horno eléctrico a 85ºC durante 72 horas. Esta temperatura fue inicialmente fijada por Pekala y colaboradores considerando que la temperatura no podía exceder los 100ºC, ya que en caso contrario se podría producir el hervor de la mezcla precursora [Pekala 1989]. En 2006, Nathalie Job y colaboradores demostraron que la modificación de la temperatura entre 50 y 90ºC no tiene un efecto significativo en las propiedades porosas del material pero sí en el tiempo de síntesis necesario para completar las etapas de reacción sol-gel y curado, que se ve incrementado al aumentar la temperatura [Job 2006a]. Este incremento de tiempo implica elevar los costes de producción sin que ello suponga una mejora en las prestaciones del producto. Por otro lado, se debe tener en cuenta que la energía aportada por unidad de tiempo mediante el dispositivo microondas es muy superior a la aportada mediante el método convencional. Como consecuencia, es posible que la variación de un grado centígrado en el horno microondas pueda tener un efecto mayor que en un horno eléctrico. Por estos motivos, en el presente estudio se consideró una variación de la temperatura de tan solo 10ºC.

- Selección de los tiempos de síntesis: Calvo y colaboradores estudiaron los efectos de sintetizar xerogeles resorcinol-formaldehído mediante calentamiento con microondas [Calvo 2013a]. Con este estudio demostraron que la utilización de la tecnología microondas como método de calentamiento da lugar a materiales cuyas propiedades son comparables a las obtenidas mediante el método convencional. En este estudio establecieron el tiempo de síntesis en 10000 segundos. Con el objetivo de determinar si es posible reducir el tiempo de síntesis, y con ello disminuir los costes de producción, en este estudio se evaluó la posibilidad de utilizar tiempos inferiores: 10000, 6000 y 2000 segundos.

- Selección del volumen de mezcla precursora: en el estudio realizado por Calvo y colaboradores mencionado anteriormente, los materiales se prepararon a partir de 30 ml de mezcla precursora [Calvo 2013a]. La aplicabilidad de la tecnología microondas a escala industrial requiere sintetizar mayores cantidades de material. Por este motivo, en este estudio se incrementó el volumen desde 30 ml hasta 3000 ml.

Todos los xerogeles utilizados para el estudio fueron sintetizados a partir de la misma concentración de reactivos fijando el valor del pH en 6.5, el grado de dilución en 5.7 y el ratio molar resorcinol-formaldehído en 0.5. La evaluación del efecto de las variables físicas sobre las propiedades de los xerogeles de carbono se llevó a cabo utilizando la versión de prueba del software estadístico comercial Design-Expert (Stat-Ease, Inc.).

Conclusiones

Los detalles experimentales y los resultados obtenidos en este estudio se describen y discuten en la Publicación II incluida al final de esta sección. Las principales conclusiones de dicha publicación se detallan a continuación:

- La variación de 10ºC en la temperatura de síntesis, entre 75 y 85ºC, no tiene ningún efecto directo en las propiedades porosas de los xerogeles de carbono. Sin embargo, modifica ligeramente el tiempo de síntesis requerido para completar la reacción sol-gel y el curado de los xerogeles RF. De modo que, cuanto menor es la temperatura, mayor es el tiempo necesario para completar la síntesis.

- El tiempo de síntesis tiene un efecto directo en la mesoporosidad del material, mientras que la microporosidad se mantiene intacta. Un aumento de un 66% en el tiempo de síntesis da lugar a un incremento de aproximadamente un 30% en el volumen de mesoporos, sin embargo el tamaño de los mesoporos apenas varía. Estos resultados se deben a que la síntesis de cada muestra finalizó en un momento distinto del proceso. A partir del registro de la energía consumida por el microondas en función del tiempo, se deduce que 2000 segundos no es tiempo suficiente para que finalice la etapa de curado. La estructura de los materiales obtenidos está poco entrecruzada y no tiene la rigidez necesaria para contrarrestar las fuerzas de capilaridad producidas durante la etapa de secado. De modo que se generan elevadas tensiones superficiales que producen la retracción de la estructura. Un aumento en el tiempo de síntesis hasta 6000 segundos permite finalizar la etapa de curado. Con ello se consiguen materiales con una estructura polimérica correctamente entrecruzada. La resistencia mecánica de estos xerogeles es suficiente para contrarrestar las tensiones superficiales evitando contracciones en la estructura. Las muestras obtenidas a partir de 10000 segundos también presentan una estructura correctamente entrecruzada. Sin embargo, durante el proceso de síntesis de estas muestras finaliza la etapa de curado y el material comienza a secarse. Tras este proceso se lleva a cabo la etapa propia de secado, de modo que el material permanece mucho más tiempo bajo el efecto de las tensiones superficiales y se produce una ligera contracción de la estructura. En consecuencia, los xerogeles RF sintetizados durante 10000 segundos presentan un volumen de mesoporos ligeramente menor al de los materiales sintetizados durante 6000 segundos.

- La síntesis de xerogeles de carbono a partir de pequeños volúmenes de mezcla precursora (30 ml) da lugar a estructuras poliméricas menos porosas que cuando se utilizan volúmenes más grandes. La energía aportada por el horno microondas es muy elevada y, cuando se sintetizan materiales a partir de 30 ml, las etapas de reacción sol-gel y curado se producen a gran velocidad. Este incremento en la velocidad de calentamiento tiene un efecto similar al de incrementar el tiempo de síntesis por encima de 10000 segundos y, por tanto, los xerogeles RF presentan menor mesoporosidad. La utilización de 200 o 3000 ml de mezcla precursora da lugar a materiales más porosos, cuyas estructuras poliméricas son prácticamente idénticas. Este resultado es de gran importancia ya que demuestra la viabilidad de escalar el proceso de síntesis, siempre y cuando se seleccione el volumen de mezcla precursora en función de la potencia del dispositivo microondas.

PUBLICACIÓN II

OPTIMIZATION OF THE PROCESS VARIABLES IN THE MICROWAVE-INDUCED SYNTHESIS OF CARBON XEROGELS

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ORIGINAL PAPER

Optimization of the process variables in the microwave-induced synthesis of carbon xerogels

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Abstract Carbon xerogels (CX) can be synthesized by microwave-assisted heating. The transfer of this technology to an industrial scale passes through the optimization of the variables that affect the process. The effect of the main operational variables, i.e., initial volume of the precursor, gelation and ageing time and temperature of the synthesis, on the final porous properties of CX has been evaluated. It was found that the development of porosity in the CX synthesised in the microwave oven is hardly influenced by the increase in the initial volume of the precursor solution. This suggests that it is feasible to scale up the production of these materials by means of microwave heating. Furthermore, the consumption of energy does not increase in proportion to the volume of xerogel synthesized. Thus, the process is energy efficient, saves a considerable amount of time and requires only a single device to carry it out. These advantages, along with the fact that a temperature variation of 10 °C is not determinative in the xerogels' final properties, indicate that CX could be produced on a large scale in a cost effective way.

Keywords Microwave · Temperature · Carbon gels · Gelation time · Gelation point · Pore size distribution

1 Introduction

Carbon gels are porous materials that are prepared by drying and carbonizing organic polymer-based gels [1]. One of the advantages of these materials is that it is possible to design their porosity and chemical properties provided that the synthesis conditions are correctly chosen [2]. Using an appropriate preparation method it is possible to tailor materials for a specific application. For this reason, over the last decade, carbon gels have been studied in a wide range of fields including adsorption [3, 4], thermal insulation [5, 6], catalyst supports [7, 8], supercapacitors [9, 10], fuel cells [11, 12], batteries [13, 14], etc.

Nowadays, the most common process used to synthesize carbon gels is based on Pekala's method [15]. The synthesis involves a sol–gel reaction between resorcinol and formaldehyde in an aqueous medium containing sodium carbonate as catalyst followed by a drying stage. Three major types of drying methods can be found in the bibliography: drying under supercritical conditions [16–18], freeze-drying [19, 20] and evaporative drying [21]. The dried gel is then subjected to secondary treatments (pyrolysis, activation, etc.) in order to obtain the final carbon gel [22–25].

The main drawback of this conventional method is the long time required for the synthesis, making the production process expensive and uncompetitive. Because of this, the synthesis method of carbon gels has been studied in depth by several research groups. Quin et al. [26] reported a semi-continuous drying process for the synthesis of carbon aerogels. They simplified the production process by eliminating the step of solvent and liquid carbon dioxide exchange. An alternative drying step by means of microwave heating has been studied in order to simplify the process and to reduce time and associated costs [27]. Ultrasonic irradiation has also been considered as a complementary technique for the synthesis of carbon xerogel (CX) [28]. Despite these improvements, several days are still required for the synthesis which is an obstacle to industrial scaling up. In 2011 a method that reduces the

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synthesis time by as much as 95 % was reported by Calvo et al. [29]. This method involves microwave radiation heating instead of conventional heating, allowing carbon gels with similar characteristics to those synthesized by the conventional method to be produced more quickly.

It is well known that the structure of carbon gels is sensitive to variations in the synthesis and processing conditions [30]. Hence, the effect of such variations on the final porous properties must be determined, especially if the objective is to optimise the process for large-scale carbon gel production. Several works published in the literature on the conventional method allude to the influence of the precursor concentration [2, 31], the temperature of synthesis [32, 33], ageing time [34], drying and pyrolysis conditions [35, 36], etc. However, there is a lack of knowledge on how the final porous properties are affected when microwave-assisted synthesis is applied. This process differs in that the heating is volumetric and involves the interaction of the materials with the microwaves, instead of convection as in conventional ovens. It is therefore necessary to know whether microwave heating technology is susceptible to the variation of operating conditions and, if so, the degree of this dependence.

Accordingly, the aim of this work was to study the influence of the operational variables of the microwave-assisted synthesis process, such as the initial volume of precursor solution, gelation and ageing time and temperature of synthesis, on the final porous properties of CX. Optimization of these variables will contribute to the transfer of microwave-assisted technology for the production of CX to an industrial scale.

2 Experimental

2.1 Preparation of precursor solutions

Organic gels were synthesized by the polycondensation of resorcinol (R) and formaldehyde (F) using deionized water as solvent and sodium hydroxide as catalyst. Resorcinol (Indspec, 99 %) was first dissolved in deionized water in an unsealed glass beaker under magnetic stirring. After dissolution, formaldehyde (Ercros, 37 wt% in water, stabilized by 10–15 % methanol) was added and the mixture was stirred until a homogeneous solution was obtained. Finally, the initial pH value was adjusted by adding sodium hydroxide.

In all cases, the precursor solutions were synthesized using the stoichiometric R/F molar ratio (i.e., 0.5) and a dilution ratio (D) fixed at 5.7. The dilution ratio parameter is defined as the molar ratio between the total solvent and reactants. Total solvent refers to the water and methanol contained in the formaldehyde and the deionized water that is added, whilst reactants refer to the resorcinol and formaldehyde. All the CX were synthesized using the same precursor solution pH, i.e. 6.5, as the aim was to evaluate the influence of the operating variables in the microwave device, i.e. temperature, time and initial volume, and not the chemical variables. However, other different pH values were also tested and the conclusions drawn from this study were valid for this entire range of pH values studied.

2.2 Synthesis conditions

Three different initial volumes of precursor solution were prepared in order to study their effect on the porous properties of the organic and CX: 30, 200 and 3,000 ml. Each solution was placed in a microwave oven at 85 °C for 10,000 s to undergo the gelation and ageing stages. At these stages a PID controller modulates de power delivered by the magnetron to the appropriate fraction of is maximum power (i.e., 700 W) in order to keep constant the settled temperature. 200 ml was selected as the most appropriate volume for studying the influence of other variables e.g., temperature or time.

The synthesis temperatures were chosen bearing in mind that: it is not advisable to set the temperature too close to the temperature of boiling water and that temperatures below 60 °C lead to a significant increase in the gelation time and in the cost of the process. This has already been reported for conventional procedures [34] and corroborated in the laboratory for microwave-assisted synthesis. Hence, the optimum temperature is between 70 and 90 °C. 75 and 85 °C were chosen as the temperatures for this study.

The time of the synthesis of the organic xerogels (OX), t_s, includes the gelation, ageing and drying stages. In this study, the time of synthesis was divided into two different variables: the time required for the sol–gel reactions and ageing, $t_{g\text{–}a}$, and the time needed to dry the excess solvent, t_d. Three values of $t_{g\text{–}a}$ were tested: 2,000, 6,000 and 10,000 s. After the formation of the polymeric structure, excess water was eliminated by continuing to heat the gel in the same microwave oven for a longer time, t_d, which will depend on the type of porous structure created. This drying step was conducted until a mass loss of over 50 % was achieved.

2.3 Microwave heating

During the synthesis process the material evolves and changes its dielectric properties [37]. These changes lead to a variation in its microwave absorption capacity and therefore in the energy consumed by the equipment to maintain the programmed temperature. Consequently, by monitoring the energy consumed by the microwave oven during the gelation and ageing stages it is possible to identify the transformations that take place during the synthesis of the OX [38]. In this study, a microwave device equipped with a power meter was used to measure the amount of energy consumed by the equipment during the gelation and ageing stages (t_{g-a}) as explained elsewhere [38].

2.4 Preparation of the carbon xerogel

Carbon xerogels were obtained by the pyrolysis of OX. The operational conditions were fixed as reported elsewhere [39]. Briefly, the pyrolysis processes were performed in a horizontal tubular furnace at 700 °C under a nitrogen flow of 500 ml/min. The residence time was 2 h and the heating rate was set at 50 °C/min.

2.5 Porous texture characterization

The porous texture of the organic and carbon gels was characterized by the analysis of nitrogen adsorption–desorption isotherms at −196 °C using a Micromeritics Tristar 3000 instrument. The specific surface area (S_{BET}) was evaluated by means of the BET equation, the micropore volume (V_{DUB}) was determined by applying the Dubinin–Raduskevich method to the nitrogen adsorption isotherms and the pore volume (V_P) was calculated from the volume adsorbed at saturation point.

2.6 Statistical study

The response surface method (RSM), in the form of central composite design (CCD), was applied in order to evaluate the effects of two of the synthesis conditions selected: temperature and t_{g-a}. The experimental design approach and the RSM were applied by using Design-Expert 8.0.7.1 Trial software. The experiments were randomized to validate the statistical results. The micropore volume (V_{DUB}), pore volume (V_P) and pore size (D_P) were selected as the responses of the system while the two process parameters, temperature and t_{g-a}, were fixed as input variables.

2.7 Sample nomenclature

Throughout the paper, the samples were labelled as follows. The letters OX and CX refer to the organic and carbon xerogel, respectively. These are followed by three different numbers separated by hyphens that correspond respectively to: (1) the initial volume, (2) gelation and ageing time and (3) temperature of synthesis. For example, the label CX-200-6000-75 corresponds to a carbon xerogel synthesized from 200 ml of precursor solution at a t_{g-a} of 6,000 s at 75 °C.

3 Results

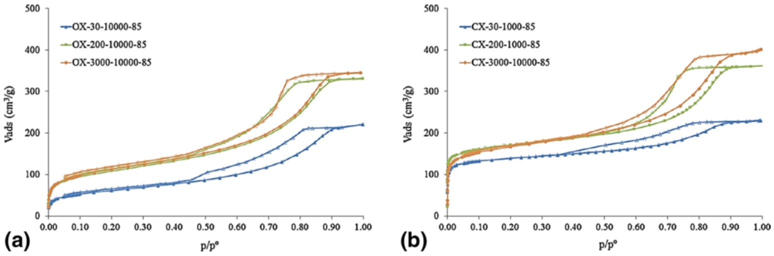
3.1 Influence of the initial volume of precursor solution

The nitrogen adsorption–desorption isotherms of the OX prepared using different initial volumes of precursor solution with a pH of 6.5, and their carbonised counterparts are shown in Fig. 1a, b, respectively. The samples shown were synthesized at a t_{g-a} of 10,000 s at 85 °C in order to ensure completion of the gelation and ageing stages.

Figure 1a exhibits isotherms of type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification, corresponding to mesoporous materials. The OX synthesized from 30 ml of initial solution presents an isotherm with a low volume of nitrogen adsorbed at low relative pressures, which indicates the presence of a small volume of micropores. Furthermore, the nitrogen adsorbed at high relative pressures is also low because of the presence of mesopores of small size. Samples OX-200-10000-85 and OX-3000-10000-85 exhibit isotherms that are almost superimposed, suggesting that porous development is not proportional to the increase in the initial volume of precursor solution.

The adsorption–desorption isotherms of the carbonised samples correspond to an isotherm combination of type I and type IV according to the IUPAC classification, indicating that they are micro/mesoporous materials (Fig. 1b).

Fig. 1 N_2 adsorption–desorption isotherms of organic (**a**) and carbon (**b**) xerogels synthesized using different initial volumes of precursor solution



These samples exhibit the same trend as their corresponding OX (Fig. 1a). That is to say CX-30-10000-85 presents the least developed structure and samples CX-200-10000-85 and CX-3000-10000-85 exhibit similar porous structures, as can be seen from Table 1.

Figure 2a, b show marked differences between the pore size distribution of the organic and CX. Thus, the micropore volumes increase notably after carbonization, whereas the mesopore size distributions seem to be narrower, although for all samples, the average pore diameter is around 8–9 nm.

The fact that samples synthesized from 200 to 3,000 ml of precursor solution exhibit similar porous structures favours the transfer of microwave-assisted technology for the production of CX to an industrial scale. However, a study of the energy consumed by the microwave is needed to perform the scaling-up. In this work, the amount of energy consumed throughout the gelation and ageing stages ($t_{g–a}$) was measured by a power meter connected to the microwave device. Greater initial volumes of precursor require a higher energy supply for the gelation and ageing stages to be completed, due to the fact that a longer time is needed to reach the programmed temperature, as can be seen from Table 2. Nevertheless, the microwave energy consumed per volume unit decreases as the initial volume of precursor increases. Initially, as the energy consumed per volume unit decreases, the development of porosity enhanced. However, a decrease to below 1,100 kJ/l in the amount of microwave energy consumed will not lead to any further development of porosity. Therefore, in order to optimize the synthesis process the optimum ratio between the energy consumed per volume unit and the porous structure obtained needs to be established.

3.2 Influence of gelation and ageing time

Figure 3a, b show the N_2 adsorption–desorption isotherms of the CX synthesized at 75 and 85 °C, respectively, for three different values of $t_{g–a}$. All the isotherms are a combination of type I and type IV according to the IUPAC classification, indicating that these samples correspond to micro/mesoporous materials.

Table 1 Porous properties of organic and CX synthesized by using different initial volumes

Samples	S_{BET} (m^2/g) ±0.5	V_{DUB} (cm^3/g) ±0.01	V_P (cm^3/g) ±0.06	D_p (nm) ±1
OX-30-10000-85	227	0.08	0.34	8
OX-200-10000-85	398	0.14	0.51	10
OX-3000-10000-85	413	0.15	0.54	10
CX-30-10000-85	535	0.21	0.36	9
CX-200-10000-85	643	0.24	0.56	9
CX-3000-10000-85	619	0.23	0.62	8

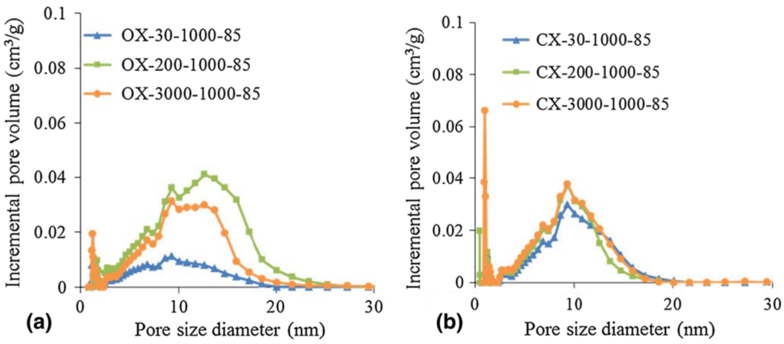


Fig. 2 Pore size distribution of organic (**a**) and carbon (**b**) xerogels synthesized using different initial volume of precursor solution

Table 2 Time and energy consumed during the microwave-assisted synthesis of OX

	OX-30-10000-85	OX-200-10000-85	OX-3000-10000-85
Time for set point [T (s)]	50 ± 20	78 ± 20	1,115 ± 20
Time of synthesis [t_s (s)]	19,020 ± 60	22,600 ± 60	23,700 ± 60
Energy consumed (kJ/l)	43,300 ± 50	8,500 ± 500	1,100 ± 50

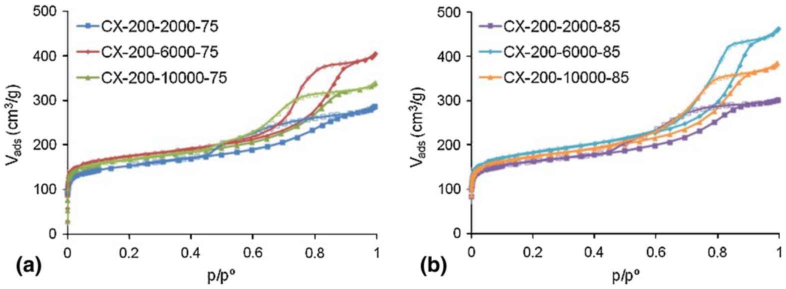


Fig. 3 N_2 adsorption–desorption isotherms of CX synthesized at 75 °C (**a**) and 85 °C (**b**)

Table 3 Time needed to complete each synthesis stage

Samples	Gelation time (visual observation), t_g (s) ±60	Gelation time (change in the slope), t_g (s) ±90	Ageing time, t_a (s)	Drying time (s)	Total synthesis time (s)
CX-200-2000-75	1,680	1,320	680	7,200	9,200
CX-200-6000-75	1,680	1,320	4,680	14,400	20,400
CX-200-10000-75	1,680	1,320	8,680	10,800	20,800
CX-200-2000-85	1,080	900	1,100	9,000	11,000
CX-200-6000-85	1,080	900	5,100	12,600	18,600
CX-200-10000-85	1,080	900	9,100	12,600	22,600

Table 4 Main porous properties of CX synthesized at 75 and 85 °C

Samples	S_{BET} (m^2/g) ±0.5	V_{DUB} (cm^3/g) ±0.01	V_P (cm^3/g) ±0.06	D_p (nm) ±1
CX-200-2000-75	578	0.22	0.44	7
CX-200-2000-85	617	0.23	0.46	7
CX-200-6000-75	660	0.25	0.63	10
CX-200-6000-85	684	0.26	0.71	10
CX-200-10000-75	635	0.24	0.52	8
CX-200-10000-85	655	0.25	0.60	9

The curves are almost superimposed up to a relative pressure of 0.4, indicating that all the samples have a similar microporosity. At both synthesis temperatures, the isotherms of the samples with a $t_{g–a}$ of 6,000 s exhibit an increase in the volume of nitrogen adsorbed at relative pressures above 0.8, which results in materials with a higher volume of mesopores.

The accumulative energy consumed by the microwave device was measured as a function of gelation and ageing time ($t_{g–a}$). As mentioned elsewhere, the representation of energy consumed versus time allows the gelation point to be established [38]. This time was also determined by visual observation. Both values are presented in Table 3. From these data it can be inferred that, under the conditions studied, the gelation times recorded visually were larger than those obtained by measuring the energy consumption. This is due to the fact that the transition from sol to gel occurs gradually, making visual determination very difficult and inaccurate.

All the samples studied were subjected to an exclusive drying stage at 85 °C after synthesis, until a mass loss of more than 50 % was achieved. The time needed for drying is also provided in Table 3.

3.3 Influence of synthesis temperature

The main porous properties of the CX synthesized at 75 and 85 °C for three different values of $t_{g–a}$ are reported in Table 4. The porosity of the samples is not greatly affected by the temperature variation studied in this work, i.e. 10 °C. This may be due to the fact that there was no significant variation in the gelation point with the variation in temperature: 1,320 and 900 s at 75 and 85 °C, respectively (Table 2). As mentioned above, temperature and $t_{g–a}$ are

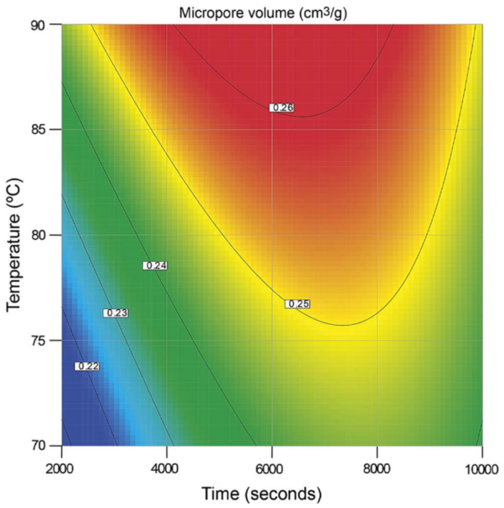


Fig. 4 Variation of the volume of micropores with t_{g-a} and temperature of synthesis

not independent variables in relation to porous textural properties. Hence, the possible interaction between these variables was evaluated by applying the RSM approach.

3.4 Response surface methodology (RSM) and statistical analysis

The implementation of RSM allows the interaction between temperature and t_{g-a} and their effect on the main porous properties to be evaluated with a minimum number of experiments. An analysis of variance (ANOVA) for each response was performed in order to determine whether the model selected was sufficiently significant to fit the experimental results. The CCD was used as the experimental design. The significance of each input variable and its interaction was determined by evaluating the *p* value. If *p* values are smaller than 0.05 the corresponding variable will have a significant effect on the response. In this study, the RSM statistical analysis showed an adequate fit of a quadratic function type.

3.4.1 Effect on the microporosity

The ANOVA results applied to microporosity indicate that time and temperature were important factors in the model. However, the interaction between these two variables was not an important factor as the *p* value was 0.2432. An R^2 value of 0.9952 was obtained, which is very close to the predicted R^2 value of 0.9477, indicating the adequacy of the model. Figure 4 shows the contour line plot corresponding to the effect of t_{g-a} and temperature on the microporosity. From the contour plot it can be inferred that, under the conditions studied, t_{g-a} has a greater effect than the variation in temperature.

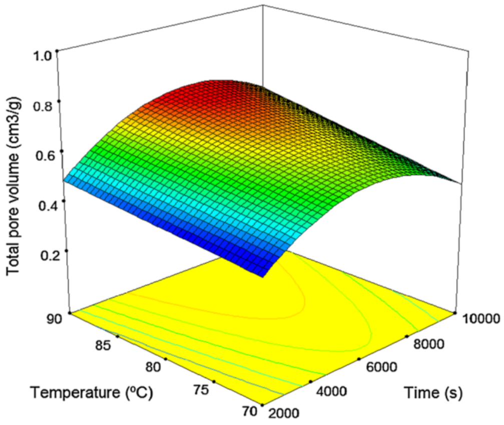


Fig. 5 Evolution of the total volume of pores with t_{g-a} and temperature of synthesis

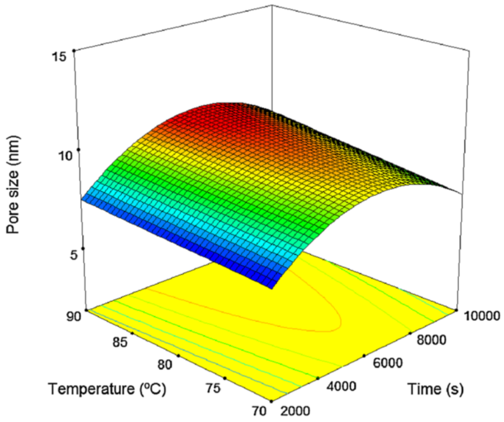


Fig. 6 Evolution of pore size with t_{g-a} and temperature of synthesis

3.4.2 Effect on the total pore volume

The model was also found suitable for the total pore volume. An R^2 value of 0.9881 was obtained, which is very close to the predicted R^2 value of 0.8403 again indicating the adequacy of the model. The *p* values obtained show that temperature is not a significant model term, while the second order effect of t_{g-a} is an important factor that affects the model. In fact, the total pore volume increases by 40 % when the time is increased from 2,000 to 6,000 s. Then it decreases when time is increased to 10,000 s. Figure 5 shows the effect of both time and temperature on the total pore volume.

3.4.3 Effect on the mean pore size

The ANOVA results applied to the mean pore size indicate that $t_{g–a}$ and its second order effect are significant model terms with *p* values of 0.0438 and 0.0214, respectively. The R^2 and predicted R^2 values were 0.9957 and 0.9531, respectively, indicating the good predictive capacity of the model. The evolution of pore size with time and temperature can be inferred from Fig. 6.

4 Discussion

The transfer of microwave-assisted technology for the production of CX to an industrial scale requires the study of the effect of the operational variables on the final porous properties of the material.

Using 30 ml of precursor solution leads to a less developed material than that obtained with higher volumes of solution. This may be due to the excess of power used in the microwave oven for such a small volume of precursor solution. However, samples synthesized from 200 to 3,000 ml of solution exhibit isotherms that are almost superimposed, suggesting that the development of porosity can be fully controlled even with a high initial volume of precursor solution. In addition, the development of porosity in these CX with microwave heating is analogous to that obtained in a conventional oven, as already reported in previous works [29].

Furthermore, by decreasing the energy consumed per volume unit it is possible to enhance the porous development of the samples. But the fact that the samples synthesized from 200 to 3,000 ml exhibit a similar porous structure indicates that a decrease to below 1,100 kJ/l in the microwave energy consumed will not lead to any further development of porosity. From these results it can be inferred that it is possible to synthesize a high amount of xerogel using less microwave energy and at the same time maintain the structural properties. This will result in a reduction in energy costs and a more competitive process. Thus, the application of microwave-assisted synthesis of carbon xerogel on an industrial scale appears feasible provided the energy consumed per volume unit is correctly chosen.

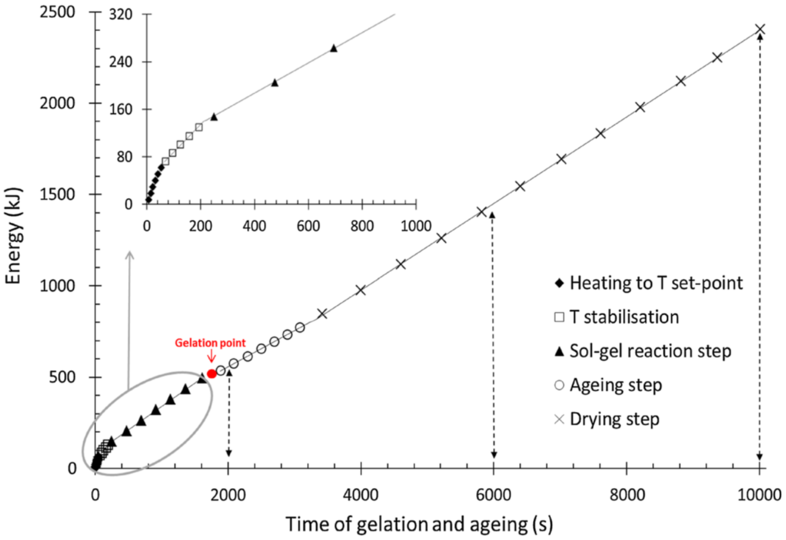
When these samples were carbonised their microporosity increased, whereas the mesopore volume decreased. These results are in accordance with those of previous works where it was demonstrated that during carbonization volatiles are released, leading to the formation of new micropores and to the reduction in size of some pores owing to the partial collapse of the pore structure [2]. The combination of both factors (micropore formation and the decrease in mesopore size) led to an increase in microporosity and a narrower mesopore size distribution, both in the case of the conventional CX widely presented in the bibliography and in the case of the CX obtained by microwave heating presented in this work.

Since the samples synthesized at pH of 6.5 from a 200 ml initial volume of precursor exhibited a well-developed porous structure, this value was chosen to study the influence of the gelation and ageing time ($t_{g–a}$) and temperature of synthesis. For both synthesis temperatures, 75 and 85 °C, the samples with a $t_{g–a}$ of 6,000 s exhibited the highest volume of mesopores. The maximum porous development was achieved when the time, $t_{g–a}$, was fixed at an intermediate value. This can be attributed to the microwave energy consumed during the synthesis process, as explained below.

The amount of energy consumed by the microwave device varies depending on the dielectric properties of the material to be heated [37]. In the case of organic gels synthesis, these dielectric properties change during the process and therefore the energy consumed by the microwave oven depends on the stage of synthesis [38]. In the present work, the accumulative energy consumed by the microwave device was measured as a function of gelation and ageing time ($t_{g–a}$). Given that the representations are similar for all the xerogels studied, only the one corresponding to sample OX-200-10000-75 is shown here as an example (Fig. 7).

Figure 7 shows five straight lines of different slope. The first one corresponds to the increase in temperature up to the set point was reached (58 s); the second one represents the stabilization of the temperature (3–4 min) and the third line indicates the sol–gel reactions step. The crosslinking and the secondary reactions take place during the transition from the sol to the gel up to the point where a stable solid material is formed. The third change in slope shown in Fig. 7 (i.e. 1,320 s) corresponds to the gelation point, which was also determined by visual observation (1,680 and 1,080 s for the samples synthesized at 75 and 85 °C, respectively, as shown in Table 3). Under the conditions established for this study, the gelation times obtained visually are longer than those obtained by measuring the change in the slope of energy consumption because the transition from gel to sol occurs gradually and is difficult to determine visually. This phenomenon is consistent with another published study where differences in the gelation time obtained by rheology and visually were reported [34]. However, the methodology followed in the present work allows the gelation point to be determined inside the synthesis device, i.e. without the need for any additional technique.

Fig. 7 Microwave energy consumption versus time of gelation and ageing (sample OX-200-10000-75)



According to the changes in slope shown in Fig. 7, a t_{g-a} of 2,000 s is not long enough for the crosslinking and the secondary reactions to be concluded. The result is a material with poorly connected primary particles and small weakly linked aggregates of nodules [33]. During the drying stage the material cannot withstand the surface tensions and probably undergoes further shrinkage [2]. These samples, regardless of the synthesis temperature, correspond to an unstable material with weakly linked clusters. During drying the shrinkage increases and the carbonised materials exhibit a porous structure that is less developed than the porosity of those synthesized for a longer time (Fig. 3).

Once a stable solid material is obtained, it is necessary to remove the solvent by drying. However, during the synthesis process itself, partial evaporation of the dissolvent occurs while the ageing process continues. At this point, when the ageing stage and partial evaporation are taking place simultaneously, more energy is required to maintain the programmed temperature [29]. This phenomenon is consistent with Fig. 7, where a change in slope appears at around 58 min (i.e. 3,500 s). During the partial evaporation of the solvent the material undergoes shrinkage. The longer the partial evaporation stage lasts, the greater the shrinkage of the material, as a consequence of which the volume of mesopores decreases. This is also in agreement with the nitrogen adsorption–desorption isotherms shown in Fig. 3, where samples synthesized for 6,000 s show a higher mesoporosity development than those synthesized for 10,000, regardless of the synthesis temperature.

It should be noted that, although ageing and partial drying occur simultaneously, all the samples studied were subjected to an exclusive drying stage at 85 °C after synthesis, until a mass loss of more than 50 % was achieved. The time needed for drying depends on the ageing time, and consequently on the t_{g-a}. High values of t_{g-a} lead to materials with more strongly linked aggregates [33]. The structure of these stable solid materials impedes the evaporation of the solvent, with the result that the drying time needs to be longer (Table 3).

Regarding the influence of the synthesis temperature, it can be concluded that the porosity of the samples is not greatly affected by the temperature variation used in this work, i.e. 10 °C. These results are in agreement with those reported by [21] where no significant influence on the final properties of CX synthesized from a precursor solution with a pH of 6.5 was observed when the temperature was increased from 70 to 90 °C in a conventional oven.

The fact that a change in temperature of 10 °C has no effect on the final porous properties is due to the non-significant variation in the gelation point, as shown in Table 2. These results were corroborated by the implementation of RSM, which showed that the interaction between these variables had a negligible effect on the porous properties under the synthesis conditions studied.

With respect to the porous properties, only a very slight effect on the microporosity was observed in the range of t_{g-a} and temperature of synthesis studied. These results are in accordance with other studies reported where no increase in microporosity development occurred when the synthesis conditions were modified in conventional synthesis [35]. The effect of the variables studied was a little more pronounced in the case of the total pore volume, which increased by 40 %

with the increase in time from 2,000 to 6,000 s. The pore size range of all the samples studied was between 7 and 10 nm and therefore the effect of both input variables on the pore size can be considered negligible. These negligible effects on the porous properties, when the time and temperature of synthesis vary, represent a great advantage for scaling up the production of CX.

5 Conclusions

The influence of the operational variables on the final porous properties of CX was studied. The results show that by means of microwave-assisted synthesis it is possible to synthesize OX from 3,000 ml of precursor solution, and produce a material with a well-developed and controlled porous structure. Furthermore, if a higher volume of precursor solution is used, the energy consumption per volume unit was lower than that needed for smaller initial volumes of precursor solution.

The time needed to complete the gelation and ageing stages plays an important role in the final porous properties. Both short and long times, i.e. 2,000 and 10,000 s, respectively, lead to materials in which the carbon structure collapses and the development of porosity decreases. Optimization of the gelation and ageing time seems to be the key to controlling porosity.

Furthermore, the porous properties of CX prepared by microwave synthesis show little susceptibility to the temperature variation in the range studied, i. e. 75–85 °C. Very little interaction between temperature and gelation time was observed in the operating conditions studied. All of the results obtained indicate that the synthesis of CX by microwave radiation produces materials analogous to those obtained by conventional synthesis, via a process that is considerably more cost-effective, as only one device and moderate conditions are needed. Thus, the production of CX on an industrial scale appears feasible.

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3.3. CONCLUSIONES

Del estudio de las variables físicas se determinan las condiciones óptimas del proceso de síntesis asistida por microondas de xerogeles resorcinol-formaldehído. Éstas consisten en fijar una temperatura de 85ºC y un tiempo de 6000 segundos, cuando se utilizan volúmenes de mezcla precursora entre 200 y 3000 ml. Sin embargo, cabe destacar que dicho estudio se llevó a cabo a partir de mezclas precursoras preparadas con las mismas concentraciones de reactivos. En función de estas concentraciones, el tiempo necesario para que se produzca la reacción sol-gel y el curado puede variar y, por tanto, cada material necesita un tiempo de síntesis acorde a la mezcla precursora seleccionada. La utilización de 10000 segundos como tiempo óptimo asegura la finalización de la reacción sol-gel y el curado de todos los materiales, independientemente de la concentración de los reactivos. Por otro lado, dado que no se encontraron grandes diferencias entre las propiedades porosas de los materiales sintetizados a partir de 200 y 3000 ml, para el desarrollo de la presente Tesis Doctoral se considera más conveniente obtener los materiales a partir de 200 ml de mezcla precursora para evitar un gasto innecesario de consumibles. En conclusión, en base a los resultados obtenidos en la Publicación II, todos los xerogeles RF obtenidos en los estudios incluidos en los siguientes capítulos se sintetizaron bajo las siguientes condiciones de síntesis: 85ºC, 10000 segundos y 200 ml de mezcla precursora.

CAPÍTULO 4

DISEÑO DE LAS PROPIEDADES POROSAS

Una de las grandes ventajas de los xerogeles de carbono es la posibilidad de diseñar a medida sus propiedades porosas de modo que encajen perfectamente en los requisitos de diferentes aplicaciones. El diseño de las propiedades se consigue mediante el control de la reacción de polimerización, ya que en función de cómo se produzca esta reacción, la estructura polimérica se forma de manera distinta y, por tanto, los materiales presentan diferentes propiedades. La reacción de polimerización depende, fundamentalmente, de la naturaleza y concentración de los reactivos. No obstante, el curso normal de la reacción puede alterarse mediante la introducción de aditivos en la mezcla precursora, proporcionando un mayor control en el diseño de las propiedades. Por lo tanto, este capítulo está enfocado al estudio del efecto que produce, sobre las propiedades porosas de los xerogeles de carbono, la modificación de la concentración de los reactivos y la introducción de agentes aditivos.

4.1. CONCENTRACIÓN DE REACTIVOS

El primer paso para diseñar las propiedades de los xerogeles de carbono consiste en determinar el papel que juega la concentración de cada uno de los reactivos en la reacción de polimerización. Estas concentraciones están directamente relacionadas con el pH de la mezcla precursora, el grado de dilución (D) y el ratio molar entre el resorcinol y el formaldehído (R/F).

El pH es una de las variables que más influencia tiene en las propiedades finales de los geles de carbono y existen numerosos estudios centrados en su efecto [Pekala 1989; Yamamoto 2001; Horikawa 2004; Job 2004; Job 2006b; Gaca 2013; Taylor 2014]. Éste puede explicarse teniendo en cuenta la reacción de polimerización entre el resorcinol y el formaldehído, detallada en el Capítulo 1 de la presente memoria. Como se explica en dicho capítulo, la reacción comienza con la abstracción del hidrógeno hidroxilo del resorcinol. Esta abstracción se ve favorecida por la presencia del hidróxido de sodio (catalizador) en la mezcla precursora, por lo que un aumento en la concentración del catalizador (valores altos de pH) aumenta el número de aniones de resorcinol disponibles para que el formaldehído se adicione. Al haber más aniones resorcinol disponibles la adición se da de forma más rápida. Es decir, la reacción de adición se ve favorecida al aumentar el pH, dando lugar a la formación de un mayor número de nódulos de pequeño tamaño (Figura 4.1a) [Taylor 2014]. Por el contrario, una baja concentración de catalizador (valores bajos de pH) genera pocos aniones de resorcinol. Esto se debe a que la adición de formaldehído ocurre en menos tiempo que en el caso de añadir más catalizador, favoreciendo la reacción de condensación y permitiendo al medio de reacción persistir más tiempo en la etapa de nucleación. El hecho de que los nódulos tengan más tiempo para crecer da lugar a una estructura con pocos nódulos de gran tamaño (Figura 4.1b). El número y tamaño de los nódulos definen la forma de la estructura porosa y, por ende, las propiedades de los geles de carbono.

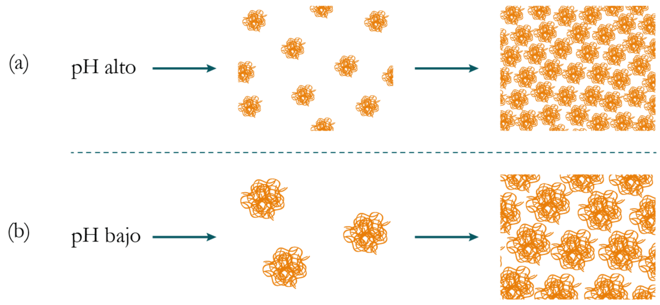

Figura 4.1. Formación y crecimiento de los nódulos en función del pH de la mezcla precursora.

Este efecto que tiene la concentración de catalizador sobre la formación de la estructura polimérica ha sido ampliamente estudiado. No obstante, la mayoría de los estudios encontrados en la bibliografía se basan en geles de carbono sintetizados a partir de la misma concentración de resorcinol, formaldehído y agua. La modificación de la concentración de estos reactivos también puede influir en la formación y crecimiento de los nódulos y, por tanto, aumentar el control sobre el diseño de las propiedades de los xerogeles de carbono. Por otro lado, cabe destacar que el efecto de cada una de las concentraciones (resorcinol, formaldehído, agua e hidróxido de sodio) se debe considerar teniendo en cuenta el efecto de las otras, ya que existe sinergia entre ellas. El hecho de que la concentración de todos los reactivos juegue un papel importante en la reacción de polimerización y que exista una sinergia entre ellas, es el motivo por el cual, durante la realización de esta Tesis Doctoral, se han llevado a cabo diversos estudios sobre el efecto de variar de forma simultánea dichas concentraciones. Para poder evaluar el efecto de cada reactivo por separado y determinar el grado de sinergia entre ellos, es necesario llevar a cabo los estudios en varias etapas. Los estudios de la primera etapa versan sobre la síntesis de xerogeles de carbono con propiedades diseñadas a medida mediante la modificación de la concentración de catalizador (pH) y agua (grado de dilución, D). En la segunda etapa, se incluyó la variación del ratio molar entre el resorcinol y el formaldehído (ratio molar R/F) como nueva variable de estudio.

4.1.1. VARIACIÓN DEL pH Y DEL GRADO DE DILUCIÓN

Objetivos

Los objetivos planteados para llevar a cabo el estudio del efecto de la variación simultánea del pH y del grado de dilución fueron los siguientes:

- ✓ Delimitar las combinaciones de valores de pH-grado de dilución (pH-D) a partir de los cuales es posible obtener de forma controlada xerogeles de carbono, preparados a partir de xerogeles resorcinol-formaldehído sintetizados mediante calentamiento con microondas.

- ✓ Evaluar estadísticamente las variaciones producidas sobre las propiedades de los xerogeles de carbono al modificar los valores de pH y grado de dilución.
- ✓ Determinar el grado de sinergia entre el pH y el grado de dilución y su efecto sobre las propiedades de los xerogeles de carbono.
- ✓ Obtener las ecuaciones estadísticas que relacionan el pH y el grado de dilución con las propiedades porosas de los xerogeles de carbono, para poder determinar las condiciones óptimas que dan lugar a materiales con las propiedades requeridas en cada aplicación.

Selección del rango de estudio

El estudio del efecto de variar de forma simultánea el pH y el grado de dilución requiere la síntesis de un amplio número de materiales. Por este motivo se aplicaron técnicas estadísticas de diseño de experimentos que permiten determinar el número mínimo de materiales que es necesario sintetizar y caracterizar para obtener conclusiones válidas y objetivas. Inicialmente se fijaron una serie de combinaciones de valores de pH-D que, en función de los resultados experimentales, se fueron ampliando hasta obtener un total de 80 materiales caracterizados. La combinación de los valores de pH-D de todos estos materiales se encuentra dentro de unos rangos determinados, cuya selección se llevó a cabo considerando los siguientes aspectos:

- ➢ El valor del pH se varió entre 3 y 9. El valor de pH mínimo corresponde al pH de la mezcla precursora previo a la adición del catalizador básico, mientras que el valor máximo se seleccionó en base a los resultados de las propiedades porosas de los materiales. Es decir, la concentración de catalizador se aumentó progresivamente, aumentando el valor del pH hasta obtener materiales que apenas presentaban porosidad.
- ➢ El valor de D se varió entre 2 y 42. El grado de dilución se define como los moles totales de disolvente, es decir, el agua añadida directamente y el agua y metanol

contenidos en la disolución de formaldehído, en función de los moles de los reactivos (resorcinol y formaldehído puro). Por definición, el valor mínimo de D corresponde a la cantidad mínima de agua y metanol que hay en la disolución de formaldehído respecto a los moles de reactivos, cuando no se añade agua (disolvente) a la mezcla precursora. La relación molar entre el resorcinol y el formaldehído se mantuvo en el valor estequiométrico (R/F = 0.5), por lo que el valor mínimo de D obtenido fue de 2. El valor máximo de D se seleccionó a medida que se desarrollaba el trabajo experimental, situándose el límite superior en aquellos valores de D para los cuales no fue posible sintetizar los xerogeles RF mediante calentamiento con microondas de forma óptima y controlada.

La evaluación del efecto de modificar de forma simultánea el valor del pH y del grado de dilución se llevó a cabo utilizando la versión de prueba del software estadístico comercial Design-Expert (Stat-Ease, Inc.).

Conclusiones

Los detalles experimentales y los resultados obtenidos en este estudio se describen y discuten en las Publicaciones III y IV, incluidas al final de esta sección. A continuación se detallan las principales conclusiones de dichas publicaciones:

- El pH tiene un efecto notable en la meso-macroporosidad de los materiales. Este fenómeno se debe a la manera en la que los nódulos se forman y crecen durante la reacción de polimerización. La utilización de valores bajos de pH da lugar a la formación de pocos nódulos de gran tamaño, resultando en un material que presenta poros de gran tamaño (materiales macroporosos). A medida que aumenta el pH, el número de nódulos aumenta y su tamaño disminuye, obteniéndose materiales con poros de menor tamaño (materiales mesoporosos). A partir de valores de pH superiores a 7 los xerogeles de carbono a duras penas presentan porosidad.
- El grado de dilución influye significativamente en la meso-macroporosidad de los materiales debido al número y tamaño de los nódulos que se forman durante la

reacción de polimerización. Considerando un mismo volumen de mezcla precursora, la utilización de un valor de D bajo implica que la concentración de resorcinol-formaldehído sea elevada. Cuanto mayor es la concentración de resorcinol mayor es el número de aniones que se generan, favoreciendo la reacción de adición. De este modo se forman muchos nódulos pequeños, dando lugar a materiales con poros de menor tamaño (materiales mesoporosos). A medida que el valor de D aumenta, es decir, el contenido en resorcinol-formaldehído disminuye, se forman menos nódulos de mayor tamaño, obteniéndose materiales con poros más grandes (materiales macroporosos). Si la concentración de agua es muy elevada, el número de nódulos que se forman es pequeño y no se llega a producir la reacción sol-gel.

- El efecto del grado de dilución es dependiente del pH de la mezcla precursora. En función de su valor, el pH puede contribuir a aumentar el efecto del grado de dilución o, por el contrario, puede contrarrestarlo. Por tanto, la modificación simultánea del pH y del grado de dilución permite obtener materiales con unas propiedades porosas que no es posible obtener modificando tan solo el pH o el grado de dilución. Es decir, la combinación de ambas variables incrementa el control sobre el diseño de las propiedades porosas de los xerogeles de carbono.

- A partir de la evaluación estadística de las propiedades porosas llevadas a cabo en estos estudios, es posible determinar la correcta combinación de valores de pH-D que da lugar a un material con unas propiedades porosas determinas. Dicho de otra manera, es posible fijar unas propiedades porosas que se ajusten exactamente a los requisitos de una aplicación concreta y, mediante las técnicas estadísticas aplicadas, determinar, antes de llevar a cabo la síntesis, la correcta combinación de pH-D que dará lugar a un material con dichas propiedades.

PUBLICACIÓN III

RF XEROGELS WITH TAILORED POROSITY OVER THE ENTIRE NANOSCALE

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RF xerogels with tailored porosity over the entire nanoscale

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ABSTRACT

Resorcinol–formaldehyde organic xerogels were synthesized by means of microwave heating using precursor solutions with pH values ranging from 2 to 9 and dilution ratios between 2 and 42. The objective of this study was to assess the effect of these two chemical variables on the final porous properties of organic xerogels synthesized by microwave heating, using optimal design of response surface methodology. An analysis of variance was applied to the results of the porous characterization of all the samples synthesized. It was found that microporosity and bulk density increased with an increase in the pH and a decrease in the dilution ratio as, under these synthesis conditions, the addition reaction was favored. Maximum mesopore and macropore volume values were achieved for opposed pH-dilution ratio combinations. Thus, when the mesopore volume increases the macropore volume decreases and vice versa. Within the range of pH-dilution ratios studied, materials with an average pore size ranging from 2 nm to 1000 nm were obtained, which covers the entire range of porosity.

1. Introduction

Carbon gels are porous materials obtained by drying and carbonizing organic polymer-based gel [1]. The most common process for synthesizing this organic gel is by polymerization of resorcinol with formaldehyde in the presence of a solvent, following Pekala's method [2]. The first step in the polymerization is the formation of resorcinol anions by hydrogen abstraction [3]. These anions are more reactive than resorcinol, and therefore, formaldehyde is added to them to form hydroxymethyl derivatives via an addition reaction [4,5]. Hydroxymethyl derivatives are linked to each other by methylene and ether bonds forming a polymeric backbone which will result in a three-dimensional interconnected structure. The final shape of this three-dimensional structure and hence the final properties of the gels depends on the pH [1,6,7], type of solvent [8,9], the concentration of reagents [10,11], the type of catalyst [12,13], the temperature and time of the synthesis [14,15], drying conditions [16,17], etc. However, the pH and the concentration of reagents are the two most influential factors that determine the final porous properties of the gels [18,19].

Several works published in the literature have reported that micropore volume is not affected by the pH of the precursor solution, whereas a decrease in the pH favors the formation of larger pores. In other words, only inter-particle voids are affected by the pH [20]. Some studies have reported that the amount of reactants, namely the dilution ratio, modifies the bulk density, pore volume and size of the pores [1,21,22], while others report that the influence of the dilution ratio on the final porous properties depends on the drying method applied [16,17]. Three major types of drying methods can be found in the bibliography: supercritical drying, freeze-drying and evaporative drying, which give rise to aerogels, cryogels and xerogels, respectively [23–27]. Some authors state that, in the case of evaporative drying, shrinkage produced by the removal of the solvent is much greater than in the other drying processes, and hence, a less-developed porous structure is obtained [17]. However, the evaporative drying method is quicker and simpler, and therefore, yields the most cost-competitive materials.

Because the final properties of the gels can be controlled by varying the synthesis conditions, the porous structure can be tailored to fit a specific application, depending on the porous properties required in each case. For instance, in the case of dynamic adsorption processes, diffusion limitations can be minimized by choosing a carbon gel containing pores large enough to overcome mass transfer limitations [28]. In the case of thermal insulation, materials with a low surface area, pores within the mesoporosity range and, in particular, a low bulk density are required [29,30]. A high hydrogen storage capacity can be achieved by using carbon gels with a highly developed microporosity and an appropriate micropore size distribution [31]. When carbon gels are to be used as electrode material, in addition to microporosity, mesopores are required in order to facilitate a good dynamic charge propagation [32].

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In short, it is evident that both organic and carbon gels are promising materials for a wide range of applications. However, in order to obtain applicable materials, the synthesis process needs to be energy-efficient and commercially competitive. In this respect, synthesis by microwave heating has been shown to be a cost-effective process as only one device and moderate conditions are needed. Moreover, this process allows the synthesis of organic gels on a large scale via a simple and rapid procedure, to yield very competitive and high value-added materials. However, the effect of adjusting the chemical variables on the final porous structure of organic gels when using microwave radiation has not yet been studied in depth.

Accordingly, the aim of the present work is to assess the effect of two chemical variables, the pH and dilution ratio, on the final porous properties of organic xerogels synthesized by microwave heating, by applying optimal design of response surface methodology to five response variables: the volume of the micropores, mesopores and macropores, the average pore size and bulk density. The optimal pH-D combinations for controlling the synthesis of xerogels were also identified.

2. Experimental

2.1. Synthesis of organic xerogels

Organic xerogels were synthesized by the polycondensation of resorcinol (R) and formaldehyde (F) using deionized water as solvent. Resorcinol (Indspec, 99%) was first dissolved in deionized water in an unsealed glass beaker under magnetic stirring. After dissolution, formaldehyde (Ercros, 37 wt.% in water, stabilized by 10–15% methanol) was added and the mixture was stirred until a homogeneous solution was obtained. All the xerogels were synthesized from 200 ml of precursor solution and the final pH value was adjusted by adding sodium hydroxide and hydrochloric acid in order to obtain basic and acid precursor solutions, respectively.

The amount of resorcinol, formaldehyde and water used for each sample depended on the dilution ratio selected (D). The dilution ratio parameter is defined as the molar ratio between the total solvent and reactants. Total solvent refers to the water and methanol contained in the formaldehyde and the deionized water that is added, whilst reactants refers to the resorcinol and formaldehyde. According to this definition, the minimum value of D corresponds to the molar ratio between the minimum amount of water and methanol contained in the formaldehyde and reactants. In the present work D reached a minimum value of 2, as all the precursor solutions were prepared using the stoichiometric R/F molar ratio, i.e., 0.5. The maximum D value was selected on the basis of the porous properties of the xerogels. D was increased gradually until the materials obtained presented a non-porous structure. The pH range of the precursor solutions was selected on the basis of the experimental results. The limits were fixed according to the pH values at which total control of the synthesis of the xerogels was achieved.

Each precursor solution was placed in a microwave oven at 85 °C for 3 h, which is long enough for gelation and ageing to be accomplished [33]. After the formation of the polymeric structure, excess water was eliminated by continuing to heat the gel in the same microwave oven until a mass loss of over 50% was achieved. The drying step lasted 1–2 h depending on the final pore structure of the material.

2.2. Sample characterization

The porous properties of the organic xerogels were characterized by nitrogen adsorption–desorption isotherm analysis and by a mercury porosimetry technique, performed at −196 °C using a Micromeritics Tristar 3020 instrument and in a Micromeritics AutoPore IV, respectively. Before each analysis, all the samples were outgassed at 120 °C and 0.1 mbar for 8 h using a Micromeritics VAc-Prep 061. These degassing conditions were previously optimized for outgassing this type of material. The micropore volume was calculated by applying the Dubinin–Raduskevich method to the nitrogen adsorption–desorption isotherms. Pore volume measurements by nitrogen adsorption are not precise enough for samples containing macropores. For this reason, mercury porosimetry was used as a complementary technique to determine the volume of the larger mesopores, the average pore size (calculated considering the overall pore size distribution) and the volume of macropores. Analysis of mercury porosimetry was based on Washburn's intrusion theory. The bulk density of all the samples was also determined by mercury porosimetry.

2.3. Experimental design

An experimental design for two of the chemical variables that play an important role in the microwave-assisted synthesis of organic resorcinol–formaldehyde (RF) xerogels was constructed based on response surface methodology (RSM). By using a suitable design of experiments (DOE) it was possible to reduce the number of experiments needed and assess the potential synergy between the variables studied: the pH and the dilution ratio. An optimal design requiring 80 experimental points, covering all the possible pH-D combinations along with repeated experimental runs, was employed to obtain a statistical model that would adequately fit the experimental results. The volume of micropores, mesopores and macropores, pore size and bulk density were selected as the responses of the system. The design matrix was generated by using a Design-Expert 8.0.7.1 Trial version from Stat-Ease Inc.

3. Results

All combinations of pH-D studied to find out whether it was possible to synthesize organic RF xerogels by microwave radiation at 85 °C for 3 h starting from a volume of precursor solution of 200 ml are presented in Fig. 1. In this figure three colored regions are highlighted. These indicate the combinations of pH-D at which: (i) it was possible to synthesize optimally controlled RF xerogels, (ii) the gelation point was not reached after 3 h of synthesis and therefore the gels were to be considered as not cost-effective

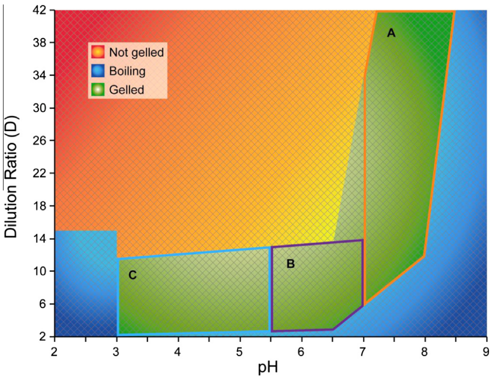

Fig. 1. pH-D combinations studied.

materials, (iii) boiling occurred in the precursor solutions and the process was therefore out of control.

In order to facilitate the subsequent statistical analysis of the results, the region corresponding to the optimal pH-D combinations (green region) was divided into three regions designated as A, B and C. The materials obtained in each region have porous structures that are totally different from those of the other two. Exclusively microporous xerogels were produced under the pH-D conditions of region A while micro-meso-macroporous and basically macropore materials were obtained from regions B and C, respectively.

From Fig. 1 it can be observed that controlled synthesis of the xerogels was achieved in the pH range between 3.0 and 6.5 when the dilution ratio was fixed at below 14. The dilution ratio can be increased by increasing the pH to above 6.5. However, dilution ratios above 42 were not studied since the xerogels displayed poorly developed porous structures. Furthermore, increasing the pH also increased the dilution ratio below which xerogels cannot be synthesized under the conditions studied.

Regardless of the dilution ratio, the xerogels catalysed with hydrochloric acid, i.e. samples with a pH value lower than 3.0, could not be synthesized under controlled conditions. However, depending on the dilution ratio the reason for this differs significantly. When a dilution ratio above a value of 15 was used, no sol–gel reaction took place within the specified 3 h, whereas with a dilution ratio below 15 the sol–gel reaction occurred though in an uncontrolled manner, which led to the boiling of the precursor solution.

3.1. Porous properties of RF xerogels

All the synthesized RF xerogels were characterized from the point of view of their porous structure. By using nitrogen adsorption–desorption analysis and the isotherm classification proposed by the IUPAC, the porous structure of each material could be readily distinguished. The nitrogen adsorption–desorption isotherms of some of the synthesized samples are shown in Fig. 2.

Each one of the samples shown in Fig. 2 was synthesized using a different pH-D combination. As can be seen, the isotherms obtained in this study show a clear difference in shape depending on their correspondence with the regions A, B or C in Fig. 1. However, the isotherms of the different materials synthesized from pH-D combinations within the same region, also exhibit differences in shape, either due to variation in the pH or the dilution ratio.

General speaking, the xerogels with a pH above 7.0 give rise to a type I isotherm, which corresponds to mainly microporous materials (region A). As the pH decreases to 5.5, the organic xerogels evolve from microporous materials to micro-mesoporous and even to macroporous materials. Indeed, the isotherms of the samples within region B range from type IV to type II, which are characteristic of micro-mesoporous materials and macroporous materials, respectively. This demonstrates that the porosity depends to a great extent on the pH and on the dilution ratio. For example, samples with a pH of 7.0 and 6.5 and dilution ratios of 23.7 and 5.7 respectively, display a pronounced hysteresis loop associated to the presence of medium size mesopores. However, the loop becomes thinner at lower pH values, indicating the presence of larger mesopores and even the presence of macropores. The low pH samples, i.e. organic xerogels with a pH below 5.5, display a type II isotherm, corresponding to macroporous solids (region C), whose pore size increases with the dilution ratio.

3.2. Statistical analysis

Statistical analyses were performed using response surface methodology (RSM). The implementation of RSM allows the interaction between the pH and the dilution ratio and their effect on the main porous properties to be evaluated with a minimum number of experiments. In order to determine whether the model selected was sufficiently significant to fit the experimental results, an analysis of variance (ANOVA) was applied to each of the five variables selected as responses: micropore, mesopore and macropore volume, pore size and bulk density. The significance of each input variable, i.e., pH and D, and their possible interaction was determined by assessing the *p*-value. If the *p*-values are smaller than 0.05, the corresponding variable will have a significant effect on the response. A point worth mentioning is that, as point out above, the samples with a pH greater than 7.0 are exclusively microporous materials and therefore, within region A the influence of pH and D was only evaluated on the basis of volume of micropores

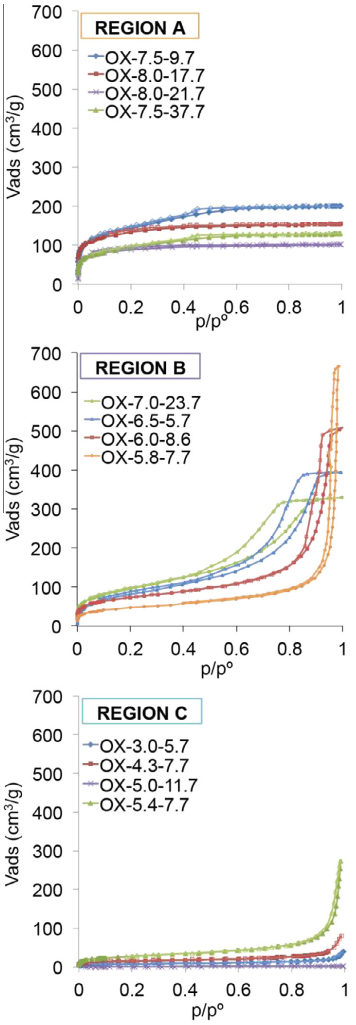

Fig. 2. N_2 adsorption–desorption isotherms of some of the samples synthesized in regions A, B and C.

and average pore size, whereas for the rest of the samples, in regions B and C, the effect of all the pH-D combinations was assessed for all the response variables.

3.2.1. Micropore volume

From Fig. 1 it can be inferred that the dilution ratio range becomes much wider as the pH increases. Applying just one statistical analysis to all the optimal pH-D combinations (green region), will lead to a model which will not fit properly to the experimental results. Consequently, the effect of modifying the pH and the dilution ratio on the micropore volume was studied for region A and regions B-C separately.

The micropore volume values for the samples synthesized using the pH-D combination from region A were adjusted to a linear function, whereas data from regions B-C were fitted to a quadratic function. The R-squared value for regions A and B-C were 0.89 and 0.83, respectively, indicating that the calculated results are in good agreement with those obtained experimentally. The results of the ANOVA applied to the microporosity from regions A and B-C are summarized in Tables S1 and S2 in the supporting information, respectively.

The data obtained by employing a least square technique indicate that, for both regions, the model is significant for microporosity. Moreover, pH and D are significant model terms based on the *p*-value ($P < 0.005$). Within region B-C, the quadratic term for the pH also has a significant effect on the volume of micropores. However, the interaction between pH and D is not a significant term, indicating that the modification of one of these variables has no effect on the influence of the other.

Three-dimensional (3D) surface plots were constructed on the basis of the model equations obtained for each region, representing the response surface curves of the independent variables, pH and D, versus the dependent variable, the volume of micropores (Fig. 3). The 3D plots show the evolution of the volume of micropores when the pH and the dilution ratio of samples with a pH value between 7.0 and 8.0 and a dilution ratio between 2 and 42 (region A) are modified and when the pH and the dilution ratio are adjusted between 3.0 and 7.0 and 2 and 14, respectively (regions B-C).

The volume of micropores for region A varies from 0.12 ± 0.01 cm^3/g to 0.20 ± 0.01 cm^3/g, indicating that all the materials exhibit microporosity. In contrast, the samples from regions B-C cover the entire range from non-microporous materials to materials with a volume of micropores as high as 0.18 ± 0.01 cm^3/g. In both the 3D plots it is can be clearly observed that the microporosity is enhanced as the pH increases and the dilution ratio decreases

3.2.2. Mesopore volume

The influence of the pH and dilution ratio on the volume of mesopores was only studied for regions B-C from Fig. 1, since the materials synthesized from the combinations of pH and D in region A, were exclusively microporous.

The mesopore volume values for the samples synthesized using the pH-D combinations from regions B-C were adjusted to a cubic function with an R-squared, correlation coefficient value, of 0.76. The results of the ANOVA applied to the mesoporosity from regions B-C are presented as Table S3 in the supporting information.

The data obtained by means of employing a least square technique indicates that the model is significant for mesoporosity. Moreover, pH and D are significant model terms based on the *p*-value ($P < 0.005$). The cubic term of pH and the quadratic term of D also have a significant effect on the volume of mesopores. The interaction is a non-significant term, indicating that the modification of one of the two chemical variables has no effect on the influence of the other.

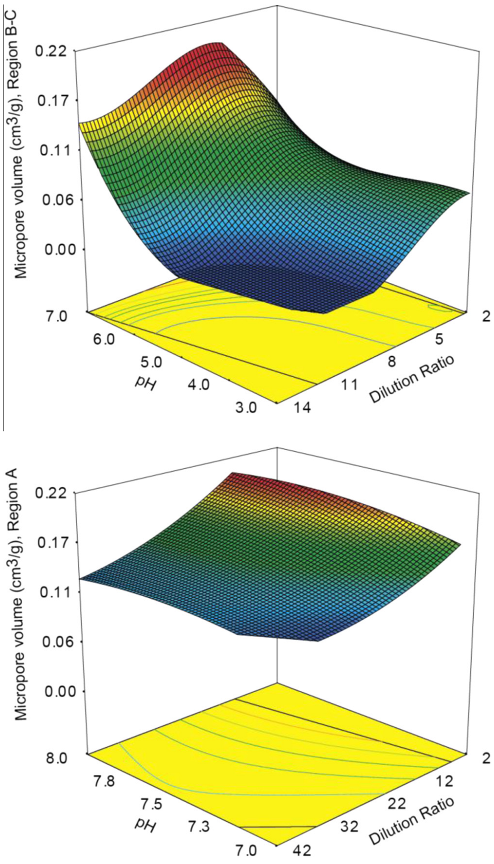

Fig. 3. Three-dimensional surface representing the effect of the pH and dilution ratio on the microporosity of region A and region B-C.

Fig. 4 shows the 3D surface plot and contour plot constructed according to the model. It shows the evolution of the mesopore volume when the pH and the dilution ratio are modified between 3.0–7.0 and 2–14, respectively. This range of pH-D combinations corresponds to the regions B-C in Fig. 1 in which the mesopore volume ranges from 0.0 ± 0.06 cm^3/g to 0.8 ± 0.06 cm^3/g.

A maximum mesopore volume value was found by adjusting the pH between 5.8 and 6.5 and the dilution ratio between 6 and 9. An increase in pH to above 6.5 leads to a decrease in the volume of mesopores. Furthermore, when the pH is decreased to below 5.5 the samples obtained are non-mesoporous materials. A non-developed microporosity was also observed in these samples, which is in good agreement with the N_2 adsorption–desorption isotherm in Fig. 2, corresponding to region C. The volume of mesopores also decreases when the dilution ratio is decreased to below 6 or increased to above 9, especially when the pH values are below 5.5.

3.2.3. Macropore volume

The effect of modifying the pH and the dilution ratio on the macropore volume was only evaluated for regions B-C, as in the case of

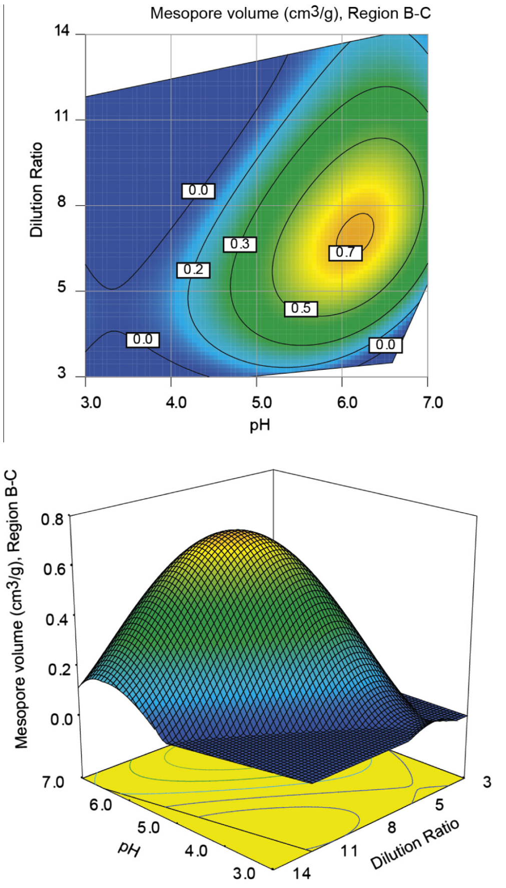

Fig. 4. Three-dimensional surface plot and contour plot for the effect of pH and dilution ratio on the mesoporosity of regions B-C.

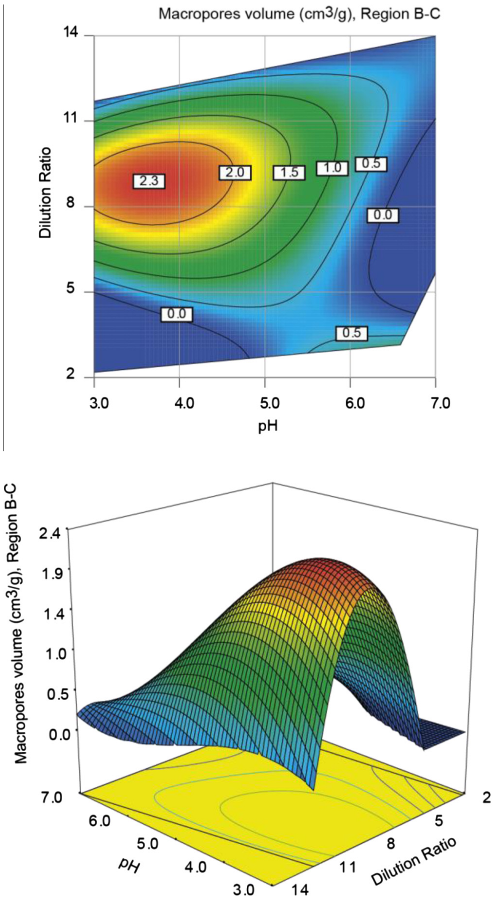

Fig. 5. Three-dimensional surface plot and contour plot showing the effect of the pH and dilution ratio on the macroporosity of regions B-C.

the mesopore volume. The values for the macropore volume for samples synthesized using the pH-D combination from regions B-C were adjusted to a cubic function with an R-squared value of 0.74. The results of the ANOVA applied to macroporosity from regions B-C are summarized in Table S4 in the supporting information.

From these data it can be inferred that the pH, the dilution ratio and their quadratic terms have a significant effect on the volume of macropores based on the *p*-value ($P < 0.005$). Furthermore, one of the interaction terms between pH and D is significant in the model, indicating that the modification of one of the two chemical variables has an effect on the influence of the other. A three-dimensional surface plot and a contour plot were constructed according to the model equations obtained for the B-C regions which represent the response surface curves for the effect of pH and D upon the volume of macropores (Fig. 5) when the pH and the dilution ratio are modified between 3.0 and 7.0 and 2 and 14, respectively. In this range of pH-D combinations the macropore volume ranges from 0.0 ± 0.04 cm^3/g to 2.3 ± 0.04 cm^3/g.

In these graphs the maximum macropore volume value can be clearly observed in the pH range of 3.0–5.0 for a dilution rate of between 7 and 11. The organic xerogels synthesized with a pH above 5.5 exhibit a negligible macropore volume, in agreement with the pH range in which the xerogels presented the maximum mesopore volume, as shown in Fig. 4. Hence, it can be stated that Figs. 4 and 5 are opposed graphs indicating that when the mesopore volume increases, the macropore volume decreases and vice versa.

3.2.4. Average pore size

The average pore size is the response variable which encompasses the greatest range of values starting from all the combinations of pH-D within the green region in Fig. 1. Indeed, the entire porosity range is covered, from microporous materials with a pore size smaller than 2 nm to macroporous materials with a pore size greater than 50 nm. Consequently, the effect of modifying the pH and the dilution ratio on the average pore size was studied for regions A, B and C, separately. The average pore size values for the three regions were fitted to a quadratic function. The correlation coefficient values for each region A, B and C were 0.96, 0.85 and 0.90, respectively. These results are in good agreement with those obtained experimentally. The results of the ANOVA applied to the average pore size from each region are presented in Tables S5, S6 and S7 in the supporting information, respectively.

The data obtained by employing the least square technique indicate that the model is significant for the average pore size in all the three regions. However, the independent variables have different effects on the dependent variable depending on the region evaluated. In the ANOVA of regions A and B the pH is the only significant term, while in region C, the pH, dilution ratio and the interaction between them also play an important role in the pore size values obtained. Indeed, in this region the effect of the pH increases greatly with the dilution ratio (D).

Three-dimensional surface plots constructed according to the model equations obtained for each region are shown in Fig. 6. In all three 3D plots it can be clearly observed that the average pore size increases as the pH decreases and the dilution ratio increases. However, the pore size varies within a different range for each region. The average pore size for region A varies by as much as 8 nm, again indicating that the organic xerogels in this region are microporous materials. Within region B, the average pore size ranges from 5 to 120 nm, i.e. they range from mesoporous materials with a small pore size to macroporous materials. In the pH-D combination range of region C the average pore size extends to thousands of nanometers indicating that most of the organic xerogels within this region are macroporous materials.

3.2.5. Bulk density

All the materials from region A present a bulk density between 1.0 and 1.2 g/cm^3. These values show that the bulk density of the organic xerogels synthesized with combinations of pH-D within region A is not related either to the pH or to the water content of the precursor solutions. Accordingly, the effect of modifying the pH and the dilution ratio was assessed only for region B-C. The bulk density values were fitted to a quadratic function with an R-squared value of 0.75. The results of the ANOVA applied to the bulk density from region B-C are presented in Table S8 in the supporting information.

The data obtained by employing the least square technique indicate that the model is significant. Moreover, pH, D and their quadratic terms have a significant effect on the bulk density based on the *p*-value ($P < 0.005$). The interaction is a non-significant term, indicating that the modification of one of the two chemical variables has no effect on the influence of the other.

A three-dimensional surface plot and a contour plot were constructed according to the model equations obtained for the B-C region, representing the response surface curves of pH and D versus the bulk density (Fig. 7) when the pH and the dilution ratio are modified between 3 and 7 and 2 and 14, respectively. In this range of pH-D combinations the bulk density ranges from 0.2 to 1.2 g/cm^3.

A minimum value for bulk density was obtained by adjusting the pH between 3.5 and 5.0 and using a dilution ratio higher than 8, corresponding to the range in which a maximum value for macropore volume was obtained (Fig. 5). The organic xerogels synthesized with a pH above 6.5 exhibit a bulk density greater than 1.0 g/cm^3 which is maintained in the xerogels with a high pH value over the entire range of dilution ratios studied.

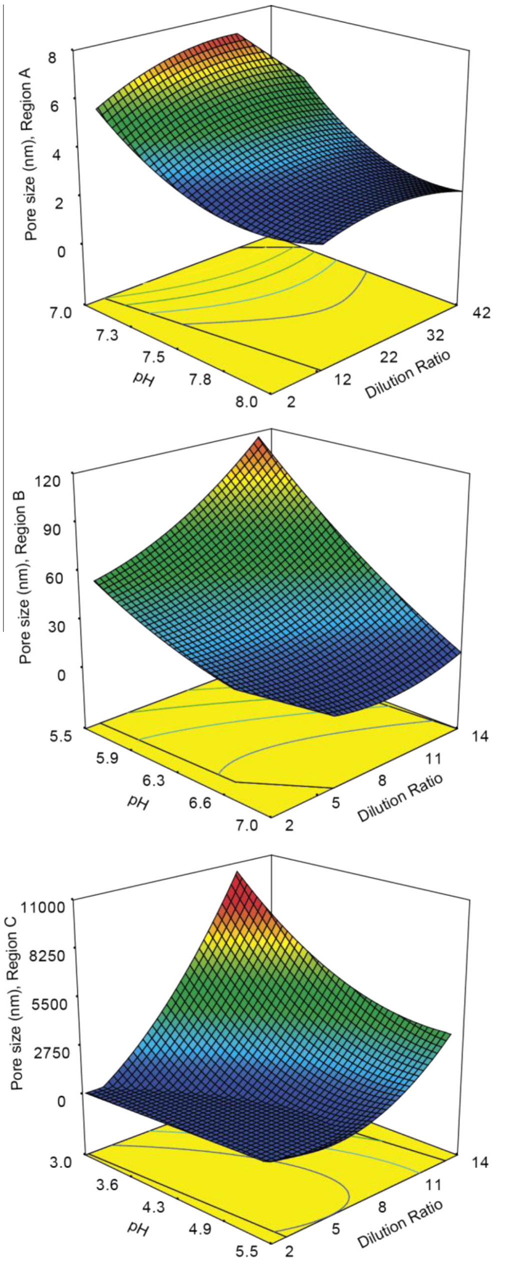

Fig. 6. Three-dimensional surface plot and contour plot showing the effect of the pH and dilution ratio on the average pore size of regions A, B and C.

4. Discussion

The results of this study show that there are limits in which organic RF xerogels can be synthesized by means of microwave heating (green region from Fig. 1). The synthesis process is completely controlled when the pH value of the precursor solutions is fixed between 3.0 and 6.5 and the D value is lower than 14.

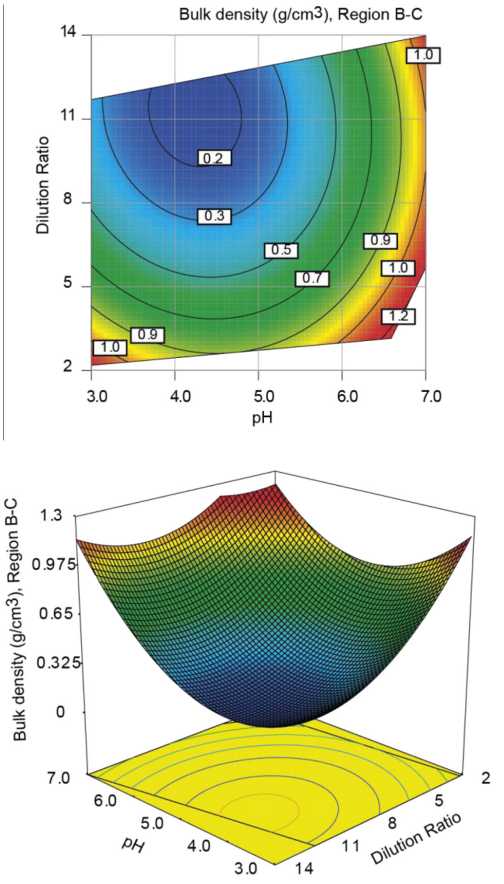

Fig. 7. Three-dimensional surface plot and contour plot showing the effect of the pH and dilution ratio on the bulk density of region B-C.

However, an increase in the dilution ratio over this value gives rise to an increase in the distance between the clusters [22], prolonging the addition reaction and impeding the formation of the polymeric structure. Consequently, the gelation point is not reached until after 3 h. On the other hand, when no water is added and the precursor solution is only composed of resorcinol and formaldehyde, the amount of catalyst relative to the amount of solvent is high and therefore the polymerization reactions take place faster, causing the temperature of the solution to rise above 100 °C.

The dilution ratio can be increased by increasing the pH above 6.5. Even at high values of D the sol–gel reaction proceeded under the conditions of this study. Nevertheless, the organic xerogels obtained from dilution ratios above 42 exhibit a poorly developed porous structure. Increasing the pH also increases the dilution ratio below which xerogels cannot be synthesized under the conditions studied. This effect could be due to the molar ratio between the amount of catalyst and the water added, since for any given dilution ratio value more catalyst is needed to increase the pH of the precursor solution. In fact, for pH values above 7.0, the amount of catalyst needed to increase the pH value by one unit, increases exponentially. As the sol–gel reaction is an exothermic reaction, the greater the amount of catalyst used, the higher the temperature of the solution becomes. Moreover, the programmed temperature of 85 °C in the microwave-assisted synthesis of organic RF xerogels is reached in less than 2 min. The large amount of microwave energy generated in the first two minutes of the process along with the heat generated by the sol–gel reaction causes a rapid increase in temperature to above 100 °C and the consequent boiling of the solution. For this reason, regardless of the water content, the synthesis of xerogels with a pH above 8.5 becomes uncontrolled.

Irrespective of the dilution ratio, the xerogels catalysed with hydrochloric acid, i. e. samples with a pH value lower than 3.0, could not be synthesized even under controlled conditions. However, the reason differs significantly depending on the dilution ratio. When dilution ratios exceeding values of 15 are used, the sol–gel reaction fails to take place within the three hours. As occurs with the samples with a pH value between 3.0 and 6.5, the amount of resorcinol and formaldehyde is low and fewer and smaller clusters are formed. This phenomenon along with the addition of a large amount of water that increases the distance between the clusters, prevents the solution from reaching the gelation point. These results are in good agreement with those reported by Kocklenberg et al. They found that an increase from 17 to 48 in the dilution factor increased the time needed for the gelation by 86% [26]. When low values of pH and D are used, the sol–gel reactions become uncontrolled, causing the precursor solution to boil as happens when pH values higher than 8.0 are used.

It should be noted that the green region in Fig. 1 could be improved. Organic xerogels synthesized from pH-D combinations within the blue region in Fig. 1 could be obtained by decreasing the temperature of synthesis to below 85 °C in order to prevent the precursor solution from boiling. Organic xerogels from pH-D combinations within the red region of Fig. 1 could be also synthesized by increasing the time of synthesis to allow the sol–gel reaction to take place. However, temperature and time of synthesis variations are not included as part of the aim of this study.

All organic xerogels synthesized from pH-D combinations within the green region of Fig. 1 were characterized from the point of view of their porous structure. The final porous structure of these xerogels formed by modifying the pH and D can be attributed to the two steps involved in the polymerization between resorcinol and formaldehyde: the addition and condensation reactions. Fig. 8 shows a schematic representation of the reaction of resorcinol with formaldehyde. Initially, resorcinol anions are formed by hydrogen abstraction [34]. These anions are more reactive than resorcinol and promote the addition of formaldehyde to form hydroxymethyl derivatives, which are the monomers necessary for polymerization to occur. Simultaneously to the addition reaction, condensation occurs. The hydroxymethyl derivatives then lose OH groups to form benzyl-type cations [5]. Each cation reacts with a benzene ring of another molecule giving rise to methylene and ether bonds [4]. As the reaction proceeds the number of bonds between the rings increases, forming the polymer backbone, which leads to three-dimensional cross-linked polymer clusters. These clusters aggregate and crosslink with each other to complete the gelation and ageing steps and to form the final solid shape of the gel [7]. Formation, growth and crosslinking between these clusters depend on the amount of catalyst added and the concentration of each of the reagents used, i.e., the pH and the dilution ratio.

The catalyst favors the addition reaction, i.e., the formation of resorcinol anions which are the active sites where formaldehyde is added during the addition reaction and where the formation of the clusters starts. Therefore, increasing the pH value of the precursor solutions causes the formation of large number of small clusters interconnected by long necks. In fact, the characterization

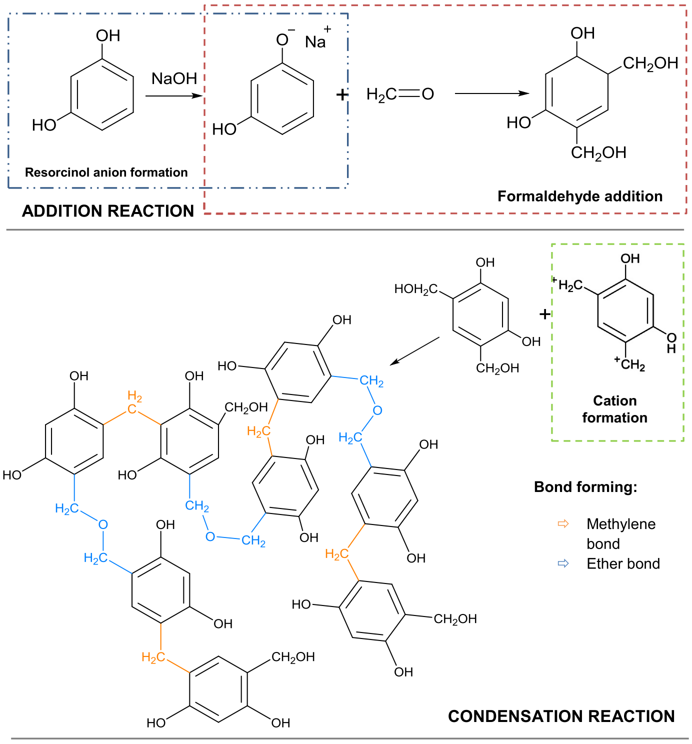

Fig. 8. Mechanism for the polymerization reaction of resorcinol with formaldehyde.

results show that, as expected, precursor solutions with a pH above 7.0 give rise to structures with a large amount of small clusters, leading to narrow pores (less than 8 nm) and a poorly developed mesoporosity (Vmeso = 0.10 ± 0.01 cm^3/g). Moreover, these samples have a highly branched structure and exhibit a maximum micropore volume value of 0.20 ± 0.01 cm^3/g and bulk densities of around 1.1 ± 0.1 g/cm^3. These results are in good agreement with other studies which report that an increase in the pH values leads to higher density gels [23].

In the case of the samples obtained from precursor solutions with a pH value below 7.0, the micropore volume decreases with the decrease in the pH values. Micropore volume values below 0.10 ± 0.01 cm^3/g are obtained when the pH values are fixed below 6.0. However, it should be pointed out that the volume of micropores can be increased by applying heat treatments such as activation. In this way, the activated xerogels can acquire similar micropore volume depending on the activation conditions used and regardless of the synthesis conditions [35].

The mesopore volume displays a maximum value when the pH is between 5.8 and 6.5 (Fig. 4). An increase in pH above 6.5 decreases the volume of mesopores due to the effect of the catalyst which promotes the addition reaction, resulting in the formation of more branched clusters of small size. When the pH is decreased to below 5.8 the mesopore volume also decreases, but in this case due to the smaller concentration of catalyst that favors the condensation reaction. The precursor solution persists longer in the nucleation step. Consequently, the number of clusters is smaller but of a larger size, resulting in a structure with a higher porosity and larger average pore sizes [7]. It is interesting to note that this behavior is opposite to that for silica gels in which larger particles are formed when the pH is increased [36]. Eventually, the pore size reaches the macroporosity range and therefore, the volume of pores should be considered as macropores rather than mesopores. When the pH is decreased to below 5.5 the volume of mesopores becomes negligible. These results agree with the data in Fig. 5. The volume of macropores displays a maximum value of 2.0 ± 0.04 cm^3/g at a pH value below 5.5 and decreases when the pH of the precursor solution is increased. These changes from mesoporous materials to macroporous materials are also in agreement with the results in Fig. 6 where the pore size scale is fixed to different ranges of values for each region B and C. As can be seen, the average pore size for region B varies from 5 to 120 nm, indicating that the organic xerogels range from mesoporous materials with a small pore size to macroporous materials. In contrast, the average pore size in region C reaches thousands of nanometers corresponding to exclusively macroporous materials.

It is now clear that the pH has a significant effect on the pore structure of organic xerogels. However, as inferred from the statistical analysis, the dilution ratio also influences the porous properties. This can be explained by the fact that the amount of water plays an important role in the drying process. After the polymerization reaction the wet gel was dried until a mass loss of over

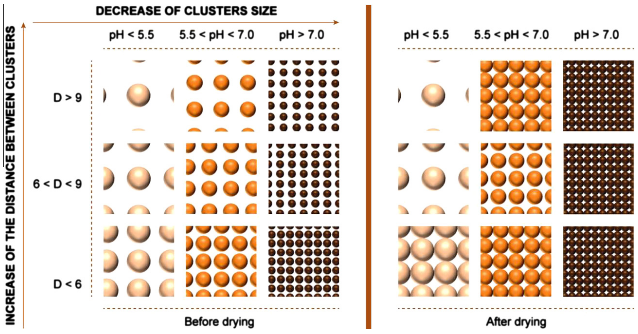

Fig. 9. Schematic representation of the influence of the pH and the dilution ratio of the precursor solution on the nanostructure of the organic RF xerogels.

50% was achieved. The evaporative drying used in this study causes the xerogel structure to contract and changes in the structure of the gel. The water in the pores causes residual surface tension, especially when the structure is composed of small clusters and small pores, favoring capillary forces. If the material has a low mechanical strength, these surface tensions cause further shrinkage of the structure. However, if the residual surface tensions are negligible in comparison to the material resistance, shrinkage during the drying can be avoided [17,22].

All the xerogels studied were prepared from the same precursor solution volume of 200 ml. An increase in the amount of water will necessarily result in a decrease in the amount of resorcinol and formaldehyde used, leading to a structure with a few weakly branched clusters. In general, the mechanical strength of these materials will be low, and therefore, during drying they will undergo further contraction, resulting in dense materials with a smaller volume of pores. However, the dilution ratio was observed to have different effect depending on the pH of the precursor solutions. Fig. 9 shows a schematic representation of the influence of both the pH and D on the structure of the organic RF gel before and after drying.

In the samples with a pH above 7.0, the dilution ratio only influences the volume of micropores, which increases by as much as 25% when D is decreased from 42 to 12. These data are consistent with those reported in another study where xerogels obtained by conventional heating presented a higher volume of micropores when the pH was increased and D was decreased from 7.3 to 5.8 and from 5.7 to 20, respectively [17].

In the case of the samples obtained from precursor solutions with a pH value between 7.0 and 5.8, when D is fixed at a value higher than 9 the clusters are weakly branched, the structure has a mechanical strength which is not able to counteract the surface tension created by the water content and the material shrinks during drying, resulting in an increase in the final bulk density (higher than 0.7 cm^3/g). The mesoporosity created during the gelation and ageing stages is slightly reduced but the size of the mesopores really decreases from 30 to 5 nm due to shrinkage. Within this pH range, when the amount of water added to the precursor solutions is low, the amount of resorcinol and formaldehyde is greater. This leads to the formation of more clusters of small size which caused the volume of the mesopores and their size to decrease. The mechanical strength is higher and no shrinkage occurs during drying. As a consequence, dilution ratios of between 6 and 9 and pH values of between 5.8 and 6.5 were found to be the ranges that produce the maximum mesopore volume values.

The large pores obtained at low pH values and for a D value of 6, facilitate the evaporation of water, thereby avoiding the appearance of capillary forces. Consequently, shrinkage is negligible and the materials show a low bulk density, a high macropore volume and a large pore size. In fact, the range of pH-D combinations in which the maximum macropore volume was obtained corresponds to samples with the lowest bulk density which is 0.2 g/cm^3, i.e. gels that do not contract during drying [23]. By decreasing the amount of water shrinkage is enhanced and the volume of pores decreases.

5. Conclusions

Statistical analysis was applied to the micropore, mesopore and macropore volume, the average pore size and bulk density of organic RF xerogels. It was found that by modifying simultaneously the pH and the dilution ratio, materials with pore volumes and average pore sizes that cannot be obtained by modifying just the pH of the precursor solution can be synthesized. It has been demonstrated that the proportion of reactants also plays an important role in the microwave-assisted synthesis of RF xerogels. The control of this variable will therefore improve the production process of xerogels with porous properties tailored for specific applications.

It was observed that the micropore volume increases when the pH is increased and the dilution ratio is decreased, as these synthesis conditions favor the addition reaction. The mesopore and macropore volume show a maximum value for opposite pH-D combinations, demonstrating that when the mesopore volume increases, the macropore volume decreases and vice versa. Within the pH-D range studied, materials with an average pore size ranging from 2 nm to a thousand nm can be obtained, indicating that organic RF xerogels over the entire range of porosity can be synthesized by means of microwave heating. The bulk density increases from 0.2 to 1.2 g/cm^3 when the pH values are increased and the dilution ratios are decreased.

By applying statistical analysis to the experimental results it is possible to predict the values of the response variables controlling the operating conditions, i.e., the pH and the dilution ratio. Hence, organic RF xerogels can be directly synthesized and tailored to have specific porous properties that fit specific application requirements without the need for endless experiments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2014.04.048.

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PUBLICACIÓN IV

A VISUAL VALIDATION OF THE COMBINED EFFECT OF pH AND DILUTION ON THE POROSITY OF CARBON XEROGELS

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Short communication

A visual validation of the combined effect of pH and dilution on the porosity of carbon xerogels

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A B S T R A C T

The hypothesis about the formation of the porous structure of carbon xerogels when the pH and the dilution ratio of the precursor solution are simultaneously modified has been validated by means of scanning electron microscope analysis. The morphology of the carbon xerogels showed that the size and number of the clusters produced during the sol–gel reaction is not only influenced by the pH but also by the dilution ratio. As with a decrease in the pH value, an increase in the dilution ratio caused the formation of a small number of large clusters, leading to materials with large pores. However, depending on the values selected the effect of the pH and dilution ratio was enhanced or diminished by the effect of the other. Hence, an appropriate adjustment of these two variables allowed microporous, micro-mesoporous and micro-macroporous materials to be obtained with pore volumes that could not be achieved by modifying the pH or the dilution ratio separately.

1. Introduction

Carbon xerogels are porous materials obtained by the carbonization of an organic gel [1]. The most frequent organic gel found in the literature is obtained by means of polymerization between resorcinol and formaldehyde in the presence of a solvent [2,3]. The porous structure and, hence, the final properties of carbon xerogels depends on a large number of variables such as the pH [1,2,4–9], type and amount of solvent [6,10,11], concentration of reactants [5,10–12], type of catalyst [1,13,14], temperature and time of synthesis [10,14,15], carbonization conditions [1,16], etc. The fact that so many variables modify the properties of these materials is a great advantage since it allows their properties to be tailored to meet the requirements of a specific application.

In the literature, a large number of studies dealing with the effect of different variables (both chemical and physical) on the porous properties of carbon xerogels can be found [1,6,8,10,11,15,17]. However, it is generally accepted that it is the chemical variables that have the greatest influence and, in particular, the concentrations of the reactants (resorcinol, formaldehyde, solvent and catalyst) [3,5,6,11,18]. The pH, which is determined by the concentration of the catalyst, has been one of the most widely studied variables as it has a great effect upon the porosity of carbon xerogels [1,2,4–8,11]. In general, it can be said that an increase in the pH value favors the addition of formaldehyde to resorcinol anions, leading to the formation of a small number of clusters of reduced size and hence to smaller pores [4,7]. On the other hand, the dilution ratio (D), which is commonly defined as the molar ratio between the total solvent and reactants, has an influence on the mechanical strength of carbon xerogels and, accordingly, on the shrinkage that takes place during the drying stage [6,11,19]. An increase in the amount of water results in a structure with low mechanical strength which during drying shrinks, leading to a material with small pores [3,6]. The effects of these two chemical variables are not isolated and the synergy between them must be taken into account when tailoring the porous properties of carbon xerogels [6,11]. However, despite the importance of the simultaneous modification of these variables on porosity, few studies in the literature focus on the effect of this synergy. Rey-Raap et al. have highlighted the importance of the synergy between pH and the dilution ratio on organic RF xerogels synthesized by microwave heating [6]. These authors provided a graphic illustration of how the pH and dilution ratio determined the size of the clusters and pores before and after the drying process. Although most studies based on carbon gels indicate that the mesoporosity and macroporosity generated during the synthesis of the organic gel is maintained during carbonization [8], some changes in the size of the clusters and pores can occur due to bonds and individual

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micropore walls breaking [7,11] and to the condensation produced during the carbonization process which may cause a slight shrinkage of the polymeric structure [7,11].

Therefore, in order to achieve total control of the tailoring of the porous structure of carbon xerogels, is worthwhile verifying whether the graphic hypothesis proposed by Rey-Raap et al. [6] for organic xerogels is also applicable to carbon xerogels. Accordingly, the aim of this study is to analyze the morphology of the structure of carbon xerogels synthesized by microwave heating through the simultaneous modification of pH and dilution ratio in the precursor solution.

2. Experimental

Organic xerogels were synthesized by the polycondensation of resorcinol (R) and formaldehyde (F) using deionized water as solvent and sodium hydroxide as catalyst, following the method described in detail elsewhere [6]. Briefly, resorcinol (Indspec, 99%) was first dissolved in deionized water in an unsealed glass beaker under magnetic stirring. After dissolution, formaldehyde (Merck, 37wt. % in water, stabilized by 10–15% methanol) was added and the mixture was stirred until a homogeneous solution was obtained. Twelve different precursor solutions were prepared with four different initial pHs ranging from 5.0 to 7.0 and three different dilution ratio values (D) ranging from 5.7 to 11.7. All the xerogels were synthesized from 200 ml of precursor solution using the stoichiometric R/F molar ratio (i.e., 0.5).

Once the reactants were selected and mixed in the appropriate proportions, each precursor solution was placed in a microwave oven at 85 °C and kept there for 3 h, which is sufficient time for gelation and curing to be accomplished. After the formation of the polymeric structure excess water was eliminated by continuing to heat the gel in the same microwave oven until a mass loss of over 50% was achieved. The drying step lasted from 1 to 2 h depending on the pore structure of the material. Carbonization was performed at 700 °C under a nitrogen flow of 150 ml/min in a horizontal tubular furnace. The residence time was 2 h and the heating rate was set at 50 °C/min. The carbon xerogels obtained were denominated CX followed by the pH value and the value of the dilution ratio.

The porous properties of the carbon xerogels were characterized by nitrogen adsorption–desorption isotherm analysis performed at −196 °C and by means of mercury porosimetry, using a Micromeritics Tristar 3020 instrument and a Micromeritics AutoPore IV, respectively. Before each analysis, all the samples were outgassed at 120 °C and 0.1 mbar for 8 h using a Micromeritics VAcPrep 061. These degassing conditions were previously optimized for outgassing this type of material. BET surface area (S_{BET}) was determined by applying BET equation to the N_2 adsorption isotherm and microporosity (V_{DUB}) was estimated by the Dubinin-Raduskevich method. Parameters such as pore size (d_p) and mesopore/macropore volume (V_{meso}, V_{macro}), were determined by mercury porosimetry, while porosity was obtained by means of envelope density analyser, using a Micromeritics GeoPyc 1360.

The morphology of the carbonaceous structures was examined using a Quanta FEG 650 scanning electron microscope. Samples were previously attached to an aluminum tap using conductive double-sided adhesive tape. An accelerating voltage of 25 kV and a secondary electron detector EDT (Everhart-Thornley) were used in all analysis.

3. Results and discussion

The porous structure of the materials studied was determined by means of nitrogen adsorption–desorption analysis and the isotherm classification proposed by the IUPAC. The nitrogen

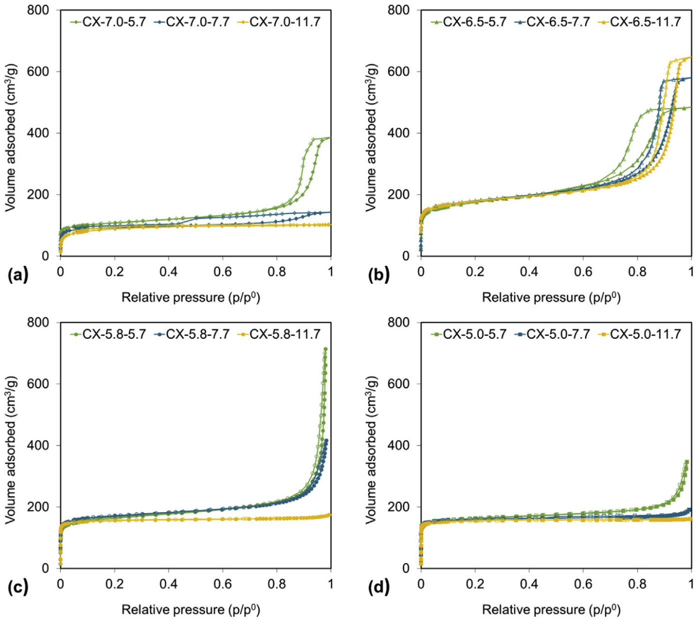

Fig. 1. N_2 adsorption–desorption isotherms of carbon xerogels.

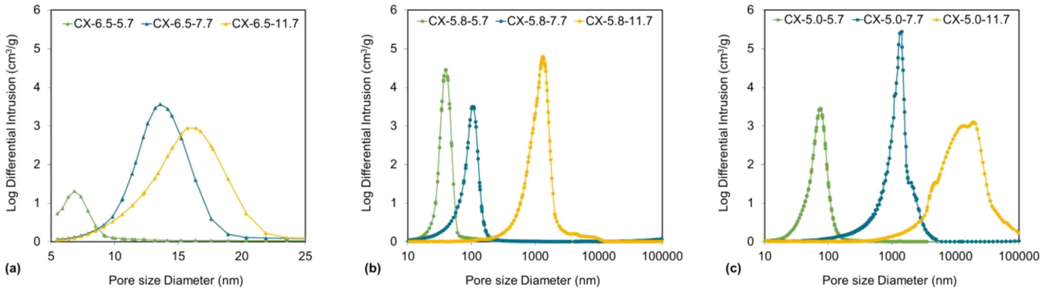

Fig. 2. Pore size distribution obtained by mercury porosimetry for carbon xerogels.

adsorption–desorption isotherms of the carbonized samples are depicted in Fig. 1, whilst the pore size distributions obtained by applying mercury porosimetry to the carbon xerogels are displayed in Fig. 2.

The N_2 adsorption–desorption isotherms presented in Fig. 1 show a clear difference in shape depending on the pH value of the precursor solution. The influence of the pH on the final properties of carbon xerogels is one of the most studied variables and almost all authors agree about its effect [1,2,5,8–10,15]. This effect can be attributed to the two steps involved in the polymerization reaction between resorcinol and formaldehyde: the addition and condensation reactions, as explained in detail elsewhere [6]. Briefly, the catalyst favors the addition reaction, i.e., the formation of resorcinol anions which are the active sites where formaldehyde is added during the addition reaction and where the formation of the clusters starts [6,7,9]. Accordingly, increasing the pH value of the precursor solution causes the formation of a large number of small clusters, resulting in materials with smaller pores as shown in Fig. 2.

In Fig. 1 it can also be seen that the shape of the isotherm of the samples synthesized from precursor solutions with the same pH value also changes due to the effect of the dilution ratio. Carbon xerogels synthesized from precursor solutions with a pH value of 7 (Fig. 1a) evolve from micro-mesoporous materials (combination of isotherm type I and IV) to exclusively microporous materials (isotherm type I) due to an increase in the dilution ratio from 5.7 to 11.7. Materials obtained from precursor solutions with a pH value of 6.5 lead to isotherms of a combination of type I and IV corresponding to micro-mesoporous materials (Fig. 1b). All these samples display a pronounced hysteresis loop associated to the presence of small-size mesopores. As D increases from 5.7 to 11.7, the hysteresis loop becomes narrower and shifts to higher relative pressures, indicating an increase in the pore size which is confirmed by the pore size distribution in Fig. 2a. At lower pH values (Fig. 1c and d), an increase in D causes the isotherms of the materials to evolve from a combination of type I and II (corresponding to micro-macroporous materials) to type I (corresponding to exclusively microporous materials). However, these carbon xerogels corresponding to a type I isotherm are not exclusively microporous but micro-macroporous materials (Fig. 2b and c). The pore size is large enough to fall exclusively within the macroporosity range and then to become inappreciable when nitrogen adsorption analysis is applied. These results can be clearly appreciated in Table 1 in which the porous properties of the carbon xerogels are listed.

In short, the pore size increases with D provided that the pH value falls below 7. The reason for this effect has not been explained in as much detail as the effect of pH [1,4,9,10]. However, some authors have reported that an increase in the amount of water leads to a structure with a small number of weakly branched clusters [6,12]. Depending on the pH (i.e. on the shape and size of the clusters) and because of the vapor–liquid interface generated during drying, shrinkage occurs to a greater or lesser extent and, hence, the porosity of organic xerogels varies. Rey-Raap et al. have provided a graphic illustration of this outcome where it was shown that the number and the size of the clusters was only pH dependent while the degree of shrinkage produced during drying was due to a combination of both the pH and the dilution ratio [6]. These results are in good agreement with the structures shown in Fig. 3, where images obtained by applying scanning electron microscopy (SEM)

Table 1
Porous properties of carbon xerogels synthesized from precursor solutions with different values of pH and dilution ratio.

Sample	S_{BET}[a] (m^2/g)	V_{DUB}[a] (cm^3/g)	V_{meso}[b] (cm^3/g)	V_{macro}[b] (cm^3/g)	d_p (nm)	Porosity[c] (%)
CX-5.0-5.7	636	0.25	0.24	0.92	70[b]	71
CX-5.0-7.7	632	0.24	0.01	2.20	1500[b]	81
CX-5.0-11.7	631	0.24	0.01	2.94	14000[b]	74
CX-5.8-5.7	661	0.25	0.98	0.10	40[b]	69
CX-5.8-7.7	656	0.25	0.13	1.04	100[b]	69
CX-5.8-11.7	632	0.24	0.01	1.87	1200[b]	76
CX-6.5-5.7	676	0.26	0.23	0.00	8[b]	45
CX-6.5-7.7	671	0.26	0.66	0.00	14[b]	59
CX-6.5-11.7	671	0.26	0.67	0.00	18[b]	59
CX-7.0-5.7	400	0.16	–	–	12[a]	28
CX-7.0-7.7	360	0.15	–	–	9[a]	25
CX-7.0-11.7	340	0.14	–	–	9[a]	27

[a] Obtained by the N_2 adsorption–desorption isotherm.
[b] Obtained by mercury porosimetry.
[c] Obtained by Geopyc.

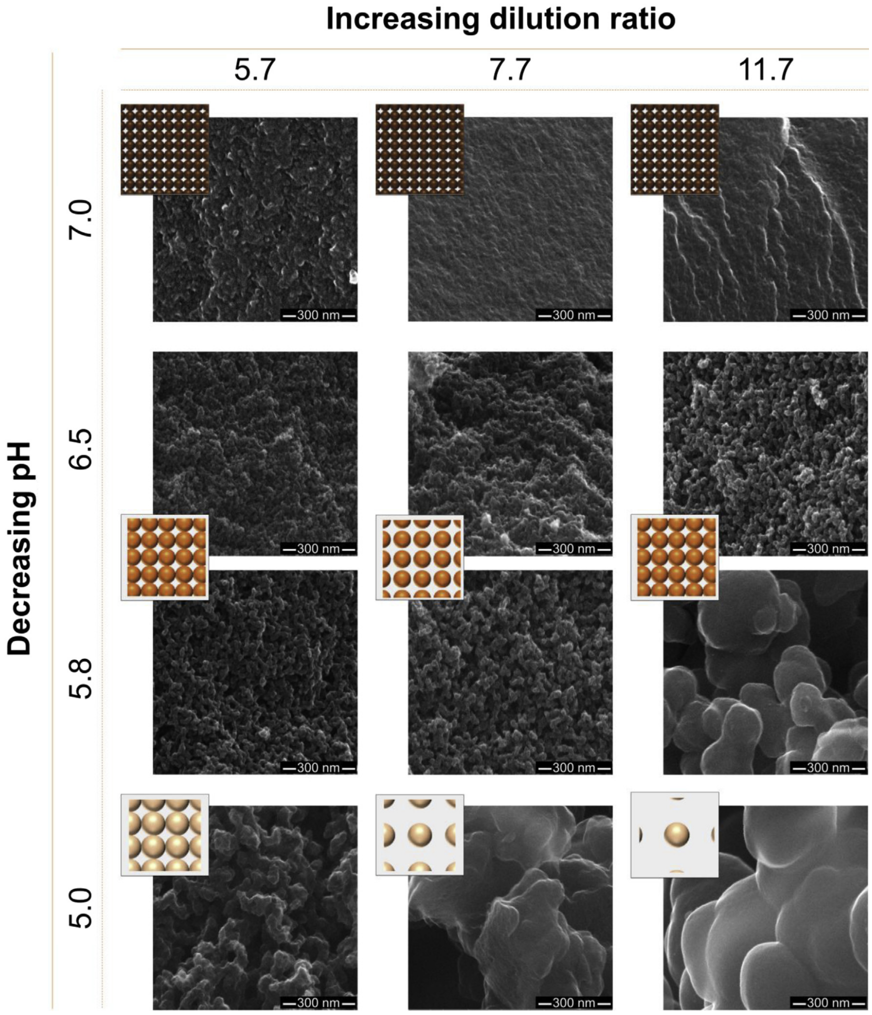

Fig. 3. SEM photographs of carbon xerogels.

to the synthesized carbon xerogels are presented. However, some differences can be appreciated between the SEM images obtained in the present study and the graphical hypothesis presented elsewhere (also shown in Fig. 3), especially with regard to the shape and size of the clusters.

On the basis of the definition of the dilution ratio and bearing in mind that all materials were prepared using the same volume of precursor solution, it can be affirmed that high values of D involve low concentrations of resorcinol and formaldehyde. The lower the concentration of resorcinol, the smaller the number of resorcinol anions generated and, consequently, structures with a reduced number of clusters are formed [6,11]. Furthermore, the addition reaction takes place more slowly, favoring the condensation reaction and, in this case, clusters of a larger size are formed. Thus, an increase in the dilution ratio gives rise to the formation of larger pores, as previously shown in Fig. 2. It should be noted, however, that the pH may increase the effect of the dilution ratio or, conversely, counteract it. Samples synthesized from a precursor solution with low pH value yield materials with a small number of large clusters. Furthermore, if the dilution ratio is high (e.g. sample CX 5.0–11.7) the size of the clusters are further increased and the combination of both these effects results in samples with exceptionally large pores (the total pore volume for sample CX-5.0-11.7 was 3.2 cm^3/g). If both values, the pH and dilution ratio, are low (e.g. sample CX-5.0-5.7), the clusters are large due to the effect of the pH, but of a smaller size than in sample CX-5.0-11.7 due to the effect of the dilution ratio. Thus the effect of one variable counteracts the effect of the other, resulting in a change in the porous structure of the materials, from being macroporous like sample CX-5.8-11.7 to being mesoporous like sample CX-5.8-5.7. Accordingly, in order to tailor the porous properties of carbon xerogels it is necessary not only to control the pH, but also to select the pH value taking into account the concentration of resorcinol and formaldehyde in the precursor solution, i.e., the dilution ratio.

4. Conclusions

In this study a scanning electron microscope was used in order to validate the combined effect of pH and dilution ratio on the porosity of carbon xerogels. It was found that the dilution ratio not only had a great influence on the degree of shrinkage but also modified the size and number of the clusters produced during the sol–gel reaction. The results of this study show that high values of dilution ratio give rise to a small number of clusters of large size. This effect is enhanced or diminished by the effect of the pH value of the precursor solution. In this way, microporous, micro-mesoporous and micro-macroporous materials with a large pore volume can be obtained provided that the appropriate pH and dilution ratio values are chosen.

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4.1.2. VARIACIÓN DEL pH, GRADO DE DILUCIÓN Y RATIO MOLAR RESORCINOL-FORMALDEHÍDO

Una vez evaluada la sinergia entre el pH y el grado de dilución y conocido el efecto que tiene su modificación simultánea sobre las propiedades porosas de los xerogeles de carbono, se incluyó el ratio molar resorcinol-formaldehído (R/F) como una nueva variable de estudio.

Objetivos

Los objetivos planteados para llevar a cabo este estudio fueron los siguientes:

- ✓ Evaluar estadísticamente las variaciones producidas sobre las propiedades de los xerogeles de carbono, sintetizados mediante calentamiento con microondas, al modificar el ratio molar resorcinol-formaldehído.

- ✓ Determinar el grado de sinergia entre el pH, el grado de dilución y el ratio molar resorcinol-formaldehído, y establecer su efecto sobre las propiedades de los xerogeles de carbono.

- ✓ Obtener las ecuaciones estadísticas que relacionan el pH, el grado de dilución y el ratio molar resorcinol-formaldehído con las propiedades porosas de los xerogeles de carbono, para poder determinar las condiciones óptimas que dan lugar a materiales con las propiedades requeridas por cada aplicación.

Selección del rango de estudio

El número mínimo de materiales que es necesario sintetizar y caracterizar, así como las combinaciones de pH-D-R/F que se deben fijar, se determinaron mediante la aplicación de técnicas de diseño de experimentos. La obtención de conclusiones válidas y objetivas se consiguió tras sintetizar y caracterizar un total de 70 xerogeles de carbono. La combinación de los valores de pH-D-R/F de todos estos materiales se encuentra dentro de unos rangos determinados, cuya selección se llevó a cabo considerando los siguientes aspectos:

- El valor del pH se varió entre 5 y 7 y el grado de dilución entre 5 y 10. Estos valores se fijaron en base a las Publicaciones III y IV incluidas en la sección anterior, donde se concluye que la combinación de pH-D dentro de estos valores da lugar a materiales mesoporos (tamaño medio de poro entre 2 y 50 nm). El propósito de centrar el estudio en este tipo de materiales se debe a que son los de mayor demanda en un gran número de aplicaciones.

- El ratio molar R/F se modificó entre 0.1 y 1. El resorcinol, junto al catalizador, es el responsable del número de nódulos que se forman, mientras que el formaldehído es el responsable de los entrecruzamientos entre nódulos. Teniendo en cuenta la reacción de polimerización entre el resorcinol y el formaldehído, cabe esperar que, modificando la proporción de ambos reactivos en el rango más amplio posible se pueda controlar de forma más exhaustiva el diseño de las propiedades.

El efecto de variar de forma simultánea el pH, el grado de dilución y el ratio molar R/F sobre las propiedades porosas de los 70 xerogeles de carbono se evaluó mediante el uso de la versión de prueba del software estadístico comercial Design-Expert (Stat-Ease, Inc.).

Conclusiones

Los detalles experimentales y los resultados obtenidos del estudio se describen y discuten en la Publicación V incluida al final de esta sección, cuyas principales conclusiones se detallan a continuación:

- El volumen de microporos no solo varía en función de las condiciones del proceso de carbonización sino también en base al ratio molar R/F. A medida que disminuye el valor de esta variable aumenta el volumen de microporos. Al introducir formaldehído en exceso parte de éste no reacciona y se elimina durante el proceso de secado, dejando libre cavidades pequeñas (microporos).

- El volumen de mesoporos se incrementa al disminuir el ratio molar R/F. El formaldehído es el responsable de formar las interconexiones entre nódulos y, por tanto, una concentración elevada de este reactivo da lugar a la formación de estructuras poliméricas con mayor resistencia mecánica. Así pues la rigidez del material permite contrarrestar las fuerzas de capilaridad producidas durante la etapa de secado, evitando retracciones en la estructura.

- El volumen de macroporos, dentro del rango de combinación de pH-D-R/F estudiado, depende, principalmente, del valor del pH de la mezcla precursora. Esto se debe a que el rango de estudio se seleccionó con el objetivo de obtener materiales mesoporosos, por lo que las variaciones en la macroporosidad al variar el grado de dilución y el ratio molar R/F son prácticamente despreciables.

- La concentración de todos los reactivos influye notoriamente en las propiedades finales de los xerogeles de carbono. Además, existe un grado considerable de sinergia entre ellas. Por ejemplo, la variación del ratio molar R/F produce un cambio en la combinación pH-D que da lugar a materiales con elevada porosidad. A medida que aumenta el ratio molar R/F desde 0.1 a 0.5, se debe disminuir el valor del pH y aumentar el del grado de dilución para poder obtener materiales con una porosidad bien desarrollada.

- La variación simultánea del pH, del grado de dilución y del ratio molar R/F permite obtener xerogeles de carbono con propiedades porosas que no es posible obtener modificando tan solo el pH o el grado de dilución. Es decir, la variación del ratio molar R/F permite controlar mejor las prestaciones de los xerogeles de carbono.

PUBLICACIÓN V

SIMULTANEOUS ADJUSTMENT OF THE MAIN CHEMICAL VARIABLES TO FINE-TUNE THE POROSITY OF CARBON XEROGELS

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Simultaneous adjustment of the main chemical variables to fine-tune the porosity of carbon xerogels

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A B S T R A C T

The objective of this study was to assess the effect of the resorcinol–formaldehyde molar ratio of precursor solutions with pH values ranging from 5.0 to 7.0 and dilution ratios between 5 and 10 upon the final porous properties of carbon xerogels synthesized by microwave heating, using an optimal design of response surface methodology. It was found that when the resorcinol–formaldehyde molar ratio was decreased the microporosity was enhanced as the addition reaction was favored. Hence, the micropore volume of carbon xerogels not only depends on the conditions used during carbonization, but also on the synthesis conditions. Mesoporosity was also increased when the resorcinol–formaldehyde molar ratio decreased while macroporosity was only influenced by the initial pH of the precursor solutions. The simultaneous variations of the three chemical variables allowed an exhaustive control of the final porous properties of carbon xerogels, which exhibited pore sizes and pore volumes that could not be obtained by modifying just the pH and the dilution ratio.

1. Introduction

Carbon gels are porous materials obtained by the polymerization of resorcinol with formaldehyde in the presence of a solvent, following Pekala's method [1]. The wet organic gel is then dried and carbonized in order to obtain the carbon gel. The final porous properties of these materials can be tailored by modifying the variables of the different stages of production: polymerization, drying and pyrolysis.

The pH, type of solvent, the concentration of reagents and the temperature and time of the synthesis are some of variables to take into consideration in the polymerization process [2]. Regarding the drying stage, three main types of drying methods can be found in the literature: supercritical drying, freeze-drying and evaporative drying, which give rise to aerogels, cryogels and xerogels, respectively [3–7]. The use of one or another method leads to materials with different properties as shrinkage produced by the removal of the solvent in the case of evaporative drying is much greater than in the other drying processes, and hence, a less developed porous structure is obtained [8,9]. Besides the conditions selected for the synthesis process and the type of drying used, certain final properties can also be modified by the carbonization process. For example, the volume of micropores can be enhanced by adjusting the time, temperature, gas type and gas flow rate used for the carbonization [10–14].

However, the variables that play a role in the polymerization process are the ones that have the greatest influence on the final properties of carbon gels and are therefore the main focus of attention in this work. Previous studies have

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reported that the final properties are not greatly influenced by the time of synthesis provided that the time is long enough for crosslinking and secondary reactions to take place [15–17]. Furthermore, it has also been reported that the final porous properties are not modified by setting the temperature of synthesis between 75 and 85 °C [17]. Hence, carbon gels with accurately controlled porous properties can be synthesized by modifying the concentrations of the reagents: resorcinol, formaldehyde, solvent and catalyst. These concentrations are reported in the literature to be related to the pH of the precursor solution, the dilution ratio and the molar ratio between the resorcinol and the formaldehyde. The influence of the pH of the precursor solution on the final properties of the carbon gel is one of the most studied variables. General speaking, a decrease in the pH favours the formation of larger pores [5,18–21]. On the other hand, an increase in the amount of water leads to a structure with a few weakly branched clusters. The mechanical strength of these materials is low, and therefore, during drying they undergo further contraction, resulting in materials with a smaller volume of pores [5,8,18,20,22].

Formaldehyde is responsible for the crosslinking between clusters that takes place during the gelation and ageing steps. An excess of formaldehyde, i.e., lower resorcinol/formaldehyde molar ratio, could lead to the formation of a high number of crosslinkages that could eventually cause a collapse of the pore structure. On the other hand, an amount of formaldehyde below the stoichiometric value could prevent the precursor solution from reaching the gelation point or could lead to a weakly branched structure leading to enhanced shrinkage during drying [11]. Accordingly, some authors state that the resorcinol/formaldehyde molar ratio should be between 0.4 and 0.7 [11,20]. However, Maldonado-Hódar et al. have reported that a higher range can be used, e.g., from 0.33 to 1.0. They found out that a decrease in the resorcinol/formaldehyde molar ratio to below the stoichiometric value (i.e., 0.5) led to an increase in the volume of micropores and to a decrease in the volume of macropores, while no variations in the volume of mesopores were observed [23]. Other authors were able to synthesize aerogels with a resorcinol/formaldehyde molar ratio below 0.4 when acidic conditions were fixed. The materials obtained hardly shrank and exhibited a well-developed mesoporous structure [24]. However, it must be noted that these studies were performed on aerogels that, in general, are materials which, depending on the drying method used, barely suffer contractions during drying. Nonetheless, different trends due to the influence of the resorcinol/formaldehyde molar ratio on the final porous properties can be found when other drying methods, such as evaporative drying, are applied. For this reason, such trends need to be studied in depth.

In order to reduce the production costs of carbon gels and to promote the marketing of these materials, microwave assisted and evaporative drying should be employed. Microwave technology for the production of carbon xerogels is a cost-effective process since the processing time is considerably reduced and only one device and moderate conditions are needed. However, to accurately tailor the final porous properties of carbon xerogels, the effect of adjusting the chemical variables involved in the synthesis process needs to be fully understood.

In this work, the influence of the resorcinol/formaldehyde molar ratio on the final porous properties of carbon xerogels obtained from precursor solutions with different values of pH and dilution ratios was studied. In order to evaluate any possible synergy between these three main chemical variables and to enhance the control of the porosity of the materials, the response surface methodology was applied to four response variables: the volume of micropores, mesopores and macropores, and the overall porosity.

2. Experimental

2.1. *Synthesis of organic and carbon xerogels*

Organic xerogels were synthesized by the polycondensation of resorcinol (R) and formaldehyde (F) using deionized water as solvent. Resorcinol (Indspec, 99%) was first dissolved in deionized water in an unsealed glass beaker under magnetic stirring. After dissolution, formaldehyde (Ercros, 37 wt.% in water, stabilized by 10–15% methanol) was added and the mixture was stirred until a homogeneous solution was obtained. All the xerogels were synthesized from 200 ml of precursor solution and the final pH value was adjusted by adding sodium hydroxide. The amount of resorcinol, formaldehyde and water used for each sample depended on the resorcinol/formaldehyde molar ratio (R/F) and the dilution ratio (D) selected. The dilution ratio parameter is defined as the molar ratio between the total solvent and reactants. Total solvent refers to the water and methanol contained in the formaldehyde and the deionized water that is added, whilst the term reactants refers to the resorcinol and formaldehyde.

The ranges of pH values of the precursor solutions were selected on the basis of previous experimental results [22]. Samples with a pH greater than 7.0 are exclusively microporous materials while samples with a pH value lower than 5.0, display averages pore sizes greater than 200 nm. Most of the applications in which carbon xerogels are promising materials require averages pore sizes below 200 nm. Consequently, in this study the pH range of the precursor solutions was fixed between 5.0 and 7.0. The range of values for the dilution ratio was selected on the basis of a previous study in which it was reported that, for all the pH values, when the dilution ratio was decreased to below 5 or increased to above 10, the materials obtained had a poorly developed porous structure. The maximum value for the resorcinol/formaldehyde molar ratio was selected on the basis of the porous properties of the xerogels, i.e., the molar ratio was increased gradually until the materials obtained presented a non-porous structure. Some xerogels did not reach the gelation point for certain dilution ratios when the resorcinol/formaldehyde molar ratio was fixed below 0.1. Hence, the resorcinol/formaldehyde molar ratio was varied from 0.1 to 1.0.

Each precursor solution was placed in a microwave oven at 85 °C for 3 h, to allow gelation and ageing to be completed [17]. After the formation of the polymeric structure, excess water was eliminated by continuing to heat the gel in the microwave oven until a mass loss of over 50% was achieved.

The drying step lasted 1–2 h depending on the final pore structure of the material.

After drying, the xerogels were carbonized at 700 °C under a nitrogen flow of 500 ml/min in a horizontal tubular furnace, using the same procedure as in previous works [10]. The residence time was 2 h and the heating rate was set at 50 °C/min.

2.2. *Sample characterization*

The porous properties of the carbon xerogels were characterized by nitrogen adsorption–desorption isotherm analysis and by a mercury porosimetry technique, performed at −196 °C using a Micromeritics Tristar 3020 instrument and in a Micromeritics AutoPore IV, respectively. Prior to each analysis, all the samples were outgassed at 120 °C and 0.1 mbar for 8 h using a Micromeritics VacPrep 061. The micropore volume was calculated by applying the Dubinin–Radushkevich method to the nitrogen adsorption–desorption isotherms. Pore volume measurements by nitrogen adsorption are not precise enough for samples with large mesopores. For this reason, mercury porosimetry was used as a complementary technique to determine the volume of mesopores and macropores and the percentage of porosity. Analysis of mercury porosimetry was based on Washburn's intrusion theory.

2.3. *Experimental design*

Response Surface Methodology (RSM) was applied to the characterization results in order to optimize the microwave-assisted synthesis of carbon xerogels. By using a suitable Design Of Experiments (DOE), namely D-optimal, it was possible to reduce the number of experiments needed and assess the possible synergy between the variables studied: the pH, the dilution ratio (D) and the resorcinol/formaldehyde molar ratio (R/F). An optimal design requiring 70 experimental points, covering all the possible pH–D–R/F combinations along with repeated experimental runs, was employed to obtain a statistical model that would adequately fit the experimental results. The volume of micropores, mesopores and macropores and the overall porosity were selected as the responses of the system. The design matrix was generated by using a Design-Expert 9.0 Trial version from Stat-Ease Inc.

3. Results

Carbon xerogels were synthesized with different pH, dilution ratio and R/F molar ratio values. These values ranged from 5.0 to 7.0, from 5 to 10 and from 0.1 to 1.0, respectively. All the carbon xerogels were characterized from the point of view of their porous structure. Fig. 1 illustrates the pore size distribution of some of the samples obtained by mercury porosimetry.

Fig. 1a includes carbon xerogels prepared from precursor solutions with the dilution ratio and the R/F molar ratio most frequently used by other authors, i.e., 5.7 and 0.5, respectively, but with different initial pHs: 6.5, 6.0, 5.5, 5.0. As can be seen from Fig. 1, the pore size distributions show a clear difference in shape and in average pore size depending on the initial pH value, ranging from less than 20 nm to pore sizes greater than 100 nm. Furthermore, as the pH decreases, not only does the pore size increase but also the volume of the pores. However, there is a wide range of pore sizes and pore volumes that cannot be achieved by only changing the pH of the precursor mixture. It is also necessary to vary the dilution ratio and the R/F molar ratio.

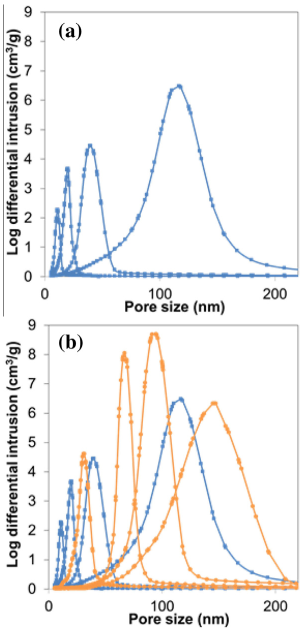

Fig. 1 – Pore size distribution of carbon xerogels prepared using (a) different initial pHs and the most commonly used dilution ratio (i.e., 5.7) and the stoichiometric R/F molar ratio (i.e., 0.5) and (b) the pore size distribution of carbon xerogels prepared by simultaneous adjustment of the pH, dilution ratio and R/F molar ratio. (A colour version of this figure can be viewed online.)

As can be seen in Fig. 1b, by modifying simultaneously these three chemical variables, materials with intermediate pore size distributions that cannot be obtained by just modifying the pH of the precursor solution can be synthesized. Furthermore, such samples not only have an intermediate average pore size but also a higher pore volume. This demonstrates that complete control of the final porous properties of carbon xerogels depends to a great extent on the pH, the dilution ratio and the R/F molar ratio.

3.1. *Statistical analysis*

Statistical analyses were performed using response surface methodology (RSM). The implementation of RSM allows the interaction between the pH, the dilution ratio and the R/F molar ratio and their effect on the main porous properties to be evaluated with a minimum number of experiments. In order to determine whether the model selected was sufficiently significant to fit the experimental results, an analysis of variance (ANOVA) was applied to each of the four variables selected as responses: volume of micropore, mesopore and macropore and percentage of porosity. The significance of each input variable, i.e., pH, D and R/F, and their possible interaction was determined by assessing the *p*-value. If the *p*-values turn out to be smaller than 0.05, the corresponding variable will have a significant effect on the response.

3.1.1. *Micropore volume*

The micropore volume values for all carbon xerogels synthesized using the selected pH–D–R/F combination were adjusted to a cubic function. The correlation coefficient value R-squared was 0.80, indicating that the calculated results were in good agreement with those obtained experimentally. The results of the ANOVA applied to the microporosity are summarized in Table S1 in the supporting information. The data obtained by employing a least square technique indicate that the model is significant for microporosity. Moreover, the quadratic term of R/F is the most significant model term based on the *p*-value ($p < 0.005$), indicating that modification of the other two chemical variables, pH and D, has no effect on the influence of the micropore volume.

Three-dimensional (3D) surface plots were constructed on the basis of the model equations obtained for different values of R/F molar ratio, representing the response surface curves of two of the independent variables, pH and D, versus the dependent variable, the volume of micropores (Fig. 2). The 3D plots show the evolution of the micropore volume in the samples with a pH value between 5.0 and 7.0 and a dilution ratio between 5 and 10, when the R/F molar ratio is fixed at 0.3, 0.5 and 0.7, respectively.

Regardless of the R/F molar ratio, the pH and the dilution ratio hardly affect the micropore volume within the range studied. However, if Fig. 2a–c are compared, clear differences can be seen when the R/F molar ratio is modified. By selecting the stoichiometric value (i.e., 0.5), all the carbon xerogels exhibit a similar micropore volume value of around $0.25 \pm 0.01\ cm^3/g$. An increase in the R/F molar ratio from 0.5 to 0.7 gives rise to a slight decrease in the volume of micropores from 0.25 ± 0.01 to $0.20 \pm 0.03\ cm^3/g$, while a large increase to above 0.7 leads to materials with a poorly developed microporous structure which display an average micropore volume of $0.15 \pm 0.02\ cm^3/g$. The micropore volume is enhanced when an R/F molar ratio below the stoichiometric value is selected. The highest micropore volume value is obtained by adjusting the R/F molar ratio to 0.2. However, below this value, the micropore volume again decreases to values of about $0.15 \pm 0.02\ cm^3/g$. The evolution of the micropore volume of the carbon xerogel over the entire range of pH–D–R/F combinations studied is shown in the animation file in the supporting information.

To the best of our knowledge, most of the publications until now have indicated that the development of the micropores takes place within the nodules during the pyrolysis step. However, in this study, variations in the volume of micropores occurred when the R/F molar ratio was modified. It would seem appropriate therefore to evaluate the variation of microporosity in the organic RF xerogel counterparts in order to see whether the volume of micropores is also influenced by the polymerization reactions. Fig. 3 shows the evolution of

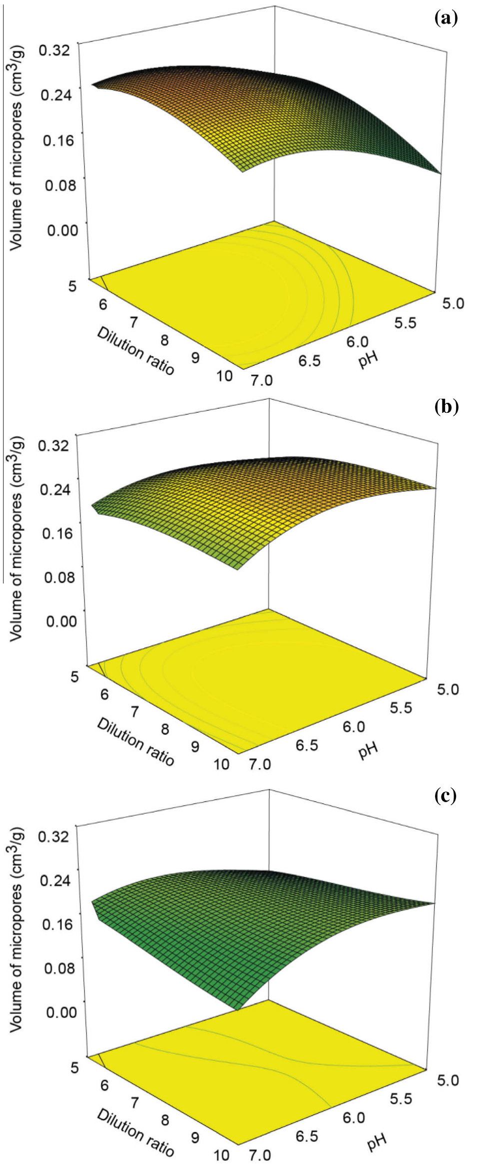

Fig. 2 – Three-dimensional surfaces representing the effect of the pH and dilution ratio on the microporosity of carbon xerogels when setting the R/F molar ratio to 0.3 (a), 0.5 (b) and 0.7 (c). (A colour version of this figure can be viewed online.)

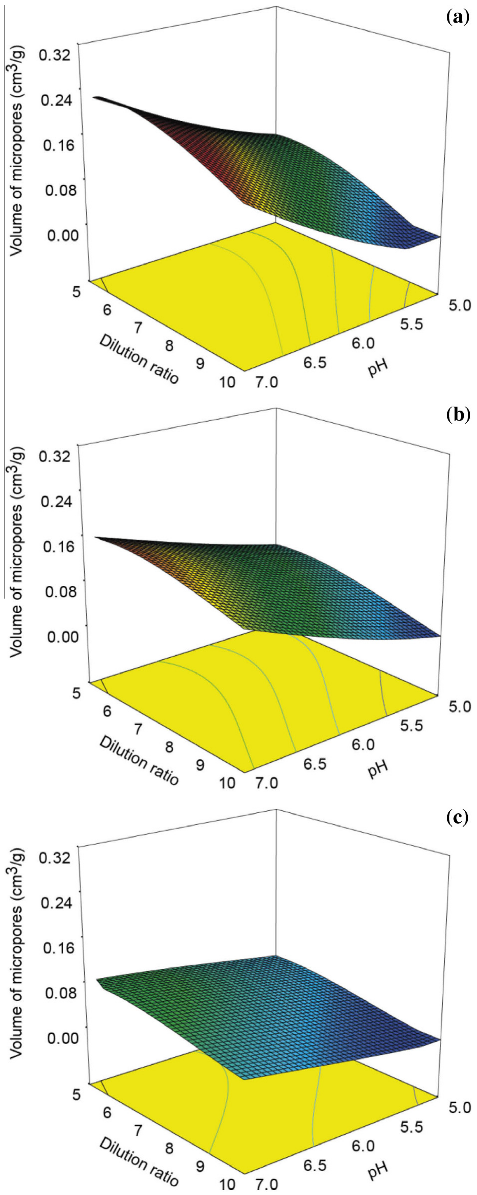

Fig. 3 – Three-dimensional surfaces representing the effect of the pH and dilution ratio on the microporosity of organic xerogels when the R/F molar ratio is set to 0.3 (a), 0.5 (b) and 0.7 (c). (A colour version of this figure can be viewed online.)

the micropore volume when the pH and the dilution ratios of organic xerogels synthesized from precursor solutions with pH values between 5.0 and 7.0 and dilution ratios from 5 to 10, are modified, while the R/F molar ratio is fixed at 0.3, 0.5 and 0.7, respectively. The micropore volume of the organic samples follows the same trend as the micropore volume of the carbonized samples (Fig. 2), i.e., the microporosity decreases when the R/F molar ratio is increased.

The extent of the improvement or increase in microporosity during the carbonization process differs greatly when the R/F molar ratio is modified. Organic xerogels synthesized from precursor solutions at the R/F stoichiometric value and an R/F molar ratio lower than the stoichiometric value display similar micropore volumes while, when the R/F molar ratio is adjusted to above the stoichiometric value, the resulting organic xerogels exhibit a poorly developed microporosity. During the pyrolysis, the microporosity of these materials is enhanced up to values close to those obtained for organic xerogels with a low R/F molar ratio. Considering that these are carbonized samples, the micropore volume is still low, even though an 86% increase is achieved. In the samples with lower values of R/F molar ratio, the increase in microporosity is about 50%. These results show that, regardless of the increase in micropore volume from carbonization, the microporosity of the carbon xerogels not only depends on the conditions established during the carbonization, but also on the microporosity of the organic counterparts and, consequently, on the synthesis conditions.

3.1.2. *Mesopore volume*

The mesopore volume values for all the samples synthesized using the pH–D–R/F combinations studied were adjusted to a cubic function with an *R*-squared value of 0.76. The results of the ANOVA applied to mesoporosity are presented in Table S2. The data obtained by employing a least square technique indicate that the model is significant for mesoporosity. Moreover, the quadratic and cubic terms of pH and the R/F are significant model terms based on the *p*-value ($p < 0.005$). The interactions between the three chemical variables are not significant, indicating that modification of one of these variables has no effect on the influence of the other two.

Three-dimensional surface plots constructed according to the model equations obtained for different values of the R/F molar ratio are shown in Fig. 4. The 3D plots show the evolution of the mesopore volume of the samples with a pH value between 5.0 and 7.0 and a dilution ratio between 5 and 10, when the R/F molar ratio is set to 0.5 and 0.2, respectively, for the carbonized samples and their corresponding organic counterparts.

In Fig. 4a a maximum mesopore volume value of about $0.65 \pm 0.05\ \mathrm{cm^3/g}$ is obtained by adjusting the pH between 5.6 and 6.0 and the dilution ratio between 5.5 and 7.0. A decrease in the R/F molar ratio to below the stoichiometric value leads to an increase in the mesopore volume, especially at low pH and dilution ratio values within the range studied. In Fig. 4b a maximum mesopore volume value of around $1.1 \pm 0.05\ \mathrm{cm^3/g}$ can be clearly observed. By increasing the R/F molar ratio to above 0.5 the volume of mesopores decreases to values below $0.1 \pm 0.05\ \mathrm{cm^3/g}$. The evolution of the mesopore volume of the carbon xerogel over the entire range of pH–D–R/F combinations studied is shown in the animation file in the supporting information.

Most of the published works relating to the carbonization of resorcinol–formaldehyde gels state that mesoporosity is

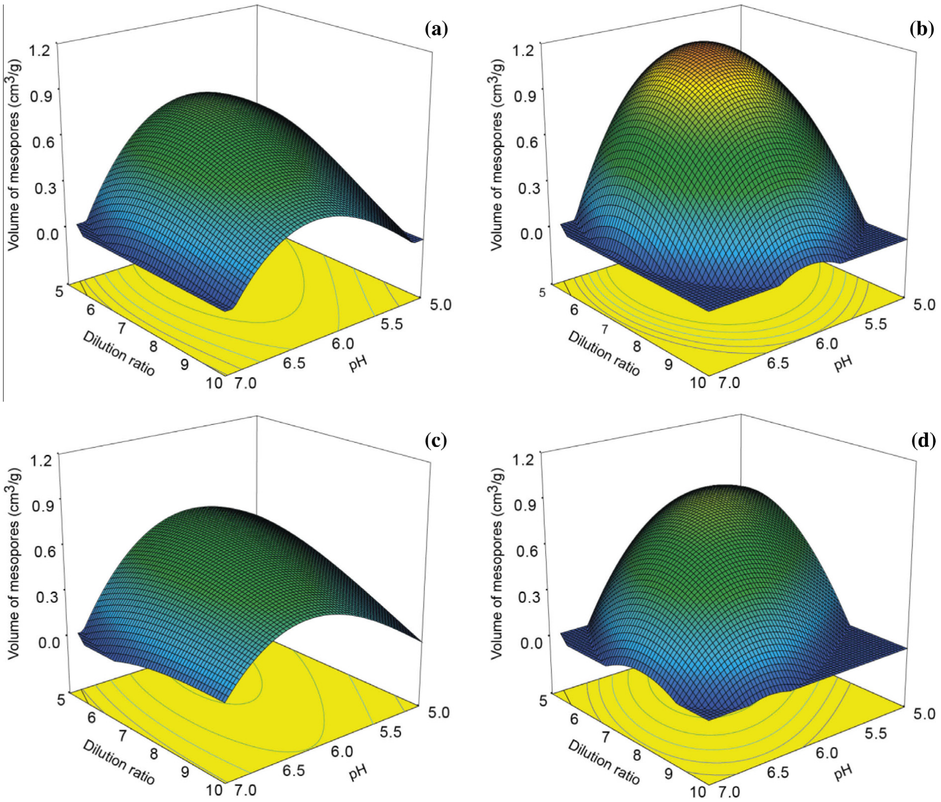

Fig. 4 – Three-dimensional surfaces representing the effect of the pH and dilution ratio on the mesoporosity of carbon xerogels when the R/F molar ratio is fixed at 0.5 (a) and 0.2 (b) and of organic xerogels when the R/F molar ratio is fixed at 0.5 (c) and 0.2 (d). (A colour version of this figure can be viewed online.)

affected by the synthesis conditions while it remains almost invariable during carbonization. This statement is in agreement with the results shown in Fig. 4a and c. The organic samples and their corresponding carbonized counterparts obtained from precursor solutions with the stoichiometric R/F molar ratio value exhibit a similar mesoporosity. In other words, during the carbonization process the mesopore volume is barely modified.

However, in Fig. 4b and d it can be clearly observed that, when the R/F molar ratio is fixed at below the stoichiometric value, the volume of mesopores increases during carbonization. The organic samples presented in Fig. 4d have an average maximum volume value of 0.82 ± 0.05 cm^3/g which, after carbonization, increases to 1.1 ± 0.05 cm^3/g (Fig. 4b).

3.1.3. *Macropore volume*

The macropore volume values of the synthesized samples were fitted to a cubic function with a correlation coefficient value of 0.80. The results of the ANOVA applied to the macropore volume are presented in Table S3 in the supporting information. The data obtained by applying the least square technique indicate that the model is significant for macroporosity. As regards the chemical variables, only the pH term appears to be significant. The dilution ratio, the R/F molar ratio and the interaction between the three variables are not significant model terms within the range of pH–D–R/F combinations studied. These results were as expected considering that the initial conditions of the precursor mixtures were selected on the basis of the average pore size, in order to cover the entire range of mesoporosity and a small range of macroporosity (average pore size from a few nanometers to 200 nm). Hence, the range of study as regards macroporosity is not wide enough for variations to be detected when the dilution ratio and the R/F molar ratio are modified.

Three-dimensional (3D) surface plots were constructed on the basis of the model equations obtained for different values of the R/F molar ratio, representing the response surface curves of the pH and D versus the macropore volume (Fig. 5). The 3D plots show the evolution of the macropore volume of the samples with a pH value between 5.0 and 7.0 and a dilution ratio between 5 and 10, when the R/F molar ratio is set to 0.4, 0.5 and 0.8, respectively.

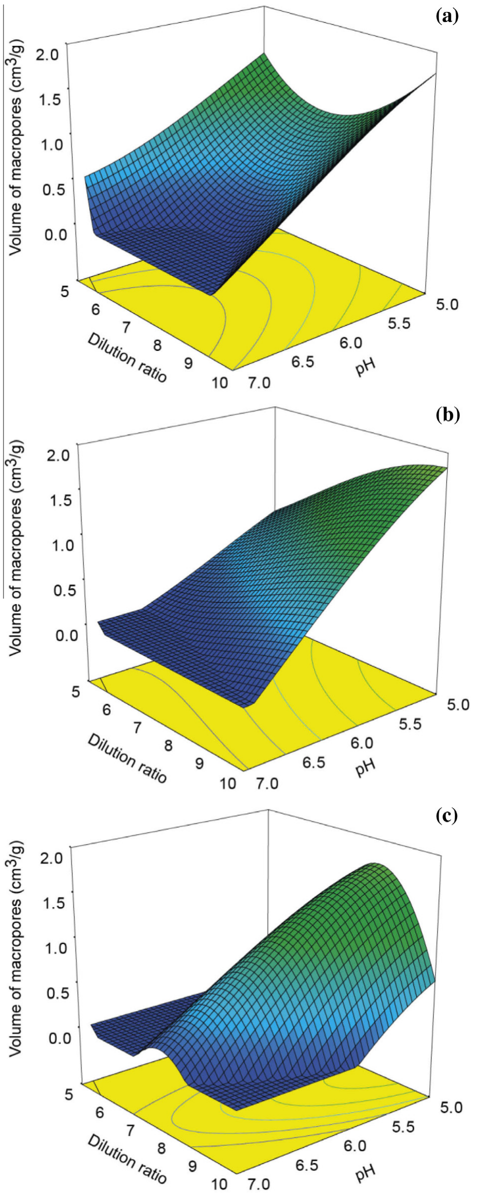

Fig. 5 – Three-dimensional surface representing the effect of the pH and dilution ratio on the macroporosity of carbon xerogels when the R/F molar ratio is fixed at 0.4 (a), 0.5 (b) and 0.8 (c). (A colour version of this figure can be viewed online.)

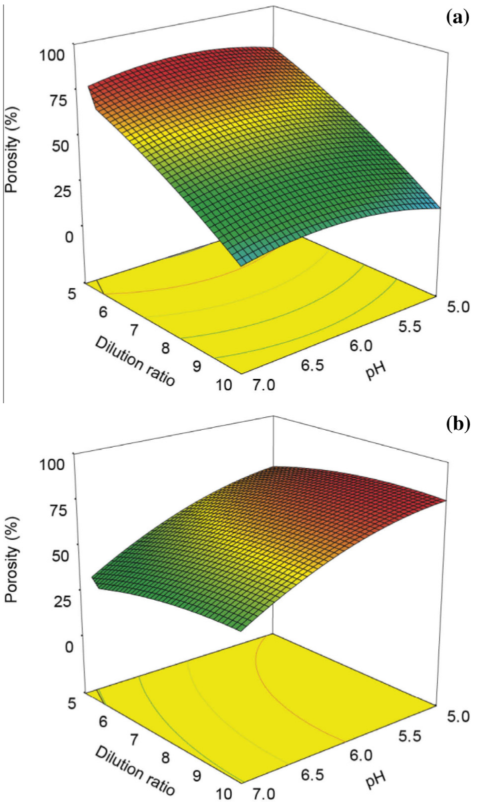

Fig. 6 – Three-dimensional surface representing the effect of the pH and dilution ratio on the porosity of carbon xerogels when the R/F molar ratio is fixed at 0.5 (a) and 0.2 (b). (A colour version of this figure can be viewed online.)

For all the combinations of pH–D–R/F studied the macropore volume ranges from 0.0 ± 0.04 cm^3/g to 1.9 ± 0.04 cm^3/g. Macroporous materials can be synthesized by adjusting the pH to below 5.5 and the dilution ratio up to 7, within a R/F molar ratio range of between 0.4 and 0.8. An increase in the R/F molar ratio to above 0.8 causes a decrease in the volume of macropores to below 0.3 ± 0.02 cm^3/g. The macroporosity also decreases when the R/F molar ratio is lower than 0.4, since under these synthesis conditions, the materials obtained are in the mesoporosity range.

3.1.4. *Porosity*

The porosity values of all carbon xerogels were adjusted to a quadratic function with an R-squared value of 0.80. The results of the ANOVA applied to porosity are summarized in Table S4. The data obtained by applying the least square technique indicate that the model is significant for porosity. The pH, the dilution ratio and the quadratic term for the three chemical variables are also significant terms. Moreover, the interaction between the dilution ratio and both the pH and the R/F molar ratio are significant, indicating that modification of one of the variables affects the influence of the other two on the porous properties of the material.

Three-dimensional surface plots constructed according to the model equations obtained for different values of R/F molar ratio are shown in Fig. 6. The 3D plots show the evolution of the porosity of carbon xerogels synthesized from precursor solutions with a pH value of between 5.0 and 7.0 and a dilution ratio of between 5 and 10, when the R/F molar ratio is fixed at 0.5 and 0.3, respectively.

Within the range of pH–D–R/F combinations studied, the materials obtained exhibit a maximum porosity of 80%. Materials with higher values of porosity can be found in the literature [5]. However, in this study the pH and the dilution ratio of the precursor solutions were selected so that most of the materials would be in the mesoporosity range, which would then display lower values of porosity. Higher porosities up to ca. 90% could be achieved by fixing lower pH values, but then the materials would fall within the range of large macroporosity and, consequently, outside the scope of this study.

Regardless of the R/F molar ratio selected, the highest porous materials are obtained when the pH is set to below 5.6. Although variation of the R/F molar ratio does not have a direct influence on the porosity, it causes a change in the range of the dilution ratio necessary to obtain highly porous materials. In fact, as the R/F molar ratio is increased from 0.1 to 0.5 the dilution ratio shifts to a range of higher values in order for materials with a well-developed porosity to be obtained. The porosity of samples synthesized from precursor solutions prepared with an R/F molar ratio greater than 0.5 decreases and displays porosity values below 40% when the R/F molar ratio is at its maximum value.

4. Discussion

Several authors have reported that the carbonization process involves the breaking of C–O bonds at low temperatures and the breaking of C–H bonds at high ones [23,25]. The breakage of bonds leads to the rearrangement of molecules resulting in a stable structure [18]. Some walls separating individual micropores will break resulting in the enlargement of narrow micropores [14]. On the other hand, the condensation produced during the carbonization process causes a slight shrinkage of the polymeric structure and, consequently, the size of the mesopores and macropores will decrease [21]. Some mesopore sizes will be smaller than 2 nm and therefore, the volume of these pores will have to be considered as micropores rather than mesopores. Both phenomena contribute to an increase in microporosity during carbonization. Accordingly, the volume of micropores depends to a great extent on the carbonization conditions.

The results of this study are in good agreement with the above explanation when carbon xerogels are synthesized from precursor solutions with the stoichiometric value of the R/F molar ratio. Under these conditions the variation in microporosity when the pH and the dilution ratio are modified is negligible. However, when the R/F molar ratio is modified the microporosity is enhanced. The increase in microporosity produced by modifying the R/F molar ratio can be attributed to the polymerization between resorcinol and formaldehyde.

Initially, resorcinol anions are formed by hydrogen abstraction. These anions are more reactive than resorcinol and promote the addition of formaldehyde to form hydroxymethyl derivatives, which are the monomers necessary for polymerization to occur [9]. At the same time as the addition reaction, condensation occurs. The hydroxymethyl derivatives then lose OH groups to form benzyl-type cations. Each cation reacts with a benzene ring of another molecule giving rise to a methylene bond [21]. As the reaction proceeds the number of bonds between the rings increases, forming the polymer backbone, which leads to three-dimensional cross-linked polymer clusters or, as defined by other authors, primary particles [26]. An increase in the concentration of formaldehyde, i.e., a decrease in the R/F molar ratio, shifts the chemical equilibrium toward the products, increasing the reaction rate [18]. This suggests that the clusters will form and grow faster, i.e., the addition reaction will be promoted, resulting in the formation of more branched clusters. Consequently, carbon xerogels synthesized from precursor solutions with a concentration of formaldehyde higher than the stoichiometrically required amount, display a greater number of highly branched clusters of larger size and therefore, higher micropore volumes could be achieved as shown in Fig. 2. Another possible reason can be that the over loaded formaldehyde cannot react with resorcinol and remain inside the clusters freely. This unreacted formaldehyde is removed during drying due to its low boiling point. Hence, the place left by these formaldehyde molecules may be the cause of the increased microporosity.

Another point worth mentioning is that the microporosity of the organic counterparts is also influenced by the pH and the dilution ratio apart from the R/F molar ratio. In general, regardless of the R/F molar ratio, the micropore volume increases as the pH and the dilution ratio decrease (Fig. 3). The catalyst favours the addition reaction, i.e., the formation of resorcinol anions which are the active sites where formaldehyde is added during the addition reaction and where the formation of the clusters originates [27]. Therefore, increasing the pH value of the precursor solutions causes the formation of a large number of small clusters interconnected by long necks. Meanwhile, a decrease in the dilution ratio will necessarily result in an increase in the amount of resorcinol and formaldehyde used, leading to a highly branched structure. Nonetheless, the effect of these two chemical variables disappears during the carbonization process, leaving as the only significant chemical variable the R/F molar ratio.

The addition of an excess of formaldehyde affects not only the volume of micropores, but also the mesoporous structure. When the molar ratio of resorcinol and formaldehyde is fixed at the stoichiometric value (i.e., 0.5) the maximum mesopore volume value is obtained for the combinations of pH–D between 5.5 and 6.0 and 5 and 7, respectively. The pH and D values for which the maximum mesopore volume values are obtained, are not altered by a decrease in the R/F molar ratio below the stoichiometric value. However, the volume is enhanced by 37% when the molar ratio is fixed at 0.2. This increase in mesoporosity is due to both a decrease in the R/F molar ratio and the carbonization process (Fig. 4). The excess of formaldehyde not only accelerates the formation and growth of clusters but also creates more interconnections between them, leading to a highly branched structure [1,18]. The mechanical strength of the organic xerogels is higher and therefore no shrinkage will occur during drying [8], leaving larger pores than in the case of samples synthesized from a precursor solution with the stoichiometric R/F molar ratio. As explained above, during carbonization part of that highly branched structure will break, leading to larger voids and, consequently to a higher mesoporosity. A insufficient amount of formaldehyde will lead to a weakly branched structure whose mechanical strength will not be able to counteract the surface tension created during drying and the material will shrink, resulting in the partial collapse of the structure and a decrease in the mesopore volume [11]. The collapse will be greater if the R/F molar ratio is increased, leading to a poor-developed mesoporous structure, especially when the molar ratio exceeds 0.8.

The macropore volume is not greatly influenced by the R/F molar ratio, but large variations are observed due to the initial pH of the precursor solutions. Previous studies indicate that for pH values lower than 5.5, macroporous materials are obtained when high dilution ratios are selected [22]. A decrease in the pH value will lead to the formation of a smaller number of large clusters, resulting in a structure with a higher pore volume that may come within the macroporosity range. The range of pH–D combinations used in this study falls outside the range of maximum macroporosity and thus, no large variations in the volume of macropores were observed.

The porosity of carbon xerogels decreases when the R/F molar ratio is increased from 0.1 to 0.5. The higher the concentration of formaldehyde is, the more highly branched the structure is and the lower the volume of pores. This effect can be counteracted by increasing the dilution ratio. An increase in the amount of solvent hinders crosslinkages and the volume of pores is greater. Therefore, the materials obtained have a high porosity in spite of having a R/F molar ratio below the stoichiometric value. However, if the R/F molar ratio is increased to above 0.5, i.e., less formaldehyde than the stoichiometrically required amount, the structure is weakly branched and shrinks during drying. If, in addition, the precursor solutions contain a large amount of solvent and therefore a high dilution ratio, the structure will undergo further contractions during drying, leading to poorly developed porous materials.

It is now clear that the pH, the dilution ratio and the resorcinol–formaldehyde molar ratio have a significant effect on the pore structure of carbon xerogels and hence, it seems worthwhile to assess the results from a statistical point of view. However, it is important to look at the results from a practical point of view and estimate the increase in the performance of carbon xerogels required to maximise the number of applications in which these materials can be used. The total pore volume versus the average pore size is shown in Fig. 7. In this figure three coloured regions are highlighted. Each colour indicates the materials synthesized from precursor solutions in which: (i) different pH values were used while the dilution ratio and the R/F molar ratio were fixed at the most commonly used values in the literature, i.e., 5.7 and 0.5, respectively, (ii) the pH and the dilution ratio were simultaneously modified while the R/F molar ratio was fixed at 0.5 and (iii) the three chemical variables were simultaneously modified.

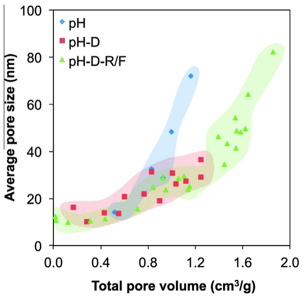

Fig. 7 – Enhanced pore control in carbon xerogels by modification of the R/F molar ratio. (A colour version of this figure can be viewed online.)

As can be seen from Fig. 7, the simultaneous adjustment of the pH, dilution ratio and resorcinol–formaldehyde molar ratio yields carbon xerogels with mean pore sizes that come within the range of pore size required for the majority of applications. Some of these pore sizes can be obtained by just changing the pH of the precursor solutions together with the dilution ratios. Moreover, by varying the R/F molar ratio it is possible to obtain materials with 40% higher pore volumes, with the result that a more accurate control of the final porous properties can be achieved.

5. Conclusions

Statistical analysis has been applied to the micropore, mesopore and macropore volume, and porosity of carbon xerogels. It was found that by modifying simultaneously the pH, the dilution ratio and the resorcinol–formaldehyde molar ratio, it is possible to synthesize materials with pore volumes and average pore sizes that cannot be obtained by modifying just the pH of the precursor solution or the pH together with the dilution ratio. It has been demonstrated that the resorcinol–formaldehyde molar ratio plays an important role in the microwave-assisted synthesis of carbon xerogels and therefore, by controlling this chemical variable, the performance of carbon xerogels can be enhanced.

It was observed that the micropore volume not only depends on the conditions of the carbonization process, but also varies depending on the resorcinol–formaldehyde molar ratio. A decrease in the value of this variable increases the micropore volume due to the fact that the excess of formaldehyde promotes the formation and growth of the clusters and creates more interconnections between them but also due to the elimination of unreacted formaldehyde during drying leaving new microporosity in the carbon gel structure. The mesopore volume is also increased due to a decrease in the resorcinol–formaldehyde molar ratio and to reactions that take place during the carbonization process. On the other hand, the macropore volume depends almost exclusively on the pH of the precursor mixture within the range of combination of pH–D–R/F studied.

By applying statistical analysis to the experimental results it is possible to predict the values of the final porous properties within the range of combinations of pH–D–R/F studied. Hence, carbon xerogels can be directly synthesised and tailored to have porous properties that fit specific application requirements.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.07.030.

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4.2. INTRODUCCIÓN DE ADITIVOS

Como se ha comentado en el Capítulo 1 de la presente memoria, la reacción sol-gel puede modificarse mediante la adición de agentes aditivos. Los aditivos más utilizados en la síntesis de xerogeles de carbono son los agentes activos de superficie, llamados comúnmente surfactantes. El objetivo principal de su utilización es minimizar las tensiones superficiales producidas en la etapa de secado para obtener volúmenes de poro elevados que se asemejen a los obtenidos en la síntesis de aerogeles y criogeles. Los surfactantes se clasifican en tres grandes grupos atendiendo a su forma de disociarse en el agua: aniónicos, catiónicos y no-iónicos.

Los surfactantes aniónicos se disocian en un anión anfífilo y un catión (generalmente un metal alcalino o un amonio cuaternario). Los más utilizados en la síntesis de geles de carbono son derivados de sodio, tales como el dodecilsulfato sódico (SDS) o el dodecilbenceno sulfonato de sodio (SDBS) [Matos 2006; Jirglová 2010; Worsley 2010; Haghgoo 2012; Allahbakhsh 2015].

Los surfactantes catiónicos se disocian en solución acuosa en un catión orgánico anfífilo y un anión generalmente del tipo halogenuro. La gran mayoría de estos surfactantes son compuestos nitrogenados del tipo sal de amina o de amonio cuaternario. En la síntesis de los geles de carbono el más utilizado es el bromuro de hexadeciltrimetilamonio (CTAB) [Lee 2002; Wu 2006; Bruno 2010b].

Los surfactantes no-iónicos no se ionizan en solución acuosa puesto que poseen grupos hidrófilos del tipo alcohol, fenol, éter o amida. Una alta proporción de estos surfactantes puede tornarse relativamente hidrofílicos gracias a la presencia de una cadena poliéter del tipo polióxido de etileno. El grupo hidrófobo es, generalmente, un radical alquilo o alquil benceno y, a veces, una estructura de origen natural como un ácido graso, sobre todo cuando se requiere una baja toxicidad. Las familias de los surfactantes no-iónicos más estudiados, debido a que es posible ajustar su hidrofilicidad son los conocidos como Span, Tween y Pluronic [Tonanon 2003; Sharma 2009; Xu 2012].

En la bibliografía se encuentran diversos estudios donde se describe el comportamiento de los distintos surfactantes en la síntesis de los geles de carbono [Tonanon 2003; Nishiyama 2005; Matos 2006; Sharma 2009; Jirglová 2010; Xu 2012; Kakunuri 2015]. Sin embargo, es difícil obtener una conclusión clara al respecto debido a que cada autor utiliza distinto método de preparación de la mezcla precursora y distinta concentración de los reactivos principales. Por otro lado, cabe destacar que el uso de la tecnología microondas como método de calentamiento también puede influir en el comportamiento de los surfactantes. El hecho de que haya tantos factores que puedan modificar el efecto de estos agentes aditivos es el motivo por el cual, durante la realización de esta Tesis Doctoral, se ha estudiado el efecto de introducir distintos agentes aditivos en las mezclas precursoras a partir de las cuales se obtienen los xerogeles de carbono.

Objetivos

Los objetivos planteados para llevar a cabo dicho estudio fueron:

- ✓ Encontrar los límites de la combinación pH-aditivo que es posible utilizar para sintetizar xerogeles de carbono mediante calentamiento con microondas de forma controlada.

- ✓ Evaluar el efecto de distintos aditivos al modificar de forma simultánea la concentración del aditivo y el pH de la mezcla precursora.

- ✓ Obtener materiales con propiedades diferentes a las obtenidas modificando la concentración de los reactivos principales.

Selección del rango de estudio

Para poder cumplir con los objetivos propuestos se sintetizaron xerogeles de carbono con diferentes cantidades de tres tipos de agentes aditivos: sulfato de sodio, CTAB y Span80. La selección del tipo y concentración de estos aditivos y la concentración de catalizador se realizaron considerando los siguientes aspectos:

- Se utilizó sulfato de sodio en lugar de un surfactante aniónico para poder evaluar si la formación de las micelas juega un papel importante en la modificación de la estructura porosa de los geles orgánicos o si, por el contrario, las fuerzas de repulsión generadas por el anión son suficientes para modificar la reacción de polimerización. Los compuestos CTAB y Span80 fueron seleccionados por ser los surfactantes catiónico y no-iónico más utilizados en la síntesis de geles de carbono.

- El porcentaje de la concentración de los agentes aditivos se varió entre 0.5% y 8% (% en peso). El porcentaje máximo de los aditivos se seleccionó a medida que se desarrollaba el trabajo experimental, ya que la concentración máxima que puede añadirse depende del pH de la mezcla precursora y de la naturaleza del aditivo.

- El valor del pH de la mezcla precursora se varió entre 3 y 7. El valor del pH cuando no se añade catalizador es de 3, correspondiendo con el valor mínimo utilizado. Los materiales obtenidos a partir de valores de pH superiores a 7 no presentan meso-macroporosidad y el volumen de microporos es considerablemente bajo. Por ello, el valor máximo de pH se situó en 7.0

Conclusiones

Los detalles experimentales y los resultados obtenidos en este estudio se describen y discuten en la publicación VI incluida al final de esta sección, cuyas conclusiones principales se detallan a continuación:

- La concentración de cada uno de los aditivos que es posible introducir en la mezcla precursora depende, principalmente, del pH inicial y de la naturaleza del aditivo. La utilización del sulfato de sodio está limitada por el incremento de la temperatura que produce el hervor de la mezcla precursora. Los límites en el uso del surfactante catiónico se deben a la aparición de precipitados, mientras que los del surfactante no-iónico vienen determinados por la modificación del pH inicial de la mezcla.

- La porosimetría de mercurio revela que la adición de sulfato de sodio incrementa el tamaño y el volumen de los poros. El grupo SO_4^- del sulfato de sodio genera fuerzas de repulsión entre el surfactante y los aniones resorcinol, provocando que la estructura polimérica se forme alejada del anión sulfato. Como consecuencia, los materiales obtenidos son principalmente macroporosos.

- La adición de CTAB tiene un efecto significativo en las propiedades porosas de los xerogeles de carbono. Este compuesto provoca la aparición de fuerzas de atracción entre las micelas del surfactante y los aniones resorcinol. Por tanto, la estructura polimérica se forma alrededor de la micela, dando lugar a materiales mesoporosos.

- La introducción de Span80 en la mezcla precursora produce una reacción de condensación entre los grupos hidroxilo de este surfactante y los del resorcinol. Esta hipótesis sobre la reacción de condensación, que tiene lugar durante la reacción sol-gel, queda verificada mediante los análisis termogravimétricos (TGA). Los perfiles TGA obtenidos indican que el surfactante no-iónico interacciona con la estructura polimérica del xerogel modificando los enlaces. Estas modificaciones son cruciales para diseñar las propiedades finales de los xerogeles de carbono, ya que un incremento en la concentración de surfactante da lugar a un aumento en el volumen y tamaño de los poros.

- La adición de aditivos permite obtener xerogeles de carbono con propiedades diferentes a las obtenidas modificando tan solo la concentración de los reactivos principales, demostrando una vez más la gran versatilidad de los xerogeles de carbono.

PUBLICACIÓN VI

THE ENHANCEMENT OF POROSITY OF CARBON XEROGELS BY USING ADDITIVES

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The enhancement of porosity of carbon xerogels by using additives

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ABSTRACT

Resorcinol-formaldehyde carbon xerogels were synthesized by means of microwave heating by using precursor solutions with pH values ranging from 3 to 7 and adding various amounts of sodium sulfate, hexadecyltrimethylammonium bromide and Span80. It was found that the amount of additive that can be introduced depends to a large extent on the final pH of the precursor solution. Characterization of the porous structure of the carbon xerogels thus synthesized demonstrated that their porosity was modified by interactions between the additives and the polymeric structure of the xerogels. It is worth noting that carbonaceous materials with a pore size that could not be obtained by merely modifying the pH could be synthesized by adding different types of additive, with the result that a significant improvement of the porous properties of the carbon xerogels was achieved. The addition of sodium sulfate increased the size of the clusters and pores due to repulsive forces created between the additive and resorcinol anions. Hexadecyltrimethylammonium bromide gave rise to a dense branched structure with pores of a small size attributable to forces of attraction between the cations of the additive and resorcinol anions. In contrast, the presence of Span80 in the precursor solution produced a condensation reaction between the resorcinol and the additive, as a result of which the amount of resorcinol available for the sol–gel reaction was reduced.

1. Introduction

Carbon gels are porous materials that are obtained by drying and carbonizing organic polymer-based gels [1]. The most common process for synthesizing this organic gel is by the polymerization of resorcinol with formaldehyde in the presence of a solvent following Pekala's method [2]. The great advantage of these materials is that their final properties can be controlled and tailored to fit specific applications by modifying the process conditions.

From a chemical point of view, the pH of the precursor solution is the variable that has the greatest influence, though the concentrations of water, resorcinol and formaldehyde are also key variables that determine the final porous structure of the carbon gels [1,3–5]. In terms of the process conditions, the drying method also plays a very important role in determining the final properties [1]. Resorcinol-formaldehyde gels can be dried under supercritical conditions, giving rise to materials known as aerogels [2,6,7] or by the sublimation of water from the pores by a lyophilization process, resulting in the formation of cryogels [8]. In both of these processes, the surface tension forces are small and hence the gel structure shrinks only slightly, leading to materials with well-developed porous structures. Although these drying methods yield highly porous materials, they involve cumbersome solvent exchange processes and complex drying stages.

The solvent can be also removed by direct evaporation, which is a simpler and quicker drying process that yields more competitive materials, known as xerogels [9–11]. However, evaporative drying causes greater shrinkage than supercritical and freezing drying, resulting in materials with less developed porous structures. It is therefore necessary to modify the synthesis process in order to avoid or reduce the effect of collapse of the polymeric structure. As a solution to this problem, some authors have proposed the addition of additives to the precursor solutions of carbon gels to prevent shrinkage during drying and to obtain well developed mesoporous materials [12,13].

The most widely used additives for synthesizing carbon gels are surfactants, which can be anionic, cationic or non-ionic. Of the possible anionic and cationic surfactants, probably the most

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commonly used for synthesizing RF gels are sodium dodecylbenzenesulfonate (SDBS) [6,9,12,14] and hexadecyltrimethylammonium bromide (CTAB) [7,9,13–16], respectively. Alternatively, the non-ionic surfactants Span and Pluronic are frequently used [9,14]. However, it is difficult to assess the effectiveness of each of these surfactants as researchers use different experimental conditions that influence the effect of these additives. Most studies on the synthesis of carbon gels by the addition of surfactants employ the emulsion technique [6,7,9,15] which requires the surfactants to be added after gelation has taken place, while other authors dissolve the surfactant in a solution of resorcinol prior to the sol–gel reaction [14,16]. Furthermore, to the best of our knowledge, all these carbon xerogels were conventionally synthesized and, there is no evidence in the literature as to what effect these additives would have on the synthesis of carbon xerogels if another heating source, such as microwave radiation, is used.

Accordingly, the aim of this work is to elucidate the effect of different additives on the formation of the polymeric structure of carbon xerogels synthesized by means of microwave heating and establish whether they can be used to tailor porous properties. All of the synthesized carbon xerogels were subjected to characterization of their porous structure to establish the effect of these additives when modifying both the initial pH of the precursor solution and the amount of additive. Moreover, possible chemical interactions between the additives and the polymeric structure were also investigated.

2. Experimental

2.1. Materials

The resorcinol was purchased from Indspec (99%). Formaldehyde (37 wt.% in water, stabilized by 10–15 wt.% of methanol), hexadecyltrimethylammonium bromide (CTAB, 98%) and Span80 were supplied by Merck. Sodium sulfate (Na_2SO_4, 99%) was purchased from VWR International. Other chemicals used included deionized water and 5 M sodium hydroxide (Analar Normapur, VWR International) solution.

Sodium sulfate, instead of sodium dodecylbenzenesulfonate (the most common anionic surfactant used to synthesize carbon gels), was used in order to investigate whether the formation of micelles, a phenomenon typical of surfactants, plays a role in the modification of the pore structure of carbon xerogels or whether the repulsive forces produced by sulfate anions are sufficient to prevent the collapse of the polymeric structure during the drying of RF xerogels.

2.2. Preparation of pure RF precursor solutions

Resorcinol was first dissolved in deionized water in unsealed glass beakers under magnetic stirring. After dissolution formaldehyde was added and the resulting mixture was stirred until a homogeneous solution was obtained. Five different precursor solutions were prepared with different initial pH values ranging from 3 to 7 by adding sodium hydroxide. All the xerogels were synthesized from 200 ml of precursor solution, using the stoichiometric R/F molar ratio (i.e., 0.5) and a dilution ratio of 5.7. The dilution ratio parameter is defined as the molar ratio between the total amount of solvent and the total amount of reactants. The term total solvent refers to the water and methanol contained in the formaldehyde and the deionized water that is added, whilst the term reactant refers to the resorcinol and formaldehyde.

2.3. Preparation of Na_2SO_4-RF precursor solutions

Resorcinol and sodium sulfate were first dissolved in deionized water in separate unsealed glass beakers under magnetic stirring. After dissolution, both solutions were mixed together and then formaldehyde was added. The resulting mixture was stirred until a homogeneous solution was obtained. Twenty different precursor solutions were prepared with different initial pH values ranging from 3 to 7 by adding sodium hydroxide and with four different concentrations of sodium sulfate (0.5, 2, 4 and 8 wt.%). All the xerogels were synthesized from 200 ml of precursor solution, using the stoichiometric R/F molar ratio (i.e., 0.5) and a dilution ratio of 5.7.

2.4. Preparation of CTAB-RF precursor solutions

Precursor solutions containing hexadecyltrimethylammonium bromide (CTAB) were prepared following the same methodology as that described above for the preparation of Na_2SO_4-RF precursor solutions (section 2.3) but dissolving CTAB instead of sodium sulfate in an unsealed glass with deionized water.

2.5. Preparation of Span80-RF precursor solutions

Resorcinol was first dissolved in deionized water in unsealed glass beakers under magnetic stirring. After dissolution formaldehyde was added. Then Span80 was introduced and the resulting mixture was stirred until a homogeneous solution was obtained. The non-ionic surfactant was added to the resorcinol-formaldehyde solution rather than to the dissolved resorcinol due to its low solubility in water (HLB value of 4.3). Twenty different precursor solutions were prepared with different initial pH values ranging from 3 to 7 by adding sodium hydroxide and with four different concentrations of Span80 (0.5, 2, 4 and 8 wt.%). All of the xerogels were synthesized from 200 ml of precursor solution, using the stoichiometric R/F molar ratio (i.e., 0.5) and a dilution ratio of 5.7.

2.6. Synthesis of organic and carbon xerogels

Each precursor solution was placed in a microwave oven (in-lab design and construction) at 85 °C for 3 h to allow gelation and curing to take place. After the formation of the polymeric structure, excess water was eliminated by continuing to heat the gel in the microwave oven until a mass loss of 50 wt.% was achieved. This drying step lasted 1–2 h depending on the final pore structure of the material. After drying, the xerogels were carbonized at 700 °C under a nitrogen flow of 150 ml/min in a horizontal tubular furnace from Carbolite Ltd. The residence time was 2 h and the heating rate was set at 50 °C/min. The carbon xerogels obtained were labeled CX followed by the pH value (from 3 to 7) and by the percentage of additive added (0.5, 2, 4 and 8 wt.%). An ‘S’, “C” or “NI” was appended to the name to indicate the type of additive added: sodium salt, cationic surfactant or non-ionic surfactant, respectively.

2.7. Sample characterization

Before being subjected to analysis, all the samples were outgassed at 120 °C and 0.1 mbar for 8 h using a Micromeritics VacPrep 061. These degassing conditions had been previously optimized for outgassing this type of material. The porous properties of the carbon xerogels were characterized by nitrogen adsorption–desorption isotherm analysis performed at −196 °C using a Micromeritics Tristar 3020 instrument. It is well known that pore volume measurements by nitrogen adsorption are not precise enough in the case of samples with macropores or even large mesopores. For this reason, mercury porosimetry (Micromeritics AutoPore IV) was used as a complementary technique to determine the pore size distribution. Analysis by mercury porosimetry was based on Washburn's intrusion theory, following the methodology described elsewhere [17] (see Supporting Information for more details). The morphology of the carbon structure was observed using a Quanta FEG 650 scanning electron microscope. Thermogravimetric analysis was performed by means of a TA instrument DSC Q600 analyzer. The weight loss of each sample was monitored in the temperature range of 25–1000 °C by purging nitrogen at 20 ml/min and at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Na_2SO_4-RF carbon xerogels

The amount of sodium sulfate, Na_2SO_4, that can be added to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions depends on the final pH value of the precursor solution. The possible pH value and sodium sulfate addition combinations are shown in Fig. 1 by the colored region.

As illustrated in Fig. 1, 0.5 wt.% of Na_2SO_4 can be added to the precursor solution when the pH value is set at a value of 4 or higher. The amount of additive can be increased as the pH value increases up to a maximum of 2 wt.% for a pH value fixed at 7. When concentrations of sodium sulfate above the levels specified in Fig. 1 are used, the sol–gel reaction still occurs but in an uncontrolled manner since the precursor solution starts to boil. This phenomenon is due to the polymerization reaction between resorcinol and formaldehyde explained in detail elsewhere [3]. First, resorcinol anions are formed by the abstraction of hydroxylic hydrogen [1]. These anions are more reactive than resorcinol and promote the addition of formaldehyde to form hydroxymethyl derivatives, which are the monomers necessary for polymerization to occur [3]. These derivatives combine through methylene and ether bonds to form the polymer chains that produce an interconnected three-dimensional structure [9,10]. Increasing the initial pH of the precursor solution (i.e. adding more catalyst) leads to the formation of more resorcinol anions, which favors the addition reaction and the formation of more clusters [3].

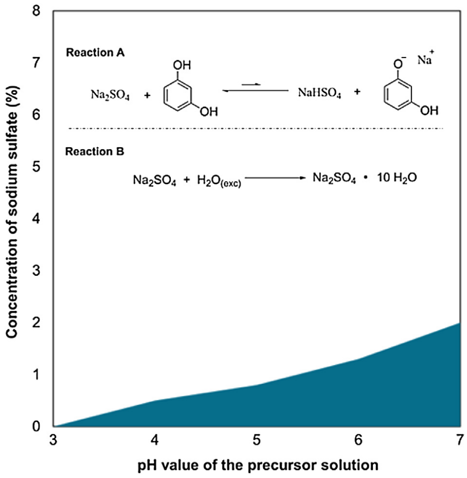

Fig. 1. Combinations of pH values and amount of sodium sulfate that it is possible to add to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions and the chemical behavior of sodium sulfate during the sol–gel reaction between resorcinol and formaldehyde.

When no catalyst is introduced into the precursor solution (pH value of 3), the SO_4^- groups originating from the dissociation of the salt in solution contribute to the deprotonation of the resorcinol via the formation of HSO_4^- molecules (Reaction A, Fig. 1). In this case, Na_2SO_4 acts as the catalyst of the reaction. Moreover, the great hygroscopic capacity of this additive leads to the hydration reaction shown in the Reaction B of Fig. 1. Both reactions shown in Fig. 1 are exothermic and, when there is an excess of additive, the synthesis temperature may increase to above 85 °C, causing the precursor solution to boil uncontrollably. When NaOH is introduced into the precursor solution it acts as the catalyst, i.e. it promotes the formation of resorcinol anions, preventing the deprotonation caused by SO_4^- groups. An excessive increase in temperature during the reaction is thereby avoided and carbon xerogels can be synthesized under controlled conditions. Thus, the greater the concentration of catalyst used, the greater the amount of sodium sulfate that can be added without causing the precursor solution to boil.

When the catalyst concentration is large enough to prevent the deprotonation of the resorcinol by the SO_4^- groups, the Na_2SO_4, which is in the solution, is in its dissociated form i.e. the solution contains SO_4^- anions and Na^+ cations. Repulsive forces are created among the SO_4^- anions and resorcinol anions generated during the addition reaction, and as a result, the formation of methylene and ether bonds is retarded. Thus, the structure of the xerogel forms more slowly and farther away from the additive anions, as shown in Fig. 2.

It is clear that the addition of sodium sulfate alters the normal course of the sol–gel reaction, leading to changes in the formation of the polymeric structure and, in turn, in the final porous properties of carbon xerogels, as demonstrated in Fig. 3, which shows the pore size distributions of carbon xerogels synthesized form precursor solutions with different pH values. Fig. 3 also includes the pore size distribution of carbon xerogels synthesized from a precursor solution with a pH value of 7 and with different amounts of sodium sulfate. The average pore size increases from 6 nm (corresponding to sample CX-7 which does not appear in the figure due to its low pore size value) to 25 nm and 150 nm as the amount of sodium sulfate increases from 0.5 to 2 wt.% respectively. In other words, the addition of sodium sulfate to the precursor solution causes the samples to evolve from micro-mesoporous to micro-macroporous materials, as shown in the nitrogen adsorption–desorption isotherm in Fig. S2 (Supporting Information). The average pore size of sample CX-6 also increases from 16 nm to 86 nm as a result of the addition of 0.5 wt.% of sodium sulfate (Fig. 3). The same trend was observed in the pore size distributions of the samples synthesized from a precursor solution with pH values of 4 and 5, which had an average pore size larger than 200 nm (the maximum value required for most applications) and, hence, they are not included in Fig. 3 (more data related to porous properties are summarized in Table S1 in the Supporting Information). In short, the addition of just a small amount of sodium sulfate gives rise to materials with pore sizes that would be impossible to obtain by just modifying the pH value, facilitating the tailoring of the porosity of carbon xerogels.

These results are in good agreement with those reported by other studies where sodium dodecylbenzenesulfonate (anionic surfactant) was used. The authors of those studies demonstrated that the addition of anionic surfactant generates repulsive forces, preventing the formation of RF-surfactant composites [6,9,12,14]. In this work, sodium sulfate also generated repulsive forces,

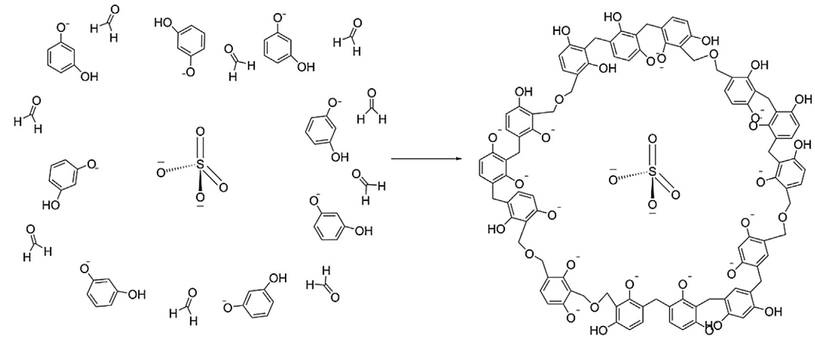

Fig. 2. Effect of Na_2SO_4 on the pore size of carbon xerogels synthesized by microwave heating.

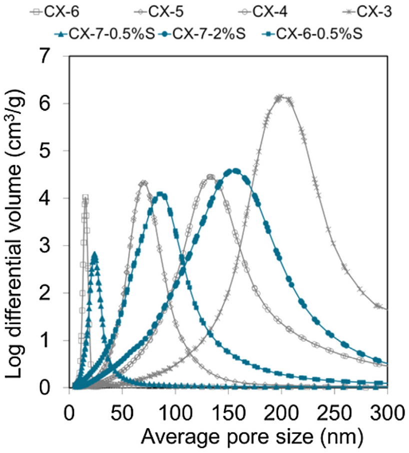

Fig. 3. Pore size distribution of carbon xerogels synthesized with and without sodium sulfate.

preventing shrinkage during drying, despite the fact that no micelles were formed when Na_2SO_4 was dissolved in water. Thus, the effect of sodium sulfate seems to be similar to that of sodium dodecylsulfate since the materials obtained by means of the anionic surfactant displayed structures with a large pore size similar to those prepared in the present work. However, Jirglovà et al. [14] have published SEM images showing that the addition of sodium dodecylbenzenesulfonate leads to the formation of needle structures, whereas the use of sodium sulfate gives rise to more spherical and homogeneous clusters, as illustrated in Fig. 4.

Repulsive forces created among the SO_4^- anions and resorcinol anions retard the development of crosslinkages. As a result, the structure forms more slowly, causing a gradual increase in the size of the clusters. In addition, the formation of clusters takes place farther away from the additive anions (Fig. 2) leading to larger voids between the clusters (Fig. 3).

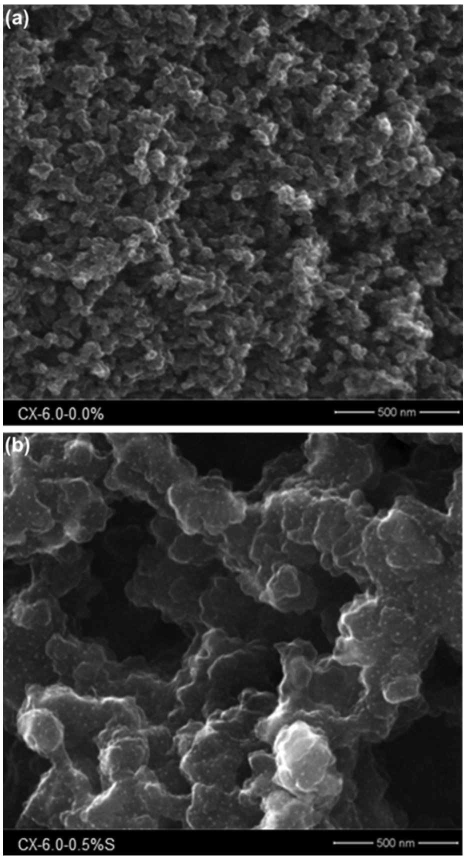

Fig. 4. SEM images of sample CX-6 (a) and CX-6-0.5%S (b).

3.2. *CTAB-RF carbon xerogels*

The amount of hexadecyltrimethylammonium bromide (CTAB) that can be added to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions also depends on the final pH value of the precursor solution. However, the behavior of CTAB is contrary to that observed with the addition of sodium sulfate, in that the lower the pH of the precursor solution, the greater the quantity of surfactant that can be added to synthesize CTAB-RF xerogels under controlled conditions, as shown in Fig. 5. In contrast to these results, Matos et al. [9] obtained carbon xerogels prepared from precursor solutions with a pH value of 6.4 and concentrations of CTAB of up to 15 wt.% without the occurrence of precipitation. This may have been due to their method of preparation. In the present work the surfactant was added to the dissolved resorcinol prior to the addition of formaldehyde, whereas Matos et al. [9] added the CTAB to the resorcinol-formaldehyde solution.

The limits to the quantities added in Fig. 5 are determined by the appearance of precipitates that modified the basicity of the solution. The resulting precipitates were analyzed by thermogravimetry together with the cationic surfactant and sample CX-6 with and without surfactant in order to establish the composition of the precipitate. The results of this analysis are shown in Fig. S3 (Supporting information). The precipitate obtained at high pH values is mostly the cationic surfactant impregnated with some RF gel. The cationic surfactant used in this study is a soluble compound in an acid media, so that as the pH increases, its solubility decreases, causing it to precipitate. However, it is necessary to point out that sample OX-6 and OX-6-0.5%C exhibit similar TGA profiles, indicating the possible formation of a CTAB-RF composite (Fig. S3). The reason for this is that the dissolved CTAB forms micelles leaving the positive charges in contact with the reaction media and the carbon chain inside the micelle [13,15]. Resorcinol anions are attracted to the cations of the surfactant, so that crosslinkages occur close to the cation, as shown in Fig. 5, giving rise to chemical interaction between the polymeric structure and the surfactant.

CTAB behavior during the polymerization reaction has a direct effect on the final porous properties of carbon xerogels. In fact, the addition of CTAB to the precursor solutions leads to the formation of a large number of small clusters, as shown in Fig. 6. Furthermore, the clusters are close to each other due to the effect of the surfactant, resulting in a very densely branched structure with pores of a small size (Fig. 6b). When the concentration of CTAB is increased, carbon xerogels evolve from macroporous material to micro-mesoporous and even to exclusively microporous materials, as confirmed by the nitrogen adsorption–desorption isotherm shown in Fig. S4 in the supporting information.

When CTAB is added, the N_2 adsorption–desorption isotherms of the carbon xerogels evolve from a combination of type I and II to a combination of type I and IV. From Fig. S4 in the supporting information it can be seen that an increase in the concentration of

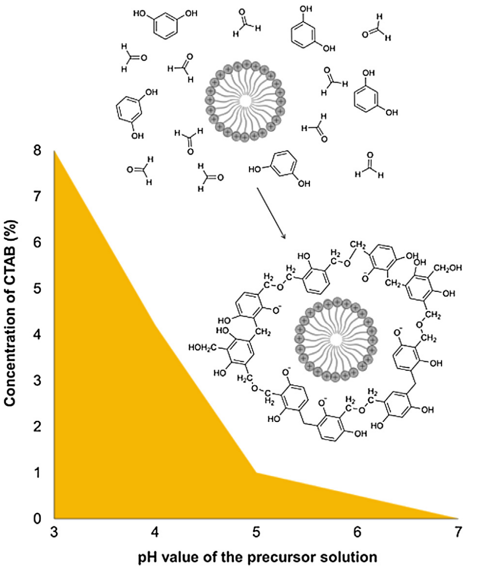

Fig. 5. Combinations of pH values and amount of CTAB that it is possible to add to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions and the effect of CTAB micelles on the formation of the polymeric structure.

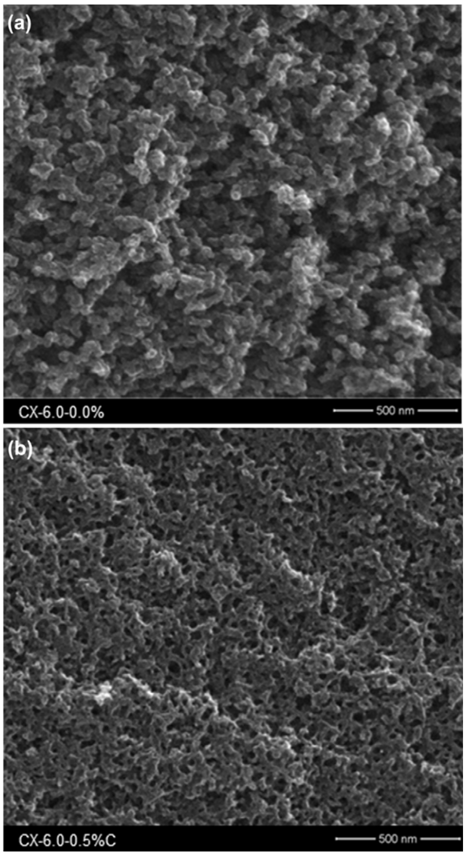

Fig. 6. SEM images of sample CX-6 (a) and CX-6-0.5%C (b).

CTAB to above 0.5 wt.%, causes a narrowing of the hysteresis loop, which indicates a decrease in the volume adsorbed at high relative pressures, resulting in structures with a smaller volume of pores and of a smaller size. Jirglovà et al. [14] and Wu et al. [7] also observed a decrease in the clusters and pore sizes when CTAB was employed, whereas Matos et al. and Bruno et al. [15] obtained materials with a larger pore size [9]. Again, the differences in the effect of the surfactant could have been due to the method of preparation. Hence, the way in which CTAB is added to the precursor solutions will result in carbon gels with different porous properties.

3.3. Span80-RF carbon xerogels

When a non-ionic surfactant is used, the maximum amount that it can be added is determined by the initial pH of the precursor solution since the surfactant used in the study, Span80, alters the initial pH values, as shown in Fig. 7a.

When no surfactant is added to the precursor solution, the initial pH value is around 3.0, whereas when 2 wt.% of Span80 is added, the initial pH value increased to 5.0. Therefore, it is not possible to synthesize Span80-RF xerogels over the whole range of pH values with the addition of Span80, unless acid catalysts are used. The use of acid catalysts for microwave-assisted synthesis was discarded for this study since the sol—gel reaction takes place via a different route and hence falls outside the scope of this work. It is worth noting that, although several works in the literature deal with the use of Span80 for the synthesis of carbon gels, to the best of our knowledge no evidence has been reported to suggest any modification of the initial pH value of the precursor solutions.

During the polymerization reaction between resorcinol and formaldehyde, hydroxymethyl derivatives are formed [3] and combine to create methylene and ether bonds that lead to a polymeric structure [14,16]. It has been conjectured that the presence of Span80 in the precursor solution produces a condensation reaction between the hydroxyl groups from the resorcinol and the alcohol groups from the surfactant, as shown in Fig. 7b. This hypothesis is verified by the TGA profiles of the Span80, OX-6 and OX-6-0.5%NI depicted in Fig. S5 (Supporting information). Sample CX-6 follows the trend of the most common thermogravimetric profile for RF gels. According to the literature [10], the TGA profile for RF gels displays three major weight losses at temperatures ranging between i) 80 and 200 °C when moisture is removed, ii) 300 and 400 °C when volatile material is eliminated and C—O bond

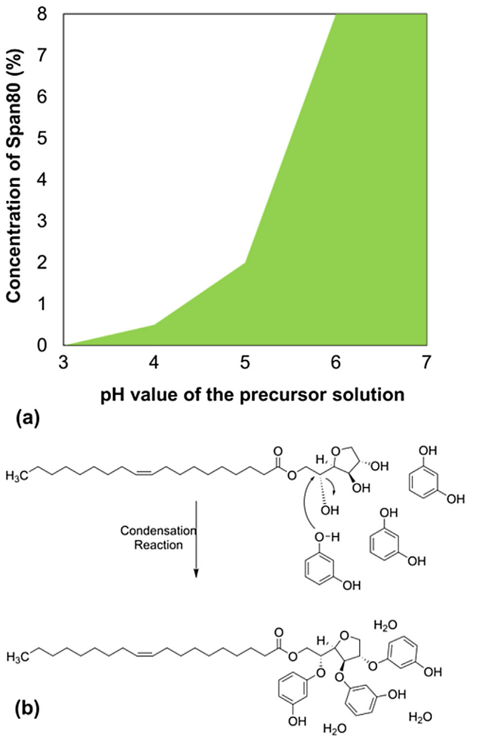

Fig. 7. Combinations of pH values and amount of Span80 that it is possible to add to the precursor solution in order to obtain carbon xerogels under controlled synthesis conditions (a) and condensation reaction between resorcinol and Span80 (b).

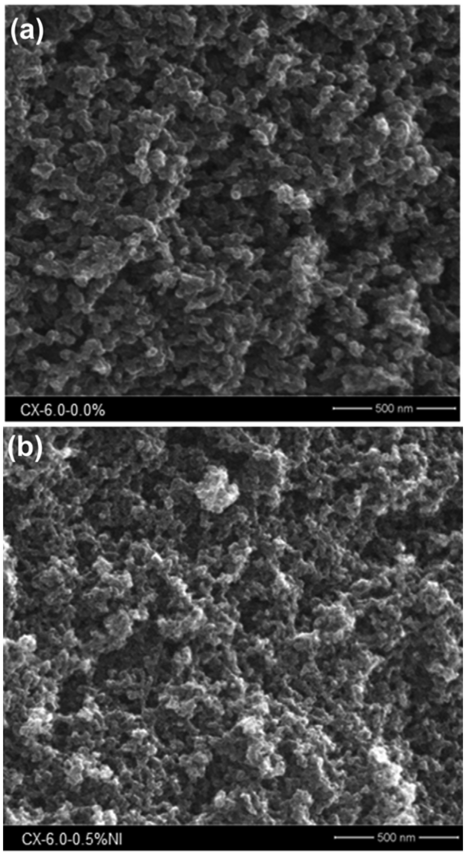

Fig. 8. SEM images of sample CX-6 (a) and CX-6-0.5%NI (b).

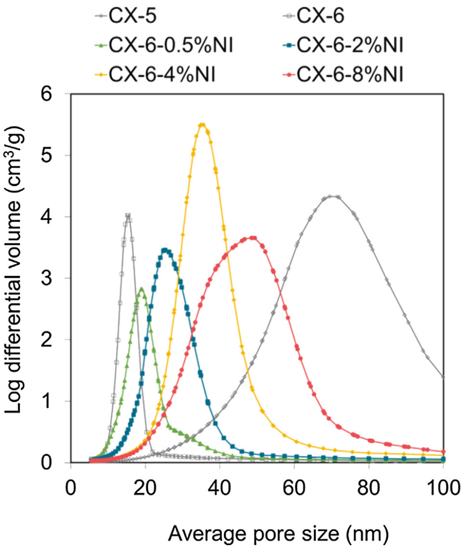

Fig. 9. Pore size distribution of samples synthesized from precursor solutions with pH values of 5 and 6 and different amount of Span80.

breakage occurs and iii) 500 and 600 °C when the C—H bonds break. As Fig. S5 shows, the mass loss in sample CX-6 is higher than in sample CX-6-0.5%NI, which indicates that the non-ionic surfactant has interacted with the polymeric structure, modifying the formation of bonds.

The fact that a condensation reaction between the non-ionic surfactant and the hydroxyl groups in the resorcinol molecule occurs means that, for a given molar ratio between resorcinol and formaldehyde, the sol—gel reaction behaves as if the proportion of resorcinol were lower, since part of this compound is retained during the condensation reaction with the surfactant. A decrease in the amount of resorcinol, i.e., a decrease in the R/F molar ratio, promotes the addition reaction that takes place during the sol—gel stage, resulting in a faster formation and growth of clusters which leads to more interconnections between them and, hence, to a highly branched structure. The mechanical strength of organic xerogels increases and therefore no shrinkage occurs during drying, giving rise to a structure with larger pore volume. This hypothesis is consistent with the SEM images in Fig. 8a and b for samples with a pH value of 6 (the same trend was observed for samples with different pH values).

The materials obtained show an increase in the volume of pores and a variation in the sizes of the pores with increasing addition of Span80 to the precursor solution (Fig. 9). As can be seen from Fig. 9, an increase in the pH by just one unit, from 5 to 6, leads to a decrease in the average pore size from 75 nm to 16 nm. By adding different amounts of Span80 a whole range of average pore sizes between 75 and 16 can be achieved (more data related to porous properties are summarized in Table S2 in the Supporting Information). These values could not be obtained by just modifying the pH value of the precursor solution. In short, the addition of Span80 facilitates the tailoring of porous properties of carbon xerogels.

4. Conclusions

Carbon xerogels with different pH values and different types and concentrations of additives were synthesized by means of microwave heating. It was found that the amount of additive that can be added to the precursor solution depends to a large extent on the pH value of the solution and the nature of the additive. Furthermore, the use of these additives modifies the formation of the polymeric structure, and hence, its addition to the precursor solution can be considered a useful alternative for tailoring the porous properties of carbon xerogels.

It was also observed that the addition of sodium sulfate causes certain sluggishness in the development of crosslinkages due to the repulsive forces produced between the additive anions and resorcinol anions, resulting in the formation of larger clusters. The addition of a cationic surfactant (CTAB) gives rise to forces of attraction between the surfactant cations and resorcinol anions, leading to chemical interaction between the surfactant and the polymeric structure. When Span80 is added, a polycondensation reaction between this additive and the resorcinol takes place, reducing the amount of resorcinol available. Thus, the effect of adding this surfactant is similar to that of decreasing the molar ratio between the resorcinol and formaldehyde.

The addition of both sodium sulfate and Span80 give rise to materials with porous properties that could not be obtained by just modifying the pH value of the precursor solution.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2015.06.003.

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4.3. CONCLUSIONES

Los resultados de los estudios mostrados a lo largo de este capítulo demuestran que es posible diseñar a medida las propiedades de los xerogeles de carbono sintetizados mediante calentamiento con microondas. Debido al gran número de variables que juegan un papel fundamental en la formación de la estructura polimérica, el diseño de las propiedades requiere la utilización de técnicas estadísticas aplicadas al proceso de síntesis. A partir de los análisis estadísticos obtenidos pueden predecirse las propiedades porosas que tendrán los xerogeles de carbono sintetizados empleando una combinación determinada de concentraciones de reactivos y aditivos. De igual forma, puede determinarse la combinación que permite obtener unas propiedades porosas concretas. Estos resultados son de gran interés ya que permiten un mayor control en el diseño de las propiedades de los xerogeles de carbono y en su adaptación a las necesidades específicas de un gran número de aplicaciones.

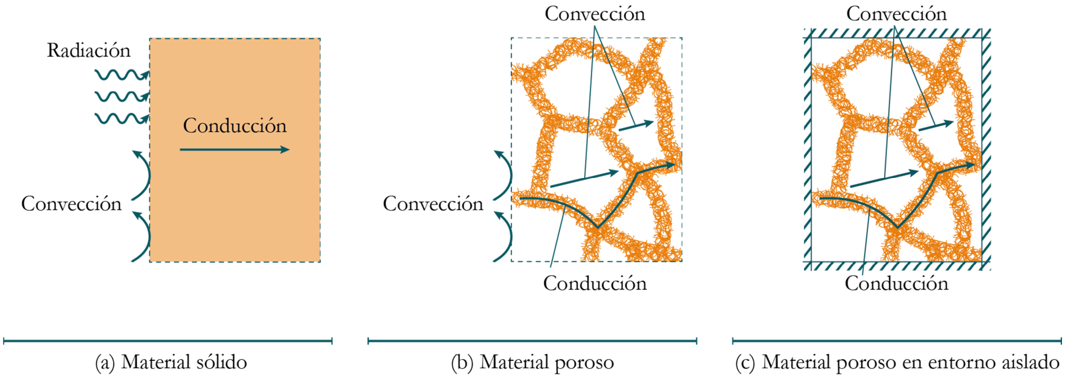
CAPÍTULO 5

APLICACIONES

El objetivo principal del trabajo desarrollado a lo largo de la presente Tesis Doctoral se basa en la optimización del proceso de síntesis inducida por microondas de xerogeles de carbono para poder obtener una amplia gama de materiales con diferentes propiedades. A lo largo del Capítulo 4 se han descrito las diferentes vías que pueden seguirse para diseñar a medida las propiedades de los xerogeles de carbono, demostrando su gran versatilidad. Este hecho hace de ellos excelentes candidatos para un gran número de aplicaciones, cuyos requisitos más relevantes se han detallado en el Capítulo 1 de esta memoria. Analizando las exigencias de cada aplicación, se observa que, en algunos casos, las propiedades que ha de tener el material se basan en la adecuación de su estructura porosa y no en el hecho de que el material esté carbonizado. Por tanto, uno de los objetivos propuestos para llevar a cabo la presente Tesis Doctoral es determinar si los xerogeles orgánicos también son materiales con potencial para ser empleados en alguna de las aplicaciones listadas en el Capítulo 1. De entre todas las aplicaciones posibles, se han seleccionado dos, de modo que este capítulo está enfocado a analizar el comportamiento de los **xerogeles orgánicos** como material para aislamiento térmico y de los **xerogeles de carbono** como material de electrodo en baterías de ion-litio.

5.1. MATERIAL PARA AISLAMIENTO TÉRMICO

Se considera que un material es aislante térmico cuando presenta una baja capacidad de conducir calor a través de su estructura. Esta capacidad de conducir calor se expresa mediante el coeficiente de conductividad térmica y se produce por las diferencias de temperaturas entre el material y su entorno. En general, la conductividad térmica total de un material sólido viene dada por la suma de los tres mecanismos de transmisión de calor: conducción, convección y radiación térmica (Figura 5.1a).



(a) Material sólido (b) Material poroso (c) Material poroso en entorno aislado

Figura 5.1. Mecanismo de transmisión de calor a través de sólidos no porosos (a) y sólidos porosos (b) y (c).

En el caso concreto de sólidos porosos, también se ha de considerar la transmisión de calor a través del fluido que ocupa los poros [Lu 1995; Cuce 2014]. Este mecanismo es asimilable al de convección anteriormente mencionado y, por tanto, en muchos casos se emplea el mismo término: convección (Figura 5.1b). Por tanto, la conductividad térmica total de un material poroso viene dada por la suma de los cuatro mecanismos de transmisión de calor que se describen a continuación:

- **Conducción a través de la estructura sólida:** la conducción de calor a través de un sólido se produce por la cesión de energía entre partículas contiguas, por lo que depende, principalmente, de la estructura interna del material [Lu 1995; Cuce 2014]. En un material poroso, la interconectividad entre las partículas se define mediante la porosidad y/o la densidad aparente. Los poros restringen la propagación del calor a través de la estructura sólida, por tanto, materiales con elevada porosidad (baja densidad aparente) presentan menor transmisión de calor por conducción [Wiener 2009; Guo 2015].

- **Convección a través del entorno:** el mecanismo de convección se debe a la transmisión de calor producido por el movimiento real de las moléculas de un fluido (gas o líquido), en el cual las partículas pueden desplazarse transportando el calor sin interrumpir la continuidad física. En un material expuesto a la atmósfera, la convección se produce a través del aire, cuya conductividad térmica tiene un valor de 24 mW/m·K [Lu 1995; Cuce 2014]. Si por el contrario el material se encuentra en un entorno aislado, la convección a través de este entorno puede considerarse nula (Figura 5.1c).

- **Convección a través de los poros:** el mecanismo de convección a través del medio gaseoso que ocupa los poros del material depende de:

  i) La conductividad del gas: en condiciones normales de operación, el gas contenido en los poros es aire a presión atmosférica y temperatura ambiente. Como ya se ha mencionado, en estas condiciones el aire presenta una conductividad térmica de 24 mW/m·K [Lu 1995; Cuce 2014].

  ii) El tamaño de los poros: en la bibliografía se encuentran diversos estudios donde se indica que el recorrido libre de las moléculas de aire a presión atmosférica es de 70 nm [Hemberger 2009; Baetens 2010]. Si el tamaño de los poros es menor que el recorrido libre medio, las colisiones ocurrirán, principalmente, entre las moléculas del gas y las paredes de los poros [Cuce 2014]. El hecho de que las moléculas no colisionen entre sí implica una disminución de la difusividad a través del gas y, en consecuencia, de la contribución de la transmisión de calor por convección.

- **Radiación:** la transmisión de calor por radiación se produce por la absorción y emisión de energía electromagnética. En materiales sólidos, esta emisión se produce con una longitud de onda comprendida entre 10^{-4} m y 10^{-7} m. Estos valores corresponden a los rangos de frecuencia que abarcan la radiación infrarroja y visible, y dependen, principalmente, de la temperatura. En el caso concreto de los geles, la transmisión de calor por radiación a temperatura ambiente es despreciable, ya que son materiales con elevado coeficiente de extinción que absorben la radiación infrarroja [Lu 1995].

En base a las definiciones de estos cuatro mecanismos de transmisión de calor, se puede concluir que la conductividad térmica total de un material sólido depende, principalmente, de las condiciones atmosféricas donde se vaya a utilizar y de su estructura porosa. En este sentido, los xerogeles de carbono se presentan como excelentes candidatos ya que, como se ha mostrado a lo largo del Capítulo 4 de la presente memoria, su estructura porosa puede diseñarse a medida. Sin embargo, el hecho de que los xerogeles de carbono estén compuestos mayoritariamente por carbono tiene como consecuencia que estos materiales puedan presentar valores de conductividad térmica por encima de 60 mW/m·K y, por tanto, no puedan considerarse aislantes térmicos, ya que la conductividad de un material aislante ha de ser inferior a 50 mW/m·K [UNE-EN-12667 2002]. Por este motivo, el estudio sobre la conductividad térmica realizado durante esta Tesis Doctoral se ha llevado a cabo utilizando los xerogeles orgánicos, ya que presentan una estructura porosa similar a la de sus correspondientes xerogeles de carbono pero con valores de conductividad térmica muy inferiores. Además, la utilización de los xerogeles orgánicos en lugar de los carbonizados supone una ventaja comercial ya que se elimina la carbonización, una de las etapas más costosas del proceso de síntesis, disminuyendo los costes de la producción del material.

Objetivos

Los objetivos planteados para realizar dicho estudio fueron los siguientes:

- ✓ Evaluar el efecto de la granulometría de los xerogeles orgánicos sobre la conductividad térmica.

- ✓ Determinar la relación entre las propiedades porosas de los xerogeles orgánicos y su conductividad térmica.

Selección del rango de estudio

El estudio sobre el uso de xerogeles orgánicos como material aislante consistió en determinar la conductividad térmica de materiales con diferentes propiedades porosas. Estos materiales se seleccionaron a partir de los resultados obtenidos en los estudios incluidos en el Capítulo 4. Debido a la gran importancia que tiene la porosidad y la densidad sobre la conductividad térmica, se seleccionaron xerogeles orgánicos con porosidad comprendida entre 30 y 85% y densidades entre 0.2 y 0.7 g/cm^3.

Conclusiones

Los detalles experimentales y los resultados obtenidos se describen y discuten en la publicación VII, incluida al final de esta sección. Las principales conclusiones de la publicación se detallan a continuación:

- o La conductividad térmica de los xerogeles orgánicos disminuye con el tamaño de partícula. Durante el proceso de molienda no se modifica la estructura porosa de las muestras, por lo que la transmisión de calor por conducción se mantiene constante. Sin embargo, muestras con partículas finas tienen mayor grado de compactación. Al compactar, se eliminan los espacios de aire entre las partículas, disminuyendo la transmisión del calor por convección. En consecuencia, la conductividad térmica total disminuye.

- o La conductividad térmica de los xerogeles orgánicos disminuye a medida que disminuye la densidad y aumenta la porosidad. Muestras con baja densidad o, lo que en general suele ser lo mismo, con elevada porosidad, presentan una estructura polimérica compuesta por nódulos de gran tamaño. El contacto entre estos nódulos es menor que entre nódulos pequeños, por lo que la transmisión de calor por conducción disminuye. No obstante, las estructuras poliméricas compuestas por nódulos grandes, dan lugar a muestras con un gran tamaño de poro. En consecuencia la transmisión de calor por convección aumenta. En base a estos resultados se concluye que es necesario llegar a un compromiso entre la densidad y el tamaño de los poros de los materiales para poder minimizar la conductividad térmica total.

- La síntesis de xerogeles orgánicos con una densidad de 0.2 g/cm^3 y un 85% de porosidad, pero con diferentes tamaños de poro, demuestra la importancia de poder diseñar a medida las propiedades de estos materiales. Una reducción en el tamaño de poro del 80% da lugar a materiales con un 9% menos de conductividad térmica.
- El valor mínimo de conductividad térmica obtenido en este estudio es de 35 mW/m·K. Este valor es similar al del poliestireno expandido (34 mW/m·K), uno de los aislantes térmicos más utilizados. Estos resultados demuestran el potencial que tienen los xerogeles orgánicos resorcinol-formaldehído como posibles materiales aislantes.

PUBLICACIÓN VII

EXPLORING THE POTENTIAL OF RESORCINOL-FORMALDEHYDE XEROGELS AS THERMAL INSULATORS

Exploring the potential of resorcinol-formaldehyde xerogels as thermal insulators

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Abstract

The contribution to the total thermal conductivity of porous materials depends mainly on the operating conditions and on its type of porosity. Accordingly, the thermal insulating capacities of several resorcinol-formaldehyde xerogels synthesized by microwave heating were investigated. First, the operating conditions were optimized, since the thermal conductivity measurements were to be performed both before and after the degassing of the organic xerogels and with various particle sizes, ranging from 3 mm to below 212 µm. Special attention was paid to the influence of the porous properties, particularly density and pore size, on the total thermal conductivity. A minimum thermal conductivity value of 0.035 W m^{-1} K^{-1} was obtained for an organic xerogel with a bulk density of 0.248 g cm^{-3} and a mean pore size of 144 nm. The results obtained suggest that RF xerogels would be highly suitable candidates for thermal insulation applications as their thermal conductivity values are comparable to those of commercial materials, such as expanded polystyrene (0.034 W m^{-1} K^{-1}).

Keywords: Resorcinol-formaldehyde xerogels; Pore size; Density; Thermal conductivity

1. Introduction

Insulating materials are used for many applications (thermal packaging, building construction, aerospace industry, etc.) to minimize energy losses, for safety purposes, to enhance the sustainability of industrial processes or even to reduce negative environmental impacts [1-3]. These materials require different properties depending on their final application, which leads to a large number of insulating materials with different benefits and costs. Some of the most widely used insulating materials are cork, polyurethane (PUR), expanded polystyrene (EPS), glass wool or silica aerogels [1-6].

The thermal conductivity (λ) of a material, i.e. its ability to conduct heat, is determined by the sum of the three mechanisms of heat transfer: radiation, convection and conduction [2, 4, 5, 7-15].

Radiation is the energy emitted by matter in the form of electromagnetic waves. No particles or fluids are involved, unlike in the processes of conduction and convection, so radiation can only be attributed to changes in the electronic configuration of atoms or molecules that constitute the matter [8, 15]. Consequently, it depends to a great extent on the temperature of the insulating material [8, 12, 16, 17]. Under normal operating conditions, the radiation mechanism of some materials exhibits a low extinction coefficient, in which case, radiation is negligible [7, 9, 14].

The mechanism of *convection* is due to the macroscopic movement of the fluid (in liquid or gas state), which leads to a relative displacement and mixes the cold part and hot part of the fluid to produce the heat transfer in the fluid [9]. The contribution of this mechanism to the total thermal conductivity depends mainly on the operating conditions [12, 16].

Heat transfer through a solid material is known as *conduction*. It is the method that most contributes to heat transfer and it occurs when there is a temperature gradient across the solid [4, 13]. Essentially, heat propagation is due to molecular vibrations, but there is no real movement of the molecules [2, 9]. The contribution of this mechanism to the total thermal conductivity depends mainly on the interconnectivity of the material, and the way in which the solid material is interconnected defines its porous structure [10, 12, 17]. In this type of mechanism, the density of the material plays an important role [13, 14, 18]. Materials with a low bulk density, that is to say, materials with high pore volumes, have good insulating properties since conduction through the solid skeleton decreases. Moreover, in porous materials, the transmission of heat between the material and the gaseous phase which occupies its inner part, i.e. porosity of the material, should be also considered [10, 12, 19]. This mechanism, named as *gaseous thermal conduction,* depends mainly on two factors: (i) gas phase conductivity and (ii) the Knudsen number (which considers the ratio between the mean free path of the fluid particles and the pore size of the material) [7, 11]. According to the above definition, under normal operating conditions, the gas embedded in the porosity is air at atmospheric pressure and room temperature. In these conditions, air has a thermal conductivity value of 0.024 W m^{-1} K^{-}

^{1} [5, 10]. On the other hand, it is well known that the free path of air molecules at atmospheric pressure is around 70 nm [7, 9, 10]. Therefore, if the material has a porous structure with a smaller pore size, transmission will occur due to collisions between the air molecules and the pore wall and not between the air molecules themselves [2, 5, 11, 14]. This phenomenon minimizes Knudsen diffusivity and, therefore, reduces the contribution of the gaseous thermal conduction mechanism to the total thermal conductivity.

It is clear that in order to obtain the lowest possible total effective thermal conductivity, the three above contributions (radiation, convection and conduction) must be minimized. Each of these heat transfer mechanisms will contribute to the total thermal conductivity as a function of the porous properties of the material and the conditions (pressure, temperature, humidity, etc.) under which they have to operate [2, 9-12, 19, 20]. In this regard, resorcinol-formaldehyde (RF) gels are excellent candidates for use as thermal insulating materials because the sol-gel synthesis process allows their porous properties to be meticulously designed [10, 12, 17, 20-28]. Several studies in literature highlight the insulating properties of carbon aerogels [11, 12, 14, 15, 17, 21, 28], while just a few are related to the use of organic RF aerogels [10, 16, 20]. For example, Lu et al. evaluated the thermal conductivity of RF organic aerogels of different density and obtained a minimum value of $\lambda = 0.012$ W m^{-1} k^{-1} for a sample with a bulk density of 0.157 g cm^{-3} [10, 16]. Another more recent example has been published by R. Tannert and co-workers, who reported in 2015 values of thermal conductivity ranging between 0.019 and 0.030 W m^{-1} k^{-1}, at atmospheric pressure, for several organic aerogels produced under different conditions of initial pH and resorcinol/water molar ratio [20]. In their work, the relevance of pore size distribution on the insulating capacity of materials was clearly demonstrated because two RF aerogels with similar densities and porosity percentages (i.e. 0.10 and 0.12 g cm^{3} and 92-93 %, respectively) but different average pore size (171 and 60 nm, respectively) exhibited λ values of 0.030 and 0.021 W m^{-1} k^{-1}.

Despite having properties suitable for thermal insulating materials, the large-scale production of RF aerogels is still very restricted, since the synthesis process involves several steps and requires supercritical conditions to remove the solvent [10, 12, 20, 22, 24-26]. This process entails excessive production costs and, hence, their use is limited to high-tech applications, where their excellent properties take precedence over their high price. In this situation, resorcinol-formaldehyde xerogels come into their own since, in addition to being amorphous materials with a low density and a high porosity, they can be obtained easily by means of microwave radiation [23, 27]. In this way, the costs of production are reduced and it is possible to increase their competitiveness against other materials available in the thermal insulation industry.

In order to properly design the properties of the RF xerogels and be able to use them as thermal insulators, the effect of the three heat transfer mechanisms through these porous materials should be considered. The contribution of radiation for RF xerogels can be considered insignificant [9, 12, 13], so the total thermal conductivity will depend primarily on the conduction and convection mechanisms. Convection depends mainly on the operating conditions while conduction varies depending on the porous properties. However, it needs to be taken into account that the different porous properties do not affect the mechanism of heat transfer in the same way. For example, heat transfer by gaseous thermal conduction rises as pore size increases, whereas conduction through the solid skeleton decreases as bulk density is reduced, due to the lower connectivity of the solid structure [9, 10]. Therefore, in order to reduce both contributions and minimize thermal conductivity, that is to say, to obtain a material with an excellent thermal insulation performance, it is necessary to strike a balance between these two mechanisms by means of a careful design of the porous structure of the material.

In this work, the thermal insulation capacity of various RF organic xerogels with different porous structures is evaluated in order to determine their influence on the thermal properties of these polymeric materials. The organic xerogels analyzed were produced by means of microwave radiation by adjusting the pH, dilution ratio and resorcinol-formaldehyde molar ratio. In addition, the thermal conductivity measurements were performed with samples of different granulometry, in order to determine the optimal particle size.

2. Experimental Section

2.1. Sol-gel synthesis of RF xerogels

A series of amorphous resorcinol-formaldehyde xerogels was prepared by the polycondensation of resorcinol (R) and formaldehyde (F), using sodium hydroxide solutions as catalyst (C) and deionized water (W) as solvent. The sol-gel synthesis process, carried out by microwave heating, is explained in detail elsewhere [23, 27]. In short, it is a rapid and simple process, performed in a compact microwave oven consisting of two main stages: (i) the RF precursor mixture (200 mL) is subjected to a temperature of 85 ºC for ca. 3 hours during which polymerization reactions between the monomers R and F take place (gelation and curing steps) and, (ii) evaporation of the solvent until a mass loss of 50 wt. % is obtained, this stage generally lasting no more than 2 hours (drying step).

Variables such as the pH, dilution ratio (D) and R/F molar ratio were modified in order to obtain a variety of organic xerogels of different porosity, specifically, with different bulk density and pore size. It should be pointed out that the values of pH, D and R/F were selected on the basis of results previously published by our research group [23]. The ranges used in this study were from 3 to 6.5 for the initial pH, from 4.7 to 7.7 in the case of the dilution ratio while the R/F molar ratio was varied between 0.10 and 0.50. The samples synthesized were labeled as follows: some samples were designated as OX (organic xerogel) followed by a number, corresponding to the value of their bulk density, while other samples were labeled as OX-ρ-d_p, since they are xerogels of a similar density, 0.2 g cm^{-3}, but with a different mean pore size.

2.2. Sample characterization

2.2.1. Porous properties

The porosity of the RF xerogels was investigated using two techniques: (i) adsorption-desorption nitrogen isotherms, that provide information about microporosity and narrow mesoporosity and, (ii) mercury porosimetry, by means of which it was possible to determine the meso-macroporous structure of the samples analyzed. In both cases, before the analysis, the samples were treated at 120 ºC under vacuum (0.1 mbar) for 8 hours.

The surface area (S_{BET}), total pore volume (V_p) and micropore volume (V_{micro}) were determined by means of N_2 adsorption-desorption isotherms. The analysis was carried out using a *Micromeritics Tristar 3020* instrument at -196 ºC. The Brunauer-Emmett-Teller and Dubinin-Raduskevich equations were applied to calculate the S_{BET} and V_{micro}, respectively. V_p was estimated from the nitrogen adsorbed at $p/p^o = 0.99$. It must be taken into account that most of the samples presented in this paper have large mesopores and even macropores, hence V_p does not correspond to the real total pore volume. Therefore, in order to accurately study the porous structure of these materials, it was necessary to resort to mercury porosimetry.

Mercury porosimetry was performed using an *Autopore IV 9500, Micromeritics*, apparatus, in a pressure range from atmospheric pressure to 228 MPa. In all the experiments, the surface tension and contact angle were adjusted to 485 mN m^{-1} and 130º, respectively. By means of this technique, which is based on Washburn's intrusion theory, the following parameters were determined: mesopore and macropore volume (V_{meso} and V_{macro}), average pore size (d_{pore}), percentage of porosity and bulk density. It should be mentioned that in the case of V_{meso}, mesopores were considered to be those with a size larger than 5.5 nm, since this is the lowest limit at which the device can operate.

2.2.2. Thermal conductivity measurements

The measurements were performed with a thermal conductivity analyzer (*TPS 2200, Hot Disk*), using a transiently heated plane sensor fitted with Kapton insulation (radius: 3.189 mm) and an isotropic module for low density materials. The measurements were performed on previously degassed samples (120 ºC, 0.1 mbar, 8 hours), in order to remove all moisture and other molecules adsorbed into the inner surface of the material, which might contribute to increasing thermal conductivity. Notwithstanding, the thermal conductivity of an untreated xerogel was also measured for comparison purposes and to assess the effectiveness of the degassing process. Thermal conductivity values (λ) were also obtained for materials with different granulometries (ranging from 3 mm to < 212 µm) in order to identify the particle size that would ensure the minimal thermal conductivity. Finally, the thermal conductivity of expanded polystyrene (EPS) was determined. This reference material was selected because it is widely used in the field of thermal insulation.

3. Results and discussion

3.1. Porous properties of RF xerogels

Table 1 shows the porous properties of the seven RF xerogels synthesized in this work. The results underscore the possibility of preparing a wide range of materials with different pore structure by means of slight changes upon the concentration of reactants. It can be seen from macroporous samples of very low density (as is the case of the OX-0.2-d_p xerogels) to denser xerogels with a micro-mesoporous structure and narrow mesopores size (for example, the sample labeled OX-0.7). Except in the case of this latter sample, which has a density value of 0.735 g cm^{-3}, the other xerogels reported in Table 1 are highly porous materials with a porosity of over 70 %. As pointed out in the Introduction section, a high degree of porosity does not guarantee low values of thermal conductivity, since bulk density of materials also plays a decisive role. This density is defined by both the size and volume of the pores created during the polymerization reaction. Samples with a high volume of large pores have a lower density (for instance, samples OX-0.2-d_p and OX-0.3), while samples become denser as the pore size decreases, as in the case of the other three organic xerogels, which have a porous structure mainly composed of micropores and mesopores. From these data it can be inferred that there is a clear relation between the density of the materials and the size/volume of the pores. Nevertheless, the porous properties can be further tailored by modifying the synthesis conditions. Good examples of this are samples OX-0.2-d_p, which have similar values of density and porosity but totally different mean pore sizes.

Table 1 *Summary of the porous properties of the synthesized RF xerogels*

Sample	**N_2 adsorption-desorption**			**Mercury porosimetry**				
	S_{BET} (m^2 g^{-1})	V_{micro} (cm^3 g^{-1})	V_p[a] (cm^3 g^{-1})	V_{meso} (cm^3 g^{-1})	V_{macro} (cm^3 g^{-1})	d_p (nm)	density (g cm^{-3})	porosity (%)
OX-0.7	484	0.18	0.60	0.37	-[c]	10	0.735	33
OX-0.6	445	0.15	0.80	0.53	-[c]	11	0.607	70
OX-0.4	180	0.07	0.43	0.81	0.65	40	0.438	75
OX-0.3	8	-[b]	0.01	0.02	1.93	270	0.341	76
OX-0.2-5000	18	0.01	0.02	0.02	3.31	5000	0.226	82
OX-0.2-800	37	0.01	0.06	0.03	2.64	800	0.204	83
OX-0.2-144	4	-[b]	0.01	0.04	3.00	144	0.248	80

[a] V_p, volume of N_2 adsorbed at saturation point ($p/p^o = 0.99$).

[b] Not relevant.

[c] Non-macroporous sample.

It should be mentioned that the low-density xerogels have a poorly developed microporosity ($S_{BET} < 40$ m^2 g^{-1}), a point worth highlighting since samples with a large presence of micropores show a lower capacity as insulating materials due to an increase in heat transfer via the mechanism of conduction, which is a consequence of the higher interconnectivity between clusters (polymeric primary particles formed during the polymerization reaction between resorcinol and formaldehyde [23]). This is one of the reasons why organic xerogels are used instead of carbonized samples, apart from the fact that they are cheaper materials due to the last stage of the manufacturing process is suppressed (i.e. the thermal treatment conducted under an inert atmosphere at temperatures above 700 ºC).

3.2. Insulating capacity of RF xerogels

3.2.1. Effect of the degassing conditions and particle size

The first measurements of thermal conductivity (λ) were performed in ambient conditions (25 ºC, 1 atm) with OX-0.6 xerogel of different granulometry, before and after having been evacuated (results compiled in Figure 1). The aim of the degassing stage was to clear the porous structure of possible residual matter (mostly formaldehyde that did not completely react during the sol-gel process) and moisture, to prevent an adverse increase in the total thermal conductivity of the material.

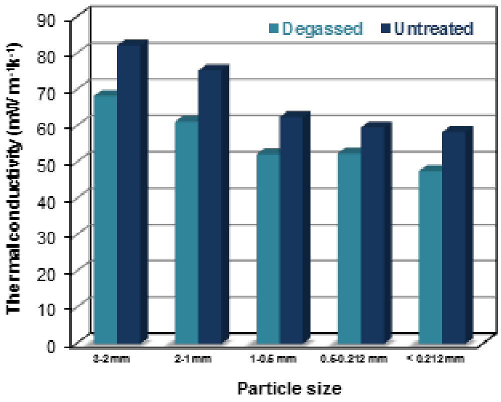

Fig 1 *Thermal conductivity as a function of particle size for OX-0.6 xerogel, before (dark color) and after (light color) degassing*

It is clear from Figure 1 that the thermal conductivity of the evacuated sample is lower. For all the particle sizes evaluated, the thermal conductivity has been reduced by around 17 % due to the conditioning of the sample, i.e. treatment under high vacuum and moderate temperature (0.1 mbar and 120 ºC). This reduction is a result of the lower heat transfer by the convection mechanism, as it has been decreased the adsorbed molecules at the inner surface of the porous material. For this reason, the rest of the λ values collected in the present work refer to degassed samples.

As regards granulometry, there is a clear decreasing tendency, with minimal thermal conductivity reaching 0.048 W m^{-1} k^{-1} in the case of the evacuated organic xerogel with a particle size below 212 µm. The smaller the particle size, the greater the compaction of the material. Consequently, the gas volume interparticle is reduced. The contribution of gaseous thermal conduction is reduced and the insulating capacity of the material is improved. Thus, the maximum compaction degree of the material must be achieved in order to minimize the air contained between the particles. Therefore, other tests were performed using particle size ranges of 212-150, 150-75, 75-50 and < 50 µm, but no improvement was observed with respect to the minimum value recorded for the particle sizes below 212 µm. Accordingly, for the other organic xerogels evaluated, no more divisions than those shown in Figure 1 were made.

3.2.2. Effect of the bulk density

Figure 2 shows the dependence of thermal conductivity on particle size for two samples of different density. The aim of this figure is to see whether granulometry produces the same effect on thermal conductivity in samples with diverse pore structures (volume/size of pores and, hence, different densities).

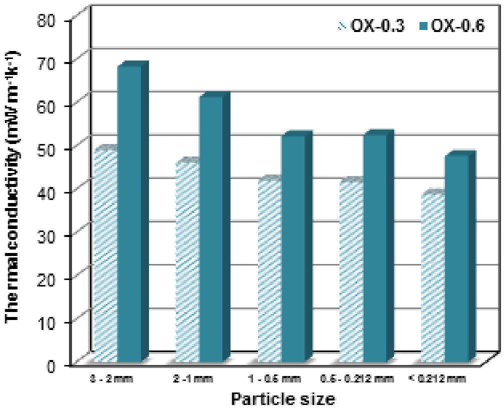

***Fig 2** Dependence of thermal conductivity on particle size for two OX of different density*

Regardless of the density, an improvement in the insulating capacity of the material (lower λ value) occurs when the particle size decreases, although it should be noted that the improvement is more evident in the case of the sample with the higher density. As mentioned above, convection diminishes with particle size, whereas conduction does not change because the internal structure of the organic xerogels is not altered by the milling process. Because radiation is negligible and conduction is not modified, the total thermal conductivity is reduced due to the lower contribution of the convection mechanism. If the λ values of both samples are compared, it can be seen that the organic xerogel of lower density (OX-0.3; 0.341 g cm^{-3}) has associated lower thermal conductivity values than sample OX-0.6 (0.039 vs. 0.048 W m^{-1} k^{-1}). A low-density material has a smaller material load and, therefore, the number of interconnections between the clusters decreases, leading to lower thermal transmission by conduction.

To explore in greater depth the variation of thermal conductivity with density, the λ values of five organic xerogels with different densities were determined. Figure 3 shows the λ values obtained for samples previously degassed and screened to below 212 µm. These values of λ vary from 0.039 W m^{-1} k^{-1} for a low-density xerogel (0.341 g cm^{-3}) to 0.064 W m^{-1} k^{-1} in the case of the xerogel with the highest density, 0.732 g cm^{-3}. As the density increases, the proportion of solid network also increases and, therefore, conduction through the solid phase is enhanced. Hence, in general terms, the variation of thermal conductivity can be considered as a function of bulk density.

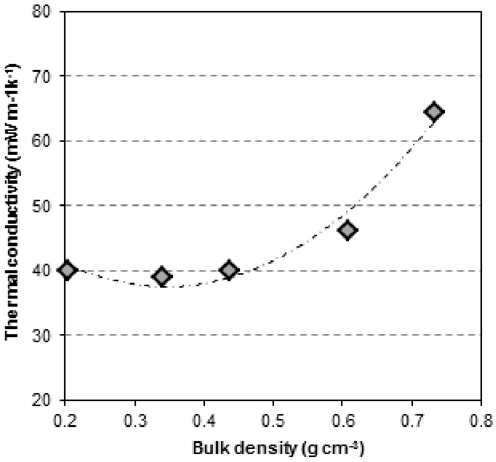

***Fig 3** Conductivity values of five RF xerogels with different bulk density. Line is drawn as guides to the eyes*

It seems clear that in order to obtain appreciable insulating properties, it is necessary to produce a material with low density. However, this is not the only determining factor. For example, virtually identical values of conductivity, 0.040 and 0.039 W m^{-1} k^{-1}, were registered for the organic xerogels OX-0.2-800 and OX-0.3, with densities of 0.204 and 0.341g cm^{-3}, respectively (Figure 3). The pore size distributions of both samples are recorded in Figure 4. The sample with the lower value of thermal conductivity (OX-0.3) displays an average pore size centered at 270 nm compared to 800 nm for the less dense sample. It can be inferred from these data that the smaller the pore size, the less heat is transmitted by gaseous thermal conduction and, hence, the insulating properties of the material are improved. This example evidences the need for a trade-off between density and pore size in order to optimize the insulating character of the material; and indeed that was the ultimate goal of the present study, to evaluate the influence of pore size on the thermal conductivity of equally dense samples.

3.2.3. Effect of the pore size

In order to exclusively evaluate the effect of pore size, three organic xerogels of similar density (~ 0.2 g cm^{-3}) and different pore size distributions were selected (PSD collected in Figure 4). The λ values of these samples, OX-0.2-5000, OX-0.2-800 and OX-0.2-144 are 0.044, 0.040 and 0.0.35 W m^{-1} k^{-1}, respectively. These results highlight the influence of pore size on the thermal conductivity of low-density samples. The value of λ has been reduced by as much as 20 %, that is to say, the insulating capacity of the RF xerogel is enhanced when samples of equal density have a narrower pore size distribution. The improvement of the insulating properties with the reduction in pore size is due to the fact that smaller pores make heat transmission by gaseous thermal conduction more difficult.

The best insulating properties are exhibited by the RF xerogel with a bulk density of 0.248 g cm^{-3} and pore size of around 144 nm, since it displays the smallest value of thermal conductivity, 0.035 W m^{-1} k^{-1}. It should be emphasized that this λ value is close to that of expanded polystyrene (EPS, 0.034 W m^{-1} k^{-1}), the reference material selected for this study because it is one of the most commonly applied commercial insulating materials.

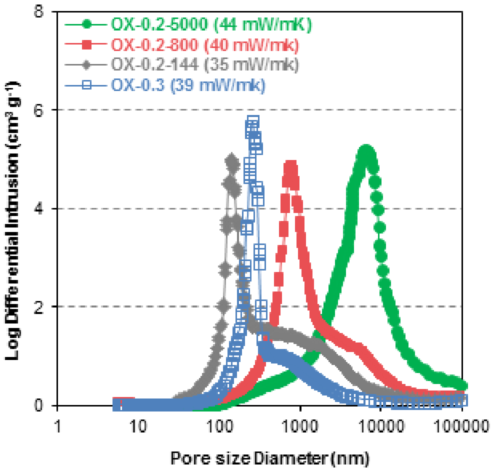

Fig 4 *Pore size distribution of low-density xerogels (OX-0.2-d_p and OX-0.3) recorded by mercury porosimetry*

4. Conclusions

The main two mechanisms of heat transmission that contribute to the thermal conductivity of RF xerogels are solid thermal conduction and gaseous thermal conduction. The porous properties of these materials, particularly density and pore size, have the opposite influence on each of these mechanisms. It is necessary therefore to achieve a compromise between them so as to minimize the total thermal conductivity. On the one hand, density influences the mechanism of conduction because the greater the density, the fewer the interconnections between the material and, therefore, conduction through the solid is minimized. On the other hand, smaller pore sizes impede collisions between the gas molecules and so heat transmission by gaseous thermal conduction is reduced. Accordingly, by tailoring carefully the porosity of the materials, thermal conductivities close to that offered by expanded polystyrene, one of the most commonly employed commercial materials, were achieved (0.035 W m^{-1} k^{-1} for a RF xerogels vs. 0.034 W m^{-1} k^{-1} for the EPS material). Thus, organic xerogels can be considered as a novel and attractive line of materials with good insulating properties since, in addition to reaching values similar to those of some commercial materials, thermal conductivity can be reduced by means of a meticulous design of the porous properties of RF xerogels, i.e. an appropriate combination of their density, pore volume and pore size.

Acknowledgements

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5.2. MATERIAL DE ELECTRODO PARA BATERIAS DE ION-LITIO

Las baterías de ion-litio son dispositivos electroquímicos capaces de convertir la energía liberada por una reacción química en energía eléctrica. Cada batería puede estar compuesta por una o varias unidades electroquímicas llamadas celdas. Las celdas están compuestas por dos electrodos (un ánodo y un cátodo), un separador y un electrolito [Roberts 2014]. El electrolito más utilizado es una solución líquida constituida por sales de litio disueltas en disolventes orgánicos y el separador suele ser una matriz polimérica impregnada por la solución de electrolito que permite la transferencia de los iones litio entre ambos electrodos [Wang 2015b]. Los materiales más utilizados como electrodo positivo (cátodo) son óxidos de litio con un metal de transición, mientras que el electrodo negativo (ánodo) suele estar compuesto por materiales carbonosos como el grafito o nanotubos y fibras de carbono [Mirzaeian 2009b; Ni 2015].

Actualmente el grafito es el material activo más utilizado como ánodo ya que la inserción de los iones litios ocurre de forma reversible entre las capas basales [Scrosati 2010; Collins 2015]. Sin embargo, el grafito solo permite obtener una capacidad teórica limitada (372 mAh/g). Por este motivo, en los últimos años se ha intentado utilizar otro tipo de materiales, como compuestos intermetálicos de estaño y silicio o sales ternarias, que permiten obtener mayores capacidades electroquímicas [Ortiz 2007; Hassoun 2011]. Sin embargo, estos materiales, aunque permiten obtener baterías de ion-litio con mayor capacidad que el grafito, sufren pérdidas de capacidad volumétrica durante el primer ciclo, lo que limita enormemente su uso en baterías comerciales. Una de las posibles soluciones para evitar este efecto es la síntesis de materiales compuesto metal-carbono. El material carbonoso amortigua la expansión volumétrica del metal, mejorando notablemente el rendimiento del dispositivo [Hassoun 2011]. Por tanto, en esta aplicación concreta se requiere un material carbonizado de elevada conductividad eléctrica. En este sentido, la utilización de los xerogeles de carbono se presenta como una alternativa con un gran potencial ya que el dopaje de estos materiales puede llevarse a cabo mediante un proceso sencillo y rápido. No obstante, el proceso de preparación de los electrodos a partir de xerogeles de carbono presenta dos inconvenientes que dificultan la obtención de baterías ion-litio competitivas:

i) El proceso más común para preparar los electrodos a partir de materiales carbonosos consiste en mezclar el material activo con polifluoruro de vinilideno (PVDF, aglutinante) disuelto en N-metil pirrolidina (NMP, disolvente) [Liu 2014; Yang 2015]. Este último compuesto, el disolvente, aunque tiene una toxicidad relativamente baja para el medio ambiente y los sistemas acuáticos, presenta un gran riesgo para la salud humana ya que se absorbe fácilmente a través de la piel. Se trata una sustancia irritante para la piel y las mucosas, neurotóxica y tóxica para la reproducción y, por tanto, aunque es el disolvente más utilizado en la preparación de los electrodos de las baterías de ion-litio, es conveniente su sustitución por disolventes menos dañinos [Hu 2013].

ii) A pesar de la gran importancia que tienen las propiedades porosas sobre el rendimiento electroquímico de las baterías ion-litio, todavía existe un gran desconocimiento sobre el comportamiento del litio en el interior de la estructura polimérica. Por ello, aún no están establecidas cuáles son las propiedades porosas necesarias para conseguir incrementar la capacidad electroquímica de estos dispositivos.

Objetivos

Teniendo en cuenta estos dos inconvenientes, los objetivos planteados para llevar a cabo el estudio de la adecuación de los xerogeles de carbono como material electrodo en baterías ion-litio fueron los siguientes:

- ✓ Evaluar la posible sustitución del compuesto NMP, utilizado en la preparación de electrodos, por un compuesto mucho más económico y natural como es el agua.

- ✓ Determinar el efecto de las propiedades porosas de los xerogeles de carbono sintetizados mediante calentamiento con microondas en las propiedades electroquímicas de las baterías ion-litio.

Selección del rango de estudio

El estudio sobre el uso de xerogeles de carbono como material de electrodo en batería de ion-litio se llevó a cabo durante una estancia en el Departamento de Química Aplicada de la Universidad de Lieja (Bélgica), cuyo grupo de investigación está dirigido por la Dra. N. Job. El estudio consistió en determinar la capacidad electroquímica de celdas preparadas a partir de materiales con diferentes propiedades porosas. Estos materiales se seleccionaron a partir de los resultados obtenidos en los estudios incluidos en el Capítulo 4. Debido a la gran importancia que tiene el tamaño de poro sobre la capacidad electroquímica, se seleccionaron xerogeles de carbono con tamaños de poro comprendidos entre 10 y 200 nm.

Conclusiones

Los detalles experimentales y los resultados obtenidos se describen y discuten en la publicación VIII incluida al final de esta sección, cuyas conclusiones principales se detallan a continuación:

- El uso de un mismo xerogel de carbono con dos disolventes distintos, NMP y agua, da lugar a materiales de electrodo con diferentes áreas superficiales. Esto se debe a que el disolvente orgánico (NMP) presenta mayor afinidad por el carbón que el agua y, por tanto, moja mejor la superficie carbonosa. Como consecuencia, el NMP se difunde hacia la parte más interna de la estructura porosa. Es probable que esto produzca el bloqueo de la microporosidad y, por tanto, se modifique el área superficial del material de electrodo.

- Las diferencias en el área superficial debido al método de preparación de los electrodos no conlleva ninguna modificación en las propiedades electroquímicas de las baterías ion-litio. Esto demuestra que es posible sustituir el NMP por agua sin que ello suponga una pérdida en el rendimiento electroquímico de los dispositivos.

- Independientemente del xerogel de carbono utilizado para preparar los electrodos, los valores de capacidad reversible de las celdas electroquímicas se mantienen prácticamente constantes (250-300 mAh/g). No obstante, sí existe una variación en la capacidad irreversible (desde 800 hasta 400 mAh/g) relacionada con el área superficial de los xerogeles de carbono. Las celdas electroquímicas presentan menor capacidad irreversible cuando se utilizan materiales con mayor tamaño de poro, es decir, con menor área superficial.

PUBLICACIÓN VIII

A COMPARISON OF ORGANIC AND AQUEOUS INKS IN THE PREPARATION OF LITHIUM-ION BATTERY ELECTRODES BASED ON CARBON XEROGELS WITH DIFFERENT MESO-MACROPORE SIZES

A comparison of organic and aqueous inks in the preparation of lithium-ion battery electrodes based on carbon xerogels with different meso-macropore sizes

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ABSTRACT

The electrochemical performance of lithium-ion batteries depends to a great extent on the method used to prepare the electrodes and on the pore texture of the active material. In the present study, carbon xerogels with different pore sizes and pore volumes were synthesized by means of microwave heating. These carbonaceous materials were used to prepare lithium-ion battery anodes. Generally, electrodes are prepared by coating a slurry made of an active material, a binder and N-methyl-2-pyrrolidone as organic solvent. The disadvantage of this solvent is that it is both toxic and costly. In this work, the use of water instead of the organic solvent yielded electrodes with similar electrochemical performances making the battery assembly process more economic and environmentally friendly. The results of this study also confirm that the use of an aqueous preparation pathway does not undermine the interdependence between the electrochemical properties of the cells and meso-macroporosity of the carbon xerogels, previously observed in electrodes prepared using organic solvents.

1 Introduction

Lithium-ion batteries are devices that transform chemical energy into electrical energy [1]. Each battery is composed of one or several electrochemical units known as cells. A cell is made up of an assembly of two electrodes, a separator and an electrolyte [2, 3]. The most common electrolyte used is composed of lithium salts dissolved in an organic solvent which impregnates the separator (usually a polymeric matrix), allowing the transport of lithium ions between the electrodes [2, 4]. Lithium oxides with different transition metals are frequently used as cathode active material [1, 4, 5], whereas carbonaceous materials such as graphite, carbon nanotubes and fibers are employed at the anode [5, 6]. On each side, the manufacture of an electrode involves the dispersion of the active material in a solvent in the presence of a binder, producing an ink or slurry that can then be coated on a current collector.

The working principle of a lithium-ion battery is based on the reversible extraction of lithium ions from the cathode during the charge stage, after which they migrate through the electrolyte to intercalate into the structure of the carbon-based anode material [3, 7, 8]. Reversible reactions take place and, during discharge, the lithium ions migrate back to the cathode [7, 8]. During the intercalation of the lithium ions, secondary reactions also occur, especially during the first cycle, leading to the formation of a stable passivation layer, known as the solid-electrolyte interface (SEI) [3, 7]. This reaction is irreversible and entraps the lithium ions [1, 9]. However, this layer acts as a barrier to further degradation and its formation ensures the stability of the cell. The formation of the SEI layer and the diffusion of lithium ions through the anode material is a complex mechanism that depends largely on the chemical composition and porous properties of the active material used as anode [3, 7, 10].

Graphite is one of the most common carbonaceous materials employed as anode active material in lithium-ion batteries [1, 8, 11]. Nevertheless, its maximum specific capacity is limited to 372 mAh/g, corresponding to 1 lithium atom for 6 carbon atoms. Moreover, changes in volume occurring during the successive insertion-deinsertion cycles can cause cell failures with long-term use [1, 8, 11]. Studies in which other carbons have been used show that it is possible to achieve higher capacities than that of graphite, indicating that factors other than lithium intercalation in graphitic layers also affect electrochemical performance [6, 11-13]. The mechanisms that explain the reactions inside a lithium-ion cell are still unclear, although several studies have claimed that being able to control the pore texture of the carbonaceous materials is essential for improving the electrochemical performance of batteries [1, 3, 14]. Consequently, carbon xerogels might be considered as good candidates for studying the electrochemical behaviour of porous carbons, since their porous properties can be tailored by choosing the appropriate synthesis conditions [15, 16]. Indeed, it has recently been shown that the electrochemical behaviour of carbon xerogels, and especially the irreversible losses in the first charge-discharge cycle, are correlated to the surface of their meso-macropores and therefore, to the external surface area of these materials [17].

As mentioned above, active materials, and so in this case, the carbons to be used as anode materials in lithium ion batteries, need to be mixed with a solvent and a binder in order to obtain a homogenous mixture for coating on the current collectors. The fluidity of the mixture will depend on the casting method employed (i.e., by hand, doctor-blade or spray). These mixtures are referred to in the literature as slurry or ink. The most frequent method for preparing inks or slurries involves the use of polyvinylidene fluoride (PVDF) as binder and N-methyl-2-pyrrolidone (NMP) as solvent [9, 18-21].

This solvent is expensive, toxic and flammable [9]. Therefore, the use of an economical and more environmental friendly solvent such as water is necessary to make batteries more cost-effective. Some authors have succeeded in replacing organic solvents with water when preparing electrodes from $LiFePO_4$ [19] or carbon black [22]. However, to the best of our knowledge, no study has been published to date on the use of water for preparing electrodes when carbon xerogels are employed as electrode material.

The present work aims to take a step further towards the understanding of using porous carbons as electrode material in lithium-ion batteries via a more economical and environmental friendly route. Hence, the purpose of this study is to prepare carbon xerogel-based electrodes by replacing the solvent (NMP with water) and the binder (PVDF by sodium carboxymethyl cellulose [Na-CMC] and styrene butadiene rubber [SBR]). The effectiveness of using water instead of NMP and different types of binder is evaluated by analyzing the electrochemical behaviour of the cells. Moreover, five carbon xerogels with different pore textures are used as active material in order to determine whether the previously observed relationship between the porous properties of carbon materials and the electrochemical capacity of lithium-ion batteries is still valid for (i) carbon xerogels synthesized by microwave heating and for (ii) water-based electrodes.

2 Experimental

2.1 Synthesis of organic and carbon xerogels

Organic xerogels were synthesized by the polycondensation of resorcinol (R) and formaldehyde (F) using deionized water as solvent and sodium hydroxide as basification agent. The resorcinol (Indspec, 99%) was first dissolved in the deionized water in an unsealed glass beaker under magnetic stirring. After dissolution, the formaldehyde (Merck, 37 wt.% in water, stabilized by 10-15% methanol) was added and the resulting mixture was stirred until a homogeneous solution was obtained. Finally, the pH was adjusted by adding two different NaOH solutions: a NaOH 5 M solution prepared from solid NaOH (AnalaR Normapur, 99.9%) and a NaOH 0.1 M solution (Titripac from Merck). The concentration of each reagent (resorcinol, formaldehyde, water and NaOH) was selected on the basis of the results reported in a previous published work in order to obtain materials of different pore sizes [16]. Accordingly, the precursor solutions were prepared with pH values ranging between 4 and 6, dilution ratios between 5 and 9 and R/F molar ratios ranging from 0.5 to 0.3.

All the organic gels were synthesized from 200 mL of precursor solution. The solution was poured into an unsealed glass beaker (transparent to microwaves) which was then placed in a multimode microwave oven (in-lab design and construction [23]) at 85 ºC for 3 h, to allow gelation and ageing to be completed. After the formation of the polymeric structure, any excess water was eliminated by further heating of the gel in the microwave oven until a constant mass was achieved. The drying step lasted from 1 to 2 h depending on the final porous texture of the material. All the samples were ground prior to carbonization using a mixer mill (Retsch MM400) at 300 rpm during 60 min. The particle size distribution of the powders was obtained by means of laser diffraction analysis using a Mastersizer 2000 (Malvern Instruments) in wet mode (Hydro2000) in order to ensure that the particle size was centred at ca. 10 µm (see Supporting Information for more experimental details; the particle size distributions of the organic xerogels are shown in Figure S1a).

Finally, the organic gel powders were carbonized at 700 ºC under a nitrogen flow in a horizontal tubular furnace. The carbonization process was performed in three successive steps: (i) heating up to 150ºC at 1.7ºC/min, (ii) heating up to 400ºC at 5ºC/min and (iii) heating up to 700ºC at 5ºC/min. The residence time for each step was 15, 60 and 120 min, respectively. After the last step, samples were left to cool down to room temperature. The particle size distribution of the carbon xerogel powders was also determined prior to the preparation of the inks (see Supporting Information for more experimental details: the particle size distributions of the carbon xerogels are shown in Figure S1b). The carbon xerogels obtained are labelled CX followed by the value of the average pore size (in nm), obtained by means of mercury porosimetry (see section 2.4). For instance, sample CX-50 is a carbon xerogel with an average pore size of around 50 nm.

2.2 Preparation of organic and aqueous inks

The organic inks (labelled 'OI') were prepared by mixing under magnetic stirring 92 wt. % of carbon xerogel, 8 wt. % of polyvinylidene fluoride (PVDF, binder supplied by Alfa Aesar) and N-methyl-2-pyrrolidone (NMP, Alfa Aesar) to form a homogeneous slurry, whereas the aqueous inks (labelled 'AI') were prepared by mixing 92 wt. % of carbon xerogel, 4 wt. % of sodium carboxymethyl cellulose (Na-CMC, binder Walocel CRT 2000 PA kindly supplied by Dow Wolff Cellulosics GMBH), 4 wt. % of styrene butadiene copolymer (SBR, binder supplied by MTI Corporation) and deionized water.

2.3 Electrode and cell preparation

Each ink was sprayed onto pre-weighed stainless steel disks of diameter 15.5 mm (electrodes), and onto stainless steel rectangular strips of 1 × 5 cm. The coating was performed using a Harder & Steenbeck Evolution Silverline 2 airbrush. After the coating, the electrodes were dried at ambient temperature for 2 h and afterwards at 60ºC overnight. The thickness of the dried coating was measured on the strips by stylus profilometry (Veeco Dektak 150, stylus radius: 12.5 µm, force: 2.00 mg), with the carbon being scratched off at regular intervals to establish a baseline. The thickness was obtained as an average value taken from two different strips and applying three scans to each strip. The coated disk-electrodes were weighed to calculate the mass of the active material prior to their electrochemical characterization. Half-cells were then assembled in CR2032 coin cells, in which the carbon xerogel-based electrodes acted as the cathode and a Li-metal disk (MTI Corporation) served as the anode. Two porous polyethylene separators (Celgard®, 25 µm thickness, MTI Corporation) soaked with 80 µL of electrolyte (1 M $LiPF_6$ in Ethylene carbonate : Diethylene carbonate : Dimethyl carbonate 1:1:1, Selectilyte LP71 Merck) were placed in-between. The half-cells were assembled in a glove-box filled with Argon (MBraun).

The excess dried coating from the spraying process was collected from the support as a powder (binder-active material composite) in order to characterize the material present on the electrodes. The composites resulting from the drying of the organic and aqueous inks were labelled 'OIC' (for 'Organic Ink Composite') and 'AIC' (for 'Aqueous Ink Composite'), respectively.

2.4 Sample characterization

2.4.1 Pore texture

The pore size distribution of the carbon xerogels was measured by means of mercury porosimetry (ThermoScientific Pascal 140 and 240). Measurements were performed between 0.01 and 200 MPa. The mercury intrusion data obtained were analysed to determine the distribution of pores larger than 7.5 nm in diameter, calculated by using the Washburn equation [15].

The carbon xerogels as well as the binder-active material composites (series CX, OIC and AIC) were characterized by performing nitrogen adsorption-desorption isotherm analysis at -196 ºC on a Micromeritics ASAP 2420 instrument. Prior to taking the measurements, the samples were degassed overnight at 270°C under high vacuum (133 Pa). The total specific surface area (BET surface area, S_{BET}) was calculated by applying the Brunauer-Emmett-Teller theory to the adsorption data obtained in the relative pressure range of 0.01 to 0.10 [24]. The external surface area (S_{ext}), *i.e.* the surface corresponding to the meso-macropores, was determined following the t-plot method [25]. Since carbon xerogels can be described as a stacking-up of microporous sphere-like nodules delimiting meso-macroporous voids [15], this surface corresponds to the external area of the nodules. Finally, the micropore volume (V_{DUB}, volume of pores of width lower than 2 nm) was determined by the Dubinin-Radushkevich method [26].

2.4.2 Electrochemical measurements

Electrochemical measurements were applied to the CR2032 coin cells. At least two cells of each material were tested in identical conditions in order to ensure repeatability of the results. Charge-discharge curves were recorded at C/5 between 0.005 and 1.5 V (vs. Li^+/Li) using a Biologic VMP3 multichannel potentiostat, inside a climate chamber at 25°C. Cyclic voltammetry was also performed over the same potential range at a scan rate of 0.1 mV/s.

3 Results and discussion

3.1 Pore texture of the carbon xerogels

The N_2 adsorption-desorption isotherms of the synthesized carbon xerogels are displayed in Figure 1a. All the samples present similar volumes of nitrogen adsorbed at low relative pressures, indicating that they all have a similar specific surface area (S_{BET} ca. 600 m^2/g) and a similar micropore volume (V_{DUB} ca. 0.26 cm^3/g). However, there are striking differences between their porous properties resulting from the composition of the precursor solution. These differences are of great importance for the evaluation of the electrochemical performance of the cells. Sample CX-8 shows a combined isotherm of type I and type IV with a marked hysteresis loop at high relative pressure, characteristic of micro-mesoporous materials. When the composition of the precursor solution is modified, the hysteresis loop shifts to higher pressures due to the presence of large mesopores, which agrees with the pore size distribution in Figure 1b recorded by means of mercury porosimetry. Thus, the carbon xerogels evolve from micro-mesoporous to micro-macroporous materials (with each xerogel, CX-8, CX-20, CX-50, CX-130 and CX-200, presenting an average pore size of 8, 20, 50, 130 and 200 nm respectively). Naturally, these results are in agreement with those already published [16], since the composition of the precursor solutions was selected on the basis of the published results.

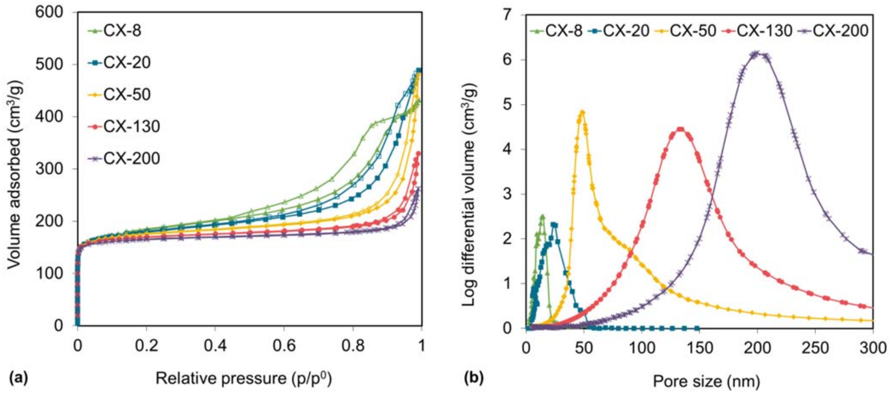

Figure 1. (a) N_2 adsorption-desorption isotherms and (b) pore size distributions taken from Hg intrusion porosimetry measurements of the carbon xerogels.

3.2 Pore texture of the active-binder material composites

The N_2 adsorption-desorption isotherms for the active-binder material composites obtained from the coating of the organic inks (OIC) and the aqueous inks (AIC) are presented in Figure S2 in the Supporting Information. The external (S_{ext}) and BET (S_{BET}) surface areas were calculated from the isotherm data and are plotted in Figure 2.

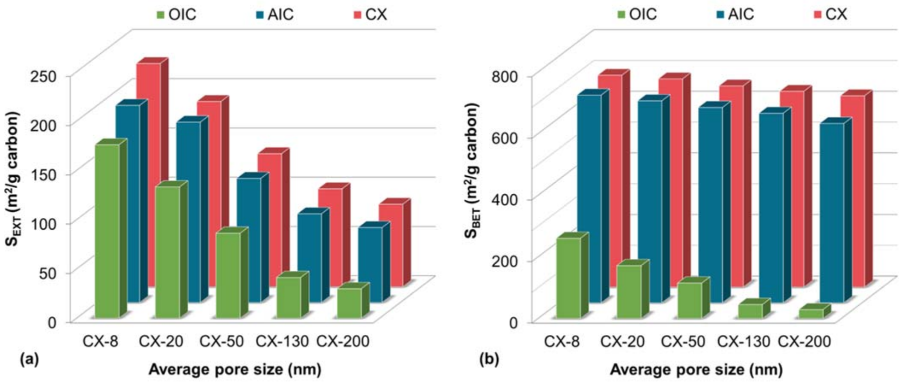

Figure 2. (a) External surface area (S_{ext}) and (b) BET surface area (S_{BET}) of the synthesized carbon xerogels (CX) and the corresponding organic solvent-based (OIC) and water-based (AIC) composites.

The external surface area (S_{ext}) of the carbon xerogels, i.e. the surface corresponding to the meso- or macropores, decreases from 227 to 84 m²/g as the pore sizes increases (see Table S1 in the supporting information). Indeed, this surface corresponds to the external area of the nodules that make up the carbon xerogel structure. The same trend is observed in the case of the composites, though the values are lower than those of the corresponding carbon xerogels, due to the incorporation of binder in the pore texture. The composites resulting from the drying of the organic solvent (OIC) and aqueous (AIC) inks show differences in S_{ext} values despite the fact that both types of ink were prepared with the same amount of binder (8 wt.%). In the case of OIC, the external surface is significantly reduced in comparison with that corresponding to the bare xerogel, whereas the reduction is much less pronounced in the case of the AIC. These differences are probably due to the fact that in the preparation of the organic solvent inks the binder penetrates more deeply into the innermost parts of the material than in the case of the aqueous inks, presumably due to the less hydrophilic nature of the carbon. These data are in agreement with the values of BET surface area (S_{BET}) displayed in Figure 2b. Indeed, the organic solvent-based composites (OIC) exhibit much lower S_{BET} values than their aqueous counterparts (AIC), even though the same amount of binder is used. This may be due to the fact that the binder penetrates more deeply during the preparation of the organic solvent inks, blocking access to the micropores and so, provoking a sharp decrease in the BET surface area.

In this study, different types of binder were used to prepare the inks, depending on the type of solvent (NMP or water). Hence, the differences in the extent of penetration by the binder inside the carbon structure must be due either to the type of solvent or the type of binder used. In order to determine which of these factors was responsible for the change, a new ink was prepared by mixing the CX-200 carbon xerogel, CMC and SBR (binder mixture used to prepare the aqueous inks and which is also soluble in NMP) and NMP (solvent used to prepare the organic inks). The resulting composite after the drying of the mixed ink was labelled 'MIC' ('Mixed Ink-based Composite').

The nitrogen adsorption-desorption isotherms of the CX-200 carbon xerogel and the corresponding active-binder material composites, obtained from the coating of the organic ink (OIC), aqueous ink (AIC) and mixed ink (MIC), are shown in Figure 3a, and the values of the external surface areas, S_{ext}, are presented in Figure 3b.

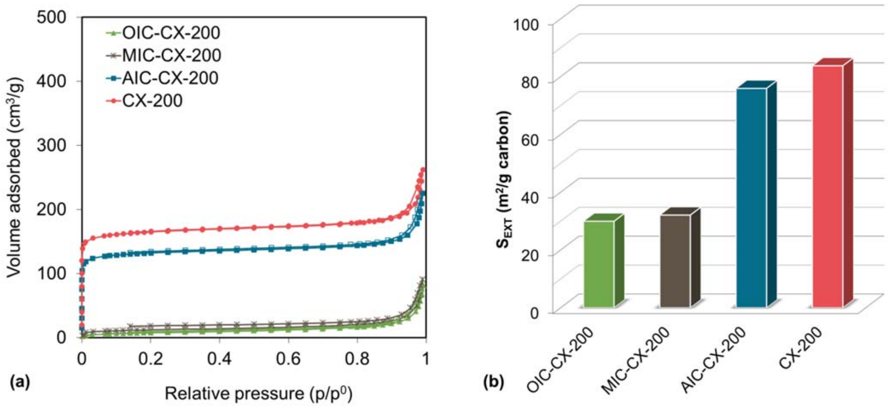

Figure 3. (a) Nitrogen adsorption-desorption isotherms and (b) external surface area values (S_{ext}) of the CX-200 carbon xerogel and its corresponding organic-based (OIC), mixed-based (MIC) and water-based (AIC) composites.

The N_2 adsorption-desorption isotherms of the three types of active-binder material composites and the carbon xerogel display the same shape at high relative pressure, suggesting that no changes occurred in the large pore region. Confirmation was not performed by mercury porosimetry due to the difficulties involved in applying this technique to binder-active material composites. A comparison of the isotherms at low relative pressure indicates that sample MIC-CX-200 has a low adsorbed volume similar to that of sample OIC-CX-200. In agreement with these data, samples MIC-CX-200 and OIC-CX-200 also exhibit similar S_{ext} values (Figure 3b). From this observation, it can be concluded that, in this case, the solvent is the chief factor influencing blockage of the microporosity by the binder. In other words, NMP allows the binder to penetrate more deeply into the pore texture of porous carbons than water. This is probably due to the chemical surface composition of the carbons which shows a greater affinity for organic solvents than for aqueous solvents, resulting in a better surface wettability. However, to explain the behaviour of carbon xerogels as anode materials as a function of their pore texture, the aqueous pathway (water-CMC system) would seem to be more appropriate than the organic pathway (NMP-PVDF system), since the electrodes should display similar textural properties to those of the initial carbon.

3.3 Electrochemical properties

The electrodes prepared from carbon xerogels with different pore textures and different types of inks were used to evaluate the behaviour of carbon xerogel-based electrodes for Li insertion-deinsertion. The thickness of the final electrodes, evaluated by profilometry, ranged from 10 to 15 μm. Their electrochemical performances were determined taking into consideration that the insertion of lithium into the carbon structure occurs during the discharge of the cell, whereas extraction of lithium occurs while the cell is being charged, due to the half-cell configuration. The galvanostatic charge-discharge technique was employed to evaluate the influence of the pore texture of five carbon xerogels. For that purpose, the carbons were employed as active material in electrodes prepared with organic solvent (series OIC) and aqueous (series AIC) based inks. The charge-discharge curves corresponding to the different half-cells during the 1st cycle are shown in Figure 4. The curves were obtained at a rate of C/5 (i.e. the current necessary to charge the battery completely in 5 h, assuming a theoretical value for graphite of 372 mAh/g). The charge-discharge curves recorded for the different half-cells in the 40th cycle are presented in Figure S3 in the Supporting Information.

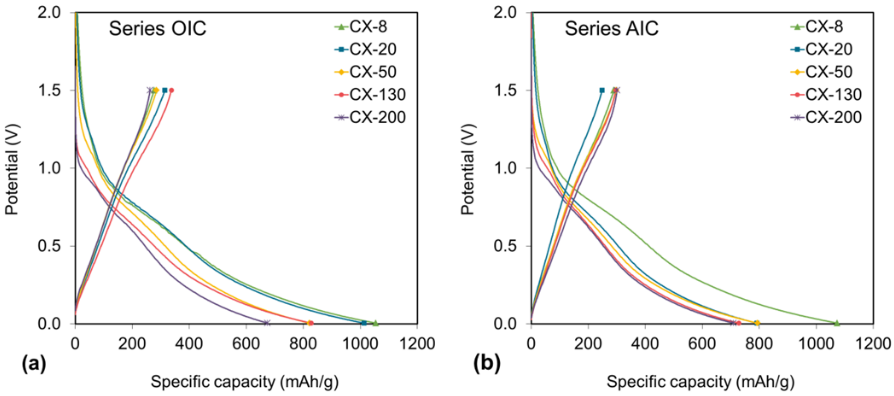

Figure 4. Charge-discharge curves at a C/5 rate for the 1st cycle of carbon xerogels of different pore size; the electrodes were prepared from organic inks (a) and aqueous inks (b).

The charge-discharge curves of the anode materials prepared from organic (series OIC) and aqueous (series AIC) inks exhibit a similar electrochemical behaviour. In agreement with data published on the use of carbons as electrode material [8, 14, 20, 21], the curves shown in Figure 4 do not exhibit a voltage plateau corresponding to the insertion-deinsertion of lithium, but rather a gradual decay in the voltage.

The calculated values of the capacities resulting from the galvanostatic cycling of the different half-cells are presented in Table 1. It should be noted that, generally, an increase in reversibility is accompanied by a rise in irreversible losses during the first charge-discharge cycle, which makes the comparison of these data difficult. In order to obtain a better insight into the behaviour of carbon xerogels as anode materials, more pertinent information can gained from the relative irreversible losses, that can be expressed by the ratio between irreversible and reversible capacity (Q_{irr}/Q_{rev}), as explained by Piedboeuf et al. [Marie-Laure]. In the present study, this ratio was employed for all the half-cell assemblies and their associated numerical values are presented in Table 1 along with the more noteworthy textural properties of the initial carbon xerogels that were used as active material.

Table 1. Textural properties and electrochemical parameters.

Carbon xerogels			Series OIC			Series AIC		
Sample	S_{BET} [a] (m^2/g)	S_{ext} [b] (m^2/g)	Q_{irr} [c] (mAh/g)	Q_{rev} [d] (mAh/g	Q_{irr}/Q_{rev} [e]	Q_{irr} [c] (mAh/g)	Q_{rev} [d] (mAh/g	Q_{irr}/Q_{rev} [e]
CX-8	688	227	778	276	2.8	784	290	2.7
CX-20	676	188	699	314	2.2	542	249	2.2
CX-50	653	135	537	285	1.9	495	298	1.7
CX-130	636	99	491	337	1.5	432	296	1.5
CX-200	621	84	558	262	1.4	408	301	1.4

[a] Calculated in the P/P_0 range of 0.01-0.10 with an accuracy of ± 5 %.
[b] Calculated by the t-plot method with an accuracy of ± 5 %.
[c] Irreversible capacity in the first cycle of charge-discharge calculated by subtraction of the first charge capacity from the first discharge capacity.
[d] Reversible capacity corresponding to the charge capacity of the half cell.
[e] Ratio between the irreversible and reversible capacity in the 1st charge-discharge cycle.

No clear tendency is observed for reversible capacity (Q_{rev}), with values remaining in the same range (ca. 300 mAh/g) for all the tested samples. On the other hand, the irreversible capacity (Q_{irr}) tends to decrease with increasing pore size. However, these absolute values have to be treated with care, in view of the degree of uncertaint surrounding the mass of active material. For that reason, the Q_{irr}/Q_{rev} ratio is much more reliable. The Q_{irr}/Q_{rev} ratio decreases as the pore size increases. Since the reversible capacities of all of the carbon xerogels are in the same range, the lower Q_{irr}/Q_{rev} ratio due to the larger pore size can be ascribed to lower irreversible losses during the first charge-discharge cycle [9]. As already pointed out in a previously published work, the lowest irreversible losses for the electrode with the carbon xerogels of large pore size can be attributed to its smallest external surface area, S_{ext}, corresponding to the surface of the carbon nodules [17]. Indeed, the S_{BET} of the carbon xerogels studied in the present work are all in the same range as shown in Table 1, indicating that there is no relationship between this parameter and the electrochemical behaviour, which is in accordance with data published by Béguin et al. and Piedboeuf et al. [10, 17].

Figure 5 shows the evolution of the Q_{irr}/Q_{rev} ratio as a function of the external surface area of the carbon xerogels used as active material in the electrodes prepared from organic and aqueous inks. A very clear relationship can be observed between the S_{ext} and the Q_{irr}/Q_{rev} ratio for all samples. These data are in good agreement with those obtained by Piedboeuf et al. for electrodes based on carbon xerogels prepared via a different route [17]. From Figure 5 it can also be seen that the relationship between the Q_{irr}/Q_{rev} ratio and the S_{ext} is maintained in all the electrodes prepared with organic solvent and aqueous inks.

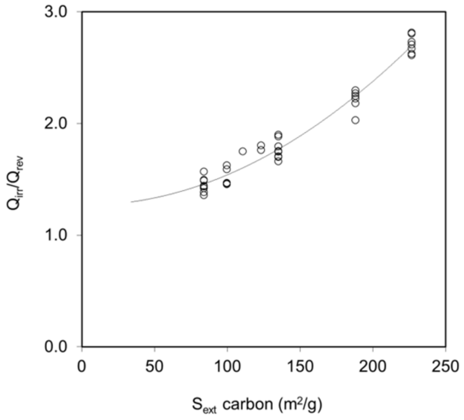

Figure 5. Irreversible-reversible capacity ratio (Q_{irr}/Q_{rev}) as a function of the external surface area of carbon xerogels.

No differences in Q_{irr}/Q_{rev} ratio can be appreciated when comparing organic solvent-based and aqueous-based electrodes prepared from the same carbon xerogel. Therefore, it can be concluded that, for the materials studied, the replacement of the NMP-PVDF system by the water-CMC/SBR system to obtain carbon xerogel-based electrodes is a viable process which avoids the use of a toxic compound without causing any significant deterioration in electrochemical behaviour when they are employed as anodes in lithium-ion batteries.

4 Conclusions

Carbon xerogels were synthesized by means of microwave heating from precursor solutions with different concentrations of reagents in order to obtain tailored micro-mesoporous or micro-macroporous carbonaceous materials with different pore textures. These materials were tested as active materials in the preparation of electrodes, where NMP was used as solvent and PVDF as binder (organic ink). The electrodes were tested for use as anode materials in Li-ion batteries. A clear relationship was observed between the electrochemical properties and the external surface area of the carbon xerogels. The same series of electrodes were also prepared using water as solvent and a mixture of CMC and SBR as binder (aqueous ink). The electrochemical capacities obtained were similar to those obtained in the electrodes prepared from organic inks and the relationship between the electrochemical properties and the external surface area S_{ext}, corresponding to the surface of the carbon nodules making up the carbon xerogel, was confirmed. As in previous works, no relationship was observed between the total specific surface area, S_{BET}, and electrochemical behaviour, whichever solvent-binder pair was used.

Thus, the NMP-PVDF system, which is commonly employed to prepare carbon-based electrodes, could be replaced with a water-CMC/SBR system in order to make way for a more environmentally friendly process without any change of electrochemical behaviour in carbon xerogel-based anode materials.

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5.3. CONCLUSIONES

En los estudios mostrados a lo largo de este capítulo se explora la posibilidad de utilizar los xerogeles orgánicos como material aislante térmico y los xerogeles de carbono como material de electrodo en baterías ion-litio.

Los **materiales aislantes térmicos** se utilizan en un gran número de aplicaciones ya sea para evitar pérdidas energéticas, por cuestiones de seguridad, para aumentar la sostenibilidad de procesos industriales o incluso para reducir impactos medioambientales negativos. En función del uso que se le vaya a dar, los materiales aislantes requieren unas características determinadas. Por ejemplo, en la fabricación de recipientes aislantes no es necesario que los materiales presenten una conductividad térmica extremadamente baja pero si es conveniente que tengan un coste de producción reducido. Sin embargo, en el caso de aplicaciones aeroespaciales priman las prestaciones por encima del coste. Esto hace que existan un gran número de materiales aislantes con diferentes prestaciones y costes. Algunos de los materiales más utilizados son el corcho, la espuma de poliuretano, el poliestireno expandido, la lana de vidrio o los aerogeles de sílice. El valor mínimo de conductividad térmica obtenido para los xerogeles orgánicos resorcinol-formaldehído sintetizados durante la realización de esta Tesis Doctoral se sitúa alrededor de 35 mW/m·K. Este valor es similar al del poliestireno expandido (34 mW/m·K), uno de los aislantes térmicos más utilizados. Aunque su coste es inferior al de los xerogeles orgánicos, el diseño de las propiedades de estos materiales puede afinarse para reducir la conductividad por debajo de 35 mW/m·K y convertirse en un producto con elevadas prestaciones y con un coste competitivo gracias a la utilización de la tecnología microondas como método de calentamiento.

El uso de los xerogeles de carbono como **material de electrodo en baterías de ion-litio** permite la sustitución del compuesto orgánico NMP por agua en la preparación de los electrodos, lo que permite utilizar un método más económico y respetuoso con el medio ambiente. Además, la relación entre el área superficial y el rendimiento de las celdas electroquímicas obtenida sirve como punto de partida para determinar qué propiedades deben tener los xerogeles de carbono para poder ser utilizados en estos dispositivos. Esto deja abierta una interesante línea de investigación, ya que la aplicación de tratamientos secundarios, como el dopaje y/o la grafitización, pueden jugar un papel fundamental en el incremento de la capacidad electroquímica de las baterías de ion-litio.

En resumen, los dos estudios incluidos en este capítulo demuestran el potencial de los xerogeles, tanto orgánicos como carbonizados, en los campos de aplicación estudiados, evidenciando el gran interés científico y comercial de estas dos líneas de investigación.

CAPÍTULO 6

EL FUTURO DE LOS GELES DE CARBONO

Como se ha visto a lo largo de la presente memoria, mediante la modificación de las condiciones de síntesis es posible diseñar las propiedades porosas de los geles de carbono para que encajen en los requisitos de la aplicación donde se quieren utilizar. Esta versatilidad hace de ellos materiales con un gran potencial comercial y, por tanto, resulta de gran interés poder sintetizarlos a escala industrial. Hoy en día, la síntesis en grandes cantidades de xerogeles orgánicos, a partir de los cuales se obtienen los geles de carbono, es posible gracias a la utilización de la tecnología microondas como método de calentamiento. No obstante, como ocurre en la gran mayoría de procesos industriales, es deseable realizar mejoras, tanto desde un punto de vista económico como medio ambiental, para poder obtener un producto más competitivo. En este sentido, en el caso concreto de los geles de carbono, un aspecto a tener en cuenta son los reactivos utilizados para preparar el gel orgánico: el resorcinol y el formaldehído. Ambas sustancias son compuestos químicos dañinos tanto para el ser humano como para el medio ambiente, siendo el resorcinol el de mayor coste económico. Llegados a este punto se debe matizar que la legislación vigente permite el uso de estos compuestos químicos a escala industrial bajo determinadas condiciones de seguridad e higiene laboral. Sin embargo, es posible que, en un futuro, debido a la aparición de nuevas restricciones legales y medioambientales, la síntesis a escala industrial de xerogeles orgánicos resorcinol-formaldehído se vea entorpecida o impedida. Por tanto, a nivel industrial resulta especialmente interesante dejar de emplearlos o, al menos, minimizar su utilización. Por este motivo, la posible sustitución del resorcinol por un compuesto más respetuoso con el medio ambiente y, en la medida de lo posible, más económico, ha sido objeto de estudio durante la realización de esta Tesis Doctoral.

La síntesis de geles orgánicos a nivel teórico puede llevarse a cabo mediante la reacción de polimerización entre un benceno hidroxilado y un aldehído en presencia de un disolvente. En la bibliografía se encuentran estudios donde se ha utilizado como benceno hidroxilado compuestos tales como el fenol o el cresol [Rojas-Cervantes 2015]. El fenol es probablemente el reactivo más estudiado como sustituto del resorcinol debido a su bajo coste. Sin embargo, su reactividad frente al formaldehído es 10-15 veces inferior a la del resorcinol [Rojas-Cervantes 2015]. Por otro lado, el cresol o mezcla de cresoles también han sido muy empleados, ya que son casi cuatro veces más baratos que el resorcinol [Rojas-Cervantes 2015]. No obstante, su solubilidad en agua es muy inferior y, en algunos casos, requiere la utilización de etanol como disolvente para conseguir su total disolución.

Aunque el fenol y el cresol son dos de los compuestos más estudiados debido a sus semejanzas químicas con el resorcinol, en las últimas décadas ha aumentado enormemente el interés por el uso de compuestos de origen natural como la celulosa, la glucosa o los taninos [Lochab 2014; White 2014; De 2015]. Los posibles precursores naturales utilizados en la síntesis de geles de carbono deben cumplir una serie de requisitos: i) deben ser susceptibles de polimerizar pasando por un estado sol-gel, ii) no deben fundirse durante el proceso de síntesis, iii) deben dar lugar, tras el apropiado tratamiento térmico, a un material con alto contenido en carbono y iv) deben ser baratos. Aunque en la bibliografía pueden encontrarse estudios donde se utilizan la celulosa o la glucosa como precursores naturales, los materiales obtenidos no presentan un elevado contenido en carbono. Para incrementarlo es necesario aplicar tratamientos hidrotérmicos, con el consiguiente aumento del coste del proceso [White 2014]. El tanino (T) es un producto comercial no tóxico, renovable, abundante y barato; por lo que se presenta como una de las opciones más viables para producir geles de carbono a escala industrial. Se trata de un compuesto fenólico, de carácter aromático, derivado de la madera, y compuesto, mayoritariamente, por unidades flavonoides (80-82% wt.) [Braghiroli 2015], cuya estructura se muestra en la Figura 6.1a. El comportamiento de los taninos es similar al del resorcinol debido a la presencia de los grupos hidroxilo (Figura 6.1) [Szczurek 2011b]. La existencia de estos grupos funcionales hace que las moléculas flavonoides presenten una reactividad, frente a aldehídos, comparable a la de la molécula de resorcinol y, por tanto, la contribución de ambas moléculas a la formación de la estructura polimérica puede considerarse análoga.

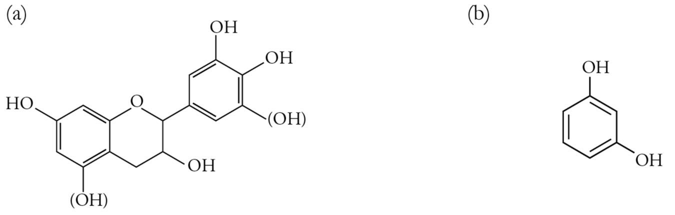

Figura 6.1. Estructura molecular de las unidades flavonoides que contienen los taninos (a) y estructura molecular del resorcinol (b).

De manera similar a la síntesis de xerogeles de carbono preparados a partir de mezclas resorcinol-formaldehído (RF), la concentración de los reactivos empleados en la reacción de polimerización entre los taninos y el formaldehído (tanino, formaldehído, disolvente y catalizador) juega un papel determinante en el diseño de las propiedades finales de estos materiales. En la bibliografía, estas concentraciones se encuentran relacionadas con el porcentaje de sólidos, la relación másica entre los taninos y el formaldehído (T/F) y el pH de la mezcla precursora. Por otro lado, cabe destacar que, en la síntesis de xerogeles a partir de taninos, es imprescindible la introducción de agentes aditivos, surfactantes, que eviten el colapso total de la estructura y permitan obtener materiales porosos [Amaral-Labat 2015]. Por tanto, la concentración del surfactante también es una variable fundamental a tener en cuenta para poder controlar las propiedades porosas de los xerogeles tanino-formaldehído (TF).

La influencia del pH sobre las propiedades finales de los geles TF es una de las variables más estudiadas y tiene una gran influencia sobre la formación de la estructura polimérica [Amaral-Labat 2015]. Al igual que ocurre en el caso de los xerogeles RF, un aumento en la concentración de catalizador, es decir, un aumento del valor del pH, favorece la reacción de adición dando lugar a materiales más densos, con menor porosidad y menor tamaño de poro. Estas propiedades pueden modificarse mediante la variación del porcentaje de sólidos [Amaral-Labat 2013b]. En general, los materiales que se encuentran en la bibliografía presentan más de un 60% de porosidad cuando se fija el porcentaje de sólidos entre 6 y 36%. La modificación del efecto del ratio másico T/F también puede influir en la formación de la estructura polimérica. A pesar de la importancia de este parámetro en el diseño de las propiedades porosas, solo en un estudio basado en la síntesis de criogeles de carbono se ha evaluado el efecto de la modificación de la relación másica T/F entre 0.5 y 0.6 [Szczurek 2011a]. No obstante, es fundamental determinar la influencia de la concentración de formaldehído en la reacción de polimerización para poder controlar las propiedades porosas de los xerogeles de carbono obtenidos a partir de mezclas tanino-formaldehído. Respecto a la introducción de surfactante, se puede resaltar que en la mayoría de los estudios que se encuentran en la bibliografía utilizan surfactantes no-iónicos [Amaral-Labat 2015]. Los aditivos empleados en dichos estudios presentan baja solubilidad en agua y es necesario añadir un disolvente orgánico en la mezcla precursora, con el consiguiente encarecimiento del producto.

El hecho de que existan estudios previos que demuestran que es posible sintetizar xerogeles tanino-formaldehído, junto a la falta de un conocimiento más profundo sobre el papel que juega la concentración de todos los reactivos en la reacción de polimerización, son algunos de los motivos por los cuales, en la presente Tesis Doctoral, se ha seleccionado el tanino como posible sustituto del resorcinol en la síntesis de xerogeles de carbono inducida por microondas. Para poder evaluar el efecto de cada reactivo por separado y determinar el grado de sinergia entre ellos, es necesario llevar a cabo el estudio en varias etapas. El estudio de la primera etapa versa sobre la sustitución progresiva del resorcinol por taninos para conseguir sintetizar xerogeles orgánicos resorcinol-tanino-formaldehído (RTF) mediante calentamiento con microondas y determinar el efecto de este precursor de origen natural sobre las propiedades porosas de los xerogeles. En la segunda etapa se evaluó el efecto sobre las propiedades porosas al variar de forma simultánea el ratio másico T/F y la concentración de surfactante. Ambos estudios se llevaron a cabo durante una estancia en el Departamento de

Ciencia de los Materiales e Ingeniería Metalúrgica del Instituto Jean Lamour (IJL-CNRS, Francia), cuyo grupo de investigación está dirigido por los Dres. A. Celzard y V. Fierro.

6.1. SÍNTESIS DE XEROGELES RESORCINOL-TANINO-FORMALDEHÍDO

Objetivos

Los objetivos planteados para desarrollar el estudio de la sustitución del resorcinol por taninos en la síntesis de xerogeles resorcinol-tanino-formaldehído (RTF) fueron los siguientes:

- ✓ Determinar el efecto de sustituir de forma progresiva el resorcinol por taninos sobre las propiedades químicas y porosas de los xerogeles RTF.
- ✓ Evaluar el efecto de introducir un surfactante que no requiera el uso de disolventes orgánicos sobre las propiedades químicas y porosas de los xerogeles RTF.
- ✓ Demostrar la posibilidad de sintetizar xerogeles tanino-formaldehído (TF) porosos mediante calentamiento con microondas.

Selección del rango de estudio

Para poder cumplir con los objetivos propuestos se seleccionó un xerogel resorcinol-formaldehído (RF), previamente sintetizado mediante calentamiento con microondas, considerando los siguientes aspectos:

- ➢ Los resultados de los estudios recogidos en el Capítulo 4 revelan que una mezcla precursora RF con un valor de pH inicial de 5.4, un grado de dilución de 7.7 y un ratio molar R/F de 0.3 da lugar a un material altamente mesoporoso con un tamaño medio de poro de 40 nm, un volumen de poro de 1.5 cm^3/g y una porosidad del 65%. En función de los valores de las concentraciones de los reactivos utilizados para preparar este xerogel de referencia, puede calcularse el porcentaje de sólidos de la mezcla precursora y el ratio másico T/F que tendría la mezcla si todo el resorcinol se sustituyera por taninos. Los valores obtenidos fueron 30% para el porcentaje de sólidos y 1.2 para el ratio másico T/F.

- Los valores del porcentaje de sólidos y del ratio másico T/F calculados a partir del xerogel de referencia son muy similares a los estudiados por Amaral-Labat y colaboradores en el año 2013 [Amaral-Labat 2013a]. En dicho estudio, se sintetizaron xerogeles TF a partir de mezclas precursoras con un 32% en peso de sólidos, un ratio másico T/F de 1.2 y diferentes valores de pH comprendidos entre 2 y 10. Obtuvieron muestras altamente porosas, 70-80% de porosidad, fijando el valor de pH entre 3 y 6. El estudio de este rango de pH implica la necesidad de utilizar catalizadores ácidos y básicos, ya que la mezcla precursora tenía un valor de pH inicial de 4.9. La síntesis de xerogeles a partir de catalizadores ácidos queda fuera del ámbito de estudio de esta Tesis Doctoral, por lo que, del estudio de Amaral-Labat et al., solo se consideraron los xerogeles obtenidos a partir de valores de pH superiores a 5.

En base a los resultados de los estudios mostrados en el Capítulo 4 y los obtenidos por Amaral-Labat y colaboradores [Amaral-Labat 2013a], todos los xerogeles utilizados en el presente estudio se prepararon a partir de mezclas precursoras con un valor de pH fijado en 5.4, un ratio másico R/F de 0.5 y un porcentaje de sólidos del 30%. A partir de este xerogel de referencia, distintos porcentajes en peso de la concentración másica de resorcinol se fueron sustituyendo por taninos (0, 25, 50, 75 y 100%), obteniéndose una serie de xerogeles llamada RTF. Esta serie RTF se sintetizó mediante calentamiento convencional y calentamiento con microondas. Así mismo, se seleccionó el surfactante aniónico dodecilsulfato de sodio (SDS) como aditivo, ya que se trata de un compuesto soluble en agua y que, tal como se indica en el Capítulo 4 de la presente memoria, puede evitar el colapso de la estructura que se produce durante la etapa de secado.

Conclusiones

Los detalles experimentales y los resultados obtenidos en este estudio se describen y discuten en la Publicación IX, incluida al final de esta sección. A continuación se detallan las principales conclusiones del estudio:

- Las propiedades porosas de los xerogeles RTF dependen en gran medida de la cantidad de taninos añadida en las mezclas precursoras. A medida que se incrementa la concentración de taninos disminuye la porosidad de las muestras. Esto probablemente se debe a que los flavonoides presentan cierto impedimento estérico que dificulta la adición del formaldehído. Por tanto, el aldehído, en lugar de adicionarse en todos los grupos hidroxilo de la molécula, podría formar cadenas poliméricas largas entre las moléculas flavonoides. Estas cadenas poliméricas, al estar poco entrecruzadas, no tendrían fuerza suficiente para contrarrestar las fuerzas de capilaridad producidas durante el proceso de secado, produciéndose el colapso de la estructura. Como consecuencia, la porosidad de los materiales disminuye.

- Las propiedades químicas de los xerogeles RTF varían en función de la cantidad de taninos añadida en las mezclas precursoras. El análisis elemental revela que, a medida que se incrementa la concentración de taninos, el contenido en carbono disminuye ligeramente, mientras que el contenido en nitrógeno, oxígeno e hidrógeno aumenta levemente. La sustitución del resorcinol por taninos en base másica y las grandes diferencias de peso molecular entre el resorcinol y los taninos, implica que la mezcla precursora contenga menor número de moléculas de tanino que de resorcinol y, por tanto menor contenido de carbono. Por otro lado, el contenido en oxígeno e hidrógeno aumenta probablemente debido al mayor número de grupos hidroxilo sin reaccionar que presentan las moléculas flavonoides tras la reacción sol-gel. El aumento en el contenido de nitrógeno se debe a las impurezas contenidas en los taninos.

- El colapso de la estructura de los xerogeles RTF producido al incrementar el contenido en tanino puede evitarse introduciendo el surfactante aniónico SDS en la mezcla precursora. El surfactante forma micelas cuya superficie, en contacto con la mezcla precursora, está cargada negativamente. Estas cargas crean fuerzas de repulsión entre la micela y los grupos hidroxilo desprotonados y la estructura se forma alejada de la micela. Debido a la presencia de estas fuerzas de repulsión, el tiempo necesario para que se produzca la reacción sol-gel aumenta, dando lugar a una estructura polimérica más entrecruzada que cuando no se utiliza surfactante. La resistencia mecánica de estos xerogeles es suficiente para contrarrestar las tensiones superficiales producidas durante el secado, evitando el colapso de la estructura.

- Las propiedades porosas de los xerogeles RTF obtenidos a partir de mezclas precursoras que contienen SDS varían en función del método de calentamiento empleado en la síntesis. El calentamiento con microondas aumenta la velocidad de la reacción sol-gel. La reacción de adición se ve probablemente favorecida, dando lugar a la formación de un mayor número de nódulos de menor tamaño. Por tanto, los xerogeles obtenidos presentan un volumen y tamaño de poro ligeramente inferior a los obtenidos mediante el método convencional.

- Las propiedades porosas de los xerogeles RTF se ven menos influenciadas por la adición de taninos cuando se utiliza la tecnología microondas como método de calentamiento. La radiación microondas provoca la rotación de los dipolos permanentes e inducidos de las moléculas polares. La mayor cantidad de grupos hidroxilo en las moléculas flavonoides favorece la absorción de energía microondas. Estos resultados demuestran que los taninos son una excelente opción como sustituto del resorcinol en la síntesis de xerogeles de carbono inducida por microondas.

PUBLICACIÓN IX

TOWARDS A FEASIBLE AND SCALABLE PRODUCTION OF BIO-XEROGELS.

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Towards a feasible and scalable production of bio-xerogels

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GRAPHICAL ABSTRACT

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ABSTRACT

Hypothesis: The synthesis process of carbon xerogels is limited, mainly due to two drawbacks that prevent their introduction onto the market: (i) the long time required for producing the material and (ii) the reagents used for the synthesis, which are costly and harmful to the environment. Microwave radiation is expected to produce a reduction in time of more than 90%, while the use of tannin instead of resorcinol will probably result in a cost-effective carbonaceous material.
Experiments: Resorcinol–tannin–formaldehyde xerogels containing different amounts of tannin, either with or without a surfactant (sodium dodecyl sulphate), were synthesized by means of two different heating methods: conventional and microwave heating. The effects of the surfactant, the heating method and the addition of tannin upon the porous structure and the chemical composition of the final materials were evaluated.
Findings: It was found that the addition of surfactant is essential for obtaining highly porous xerogels when using tannins. The heating method also plays an important role, as conventionally synthesized samples display a greater volume of large pores. However, tannins are less sensitive to microwave radiation and their use results in tannin–formaldehyde xerogels that have a porous structure and chemical composition similar to those of resorcinol–formaldehyde xerogels.

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1. Introduction

Carbon xerogels are porous materials that are obtained by drying and carbonizing an organic gel [1]. The organic gel is usually synthesized by the polymerization of hydroxylated benzenes and aldehydes in the presence of a solvent [2]. These materials have attracted interest due to the fact that their porous structure and chemical composition can be controlled by the right choice of synthesis conditions [3–5], to produce a wide range of tailor-made and purpose designed materials, whose characteristics meet the needs of specific applications. Hence, it can be said that carbon xerogels are high value-added materials that have a strong commercial potential. However, the synthesis process is handicapped by two major drawbacks that prevent their introduction onto the commercial market: (i) the conventional synthesis process, which involves heating the precursor solution in an electric furnace, requires several days to produce organic xerogels [2]; and (ii) the most common reagents used for the synthesis, resorcinol and formaldehyde, are costly and harmful to the environment [6].

In 2011, Calvo et al. addressed the first drawback by applying microwave radiation to all three stages of the synthesis process: sol–gel reaction, curing and drying. By this heating method, a reduction in time of more than 90% was achieved (from several days to 5–6 h), while the materials obtained displayed similar chemical and porous properties to those conventionally synthesized [7,8]. Organic xerogels synthesized by microwave heating are generally prepared from resorcinol and formaldehyde and, as mentioned above, these reactants are harmful to the environment. However, some authors have reported that by means of conventional synthesis it is possible to obtain carbon gels by using phenol [9], cresol [10,11], tannins [6,12] or cellulose [13] as hydroxylated benzenes and furfural [14] or hexamethylenetetramine [15] as aldehydes.

Of all the possible reagents mentioned above, tannins are considered to be the most viable option at industrial scale as they are "eco-friendly", cheap and non-toxic [16]. Condensed (flavonoid) tannins are phenolic compounds derived from wood. Because they contain reactive hydroxyl groups, they are similar to resorcinol in the way they react towards aldehydes and are transformed from sols to gels [17]. These advantageous chemical characteristics explain why in recent years the number of studies on the use of tannins for the synthesis of different carbonaceous materials has increased [16–20]. The first study to deal with the use of tannins for the synthesis of carbon gels was focused on the synthesis of aerogels and cryogels [19,20], since xerogels gave rise to highly dense materials with a poorly developed porous structure. Amaral-Labat et al. were the first to synthesize highly porous tannin-based xerogels by adding Pluronic F-127 as surfactant [17]. Nevertheless, a period of ten days was needed to obtain these conventionally synthesized xerogels. Furthermore, in order to dissolve the Pluronic, it was necessary to use an organic solvent, which increased the cost of the final product.

The aim of the present work is to address the two main drawbacks that have so far prevented the fabrication of a cost-competitive carbonaceous material at industrial scale and its commercialization, by means of the microwave-assisted synthesis of tannin–formaldehyde xerogels. An attempt has been made to synthesize organic xerogels by conventional and microwave heating using tannin instead of resorcinol. Moreover, an anionic surfactant, which does not require the addition of an organic solvent, was employed to produce highly porous materials. All of the synthesized xerogels were characterized from the point of view of their chemical and porous structure so as to determine the effect of using tannin instead of resorcinol and to ascertain possible differences in properties due to the synthesis method employed.

2. Materials and methods

2.1. Raw materials

Commercial wattle tannin extracted from Acacia Mearnsii (*De Wild*) barks was used for the present study. This raw material was kindly supplied by SilvaChimica (San Michele Mondovi, Italy) under the name Fintan OP. The industrial extraction process of tannins has been explained in detail elsewhere [16]. Briefly, fresh bark was leached in a sodium bisulphite aqueous solution at 70 °C. The resulting solutions were concentrated and then spray-dried to yield a light-brown powder containing 80–82 wt.% of phenolic flavonoid materials, 4–6 wt.% of water, 1 wt.% of amino acids, the remaining components being monomeric and oligomeric carbohydrates in the form of broken pieces of hemicellulose. As from now, the light-brown powder thus obtained will be referred to simply as tannin (T).

Other chemicals used included resorcinol (Sigma Aldrich, 99%), formaldehyde (Roth, 37 wt.% in water, stabilized by 10–15 wt.% methanol), sodium dodecyl sulphate (Sigma Aldrich) and sodium hydroxide (Carlo Erba).

2.2. Preparation of organic xerogels

Organic gels were synthesized by the polycondensation of resorcinol (R), tannin (T) and formaldehyde (F) using deionized water as solvent, sodium hydroxide as catalyst and sodium dodecyl sulphate (S) as surfactant. The method employed for preparing the precursor solutions was the same in all cases. Resorcinol was first dissolved in deionized water in unsealed glass beakers under magnetic stirring. Once the resorcinol had dissolved, tannin was added, still under stirring at room temperature, until complete dissolution. Formaldehyde was then introduced into the solution. Finally, sodium dodecyl sulphate was added and the resulting mixture was stirred until a homogeneous brown solution was obtained.

All the gels were synthesized from 20 ml of precursor solution. The final pH value was adjusted to 5.5 by adding sodium hydroxide. In all cases, the resorcinol–tannin/formaldehyde weight ratio and the percentage of solids were fixed at 1.2 and 25 wt.%, respectively. Ten different precursor solutions using different amounts of tannin, ranging from 0 to 100 wt.% to replace resorcinol either partly or completely, were prepared. Anionic surfactant was added to five of these solutions, in amounts that would ensure that their concentration was 5 wt.%, whereas the other five solutions were kept surfactant-free. Each solution was split into two batches and subjected to two different heating methods: conventional (C) or microwave (MW) heating. The resultant organic xerogels obtained after drying (see details below) were labelled 'RTF' followed by the percentage of tannin used to replace the resorcinol, i.e., 0, 25, 50, 75 and 100 wt.%. An 'S' was appended to the name of those samples containing surfactant. Finally, 'C' or 'MW' was added to indicate the type of heating applied. For example, the sample RTF-75-S-MW refers to a microwave-assisted synthesized xerogel prepared with 75 wt.% of tannin (the other 25 wt.% being resorcinol) and 5 wt.% of surfactant.

2.2.1. Conventional synthesis

The precursor solutions were poured into sealed glass tubes which were then placed in a ventilated oven at 85 °C for 72 h to undergo gelation and curing. Afterwards, the tubes were opened and introduced again into the oven at 85 °C for 48 h for the purpose of completely drying the organic gels by evaporation of the solvent. This temperature was selected according to the procedure proposed by Job et al. for the conventional synthesis of RF xerogels [2].

2.2.2. Microwave-assisted synthesis

In the case of microwave-assisted synthesis, the precursor solutions were poured into unsealed glass beakers (transparent to microwaves) which were placed in a multimode microwave oven (in-lab design and construction) at 85 °C for 3 h to undergo gelation and curing. After the formation of the polymeric structure, any excess water was eliminated by continuing to heat the gel in the microwave oven until constant mass was reached. This dying step lasted from 1 to 2 h. These heating conditions were selected from previous studies on the synthesis of RF xerogels by microwave heating [3].

2.3. Sample characterization

2.3.1. Porous properties

The specific pore volume and the average pore size were measured by means of mercury porosimetry (Autopore IV, Micromeritics) and by applying Washburn's equation to the corresponding data. Measurements were performed between 0.0035 and 414 MPa. Bulk and skeletal densities were determined by helium (Accupyc II 1340, Micromeritics) and envelope (Geopyc 1360 Envelope Density Analyzer, Micromeritics) pycnometry, respectively. The overall porosity was determined from the bulk and skeletal densities.

2.3.2. Chemical composition

The chemical composition of the samples was determined by elemental analysis (C, H, O, N, S), using an Elemental Vario Cube (from Elementar) microanalyzer.

2.3.3. FT-IR spectroscopy

The chemical structure of the RTF xerogels was investigated by using an Infrared Affinity-1 spectrometer (Shimadzu, Japan) over a range of 4000–400 cm^{-1} and by applying an average of 20 scans at a maximum resolution of 4 cm^{-1}. For this purpose, pellets were prepared by pressing 1 mg of sample ground together with 100 mg of dry potassium bromide.

2.3.4. Sample morphology

Scanning Electron Microscope observation (FEI Quanta 600 FEG) was employed to evaluate the morphology of the materials.

3. Results and discussion

3.1. Replacement of resorcinol by tannin

Fig. 1 shows the main porous properties of the resorcinol–tannin–formaldehyde xerogels prepared by the different heating methods. As explained above, the set of samples labelled RTF-MW were synthesized by means of microwave heating, while those labelled RTF-C were conventionally synthesized.

The two sets of samples showed no significant differences in properties despite the fact that the RTF-MW samples were synthesized in unsealed beakers, which should have caused them to undergo greater shrinkage due to the evaporation of the solvent throughout the synthesis process, resulting in strong capillary forces at the liquid–vapour interface [3]. However, the time required for gelation in microwave-assisted synthesis is much shorter and, although a certain degree of shrinkage did occur, the gelation time was not long enough for the polymeric structure to totally shrink [8], leading to materials with porous properties similar to those of conventionally synthesized samples (Fig. 1).

Pore volume, average pore size, porosity and density depend largely on the amount of tannin added to the precursor solutions, as illustrated in Fig. 1. Regardless of the heating method, the addition of tannin resulted in a poorer development of the porous structure (i.e. porosity decreased from 65% to 10% and from 77% to 3% in the group of RTF-C and RTF-MW samples, respectively), as shown in Fig. 1d.

The replacement of resorcinol by tannin not only led to a change in the porous properties of the RTF xerogels but also affected their chemical composition, as can be seen in Table 1. The elemental analysis data of conventionally synthesized samples depends on the amount of reactants used to prepare the precursor solutions. The data in Table 1 indicate that the replacement of resorcinol by tannin caused an increase in the content of hydrogen, oxygen and nitrogen, whereas the percentage of carbon decreased. The RTF-MW set of samples (not shown in Table 1) followed the same trend.

The increase in nitrogen content was probably due to impurities in the tannin as a result of the manufacturing process. The differences in the rest of elements can be attributed to the RT/F mass ratio chosen to prepare the precursor solutions, as the molecular weight of resorcinol and tannin is very different (110.1 g/mol for resorcinol and between 800 and 1200 g/mol for tannin). Thus, for the same volume of precursor solution, there are fewer tannin molecules in sample RTF-100-C than resorcinol molecules in sample RTF-0-C. For this reason, sample RTF-100-C contains a smaller amount of carbon, even though a tannin molecule has a greater number of carbon atoms than a resorcinol molecule. On the other hand, the large size and the lack of flexibility of tannin molecules cause steric hindrance and therefore, the addition of formaldehyde is less effective than when resorcinol is used. Consequently, even though there are fewer tannin molecules in sample RTF-100-C, more OH groups remain unreacted, leading to an increase in the percentage of oxygen and hydrogen (see Tables 1 and 3). These results are also corroborated by the infrared spectroscopy spectra presented in Fig. 2.

The absorption bands assigned to C–O–C stretching (1000–1200 cm^{-1} [12]) and C–O–H bonds attributed to aromatic rings (1200–1300 cm^{-1} [12]) are more intense in sample RTF-100-C than for RTF-0-C, which indicates more oxygen and hydrogen content in the tannin-based sample. On the other hand, sample RTF-100-C shows slightly less intense peaks in the absorption region of 1600 and 1400 cm^{-1} attributed to the characteristic mode of aromatic rings and C–H bonds, respectively [2], probably due to the lower amount of aromatic rings. The more intense bands around 2900–2800 cm^{-1}, which can be attributed to C–H bonds [2], indicates that chains between tannin molecules are larger. Finally, large peaks at 3500 cm^{-1}, characteristic of O–H bonds vibration, can be observed. Accordingly, tannin based sample probably have less amount of aromatic rings which are linked by larger chains. As a result, larger voids between clusters are formed. However, the structure is not able to withstand the surface tension created during drying and the structure collapses, resulting in a non-porous material. Nevertheless, a comparison of the RTF-100-C and RTF-0-C samples reveals that both resorcinol and tannin react with formaldehyde, leading to the same types of bond. This demonstrates the great potential that tannins offer as a substitute for resorcinol, even in a case such as this, where the complete replacement of resorcinol by tannin leads to poorly porous polymeric structures (Fig. 1).

3.2. Addition of surfactant

Fig. 3 shows the main porous properties of resorcinol–tannin–formaldehyde–surfactant xerogels prepared using the two different heating methods. Irrespective of the heating method, the effect of the surfactant is clear from a comparison of Figs. 1 and 3. As expected, the dissolved surfactant formed micelles, leaving negative charges in contact with the reaction medium, which exerted

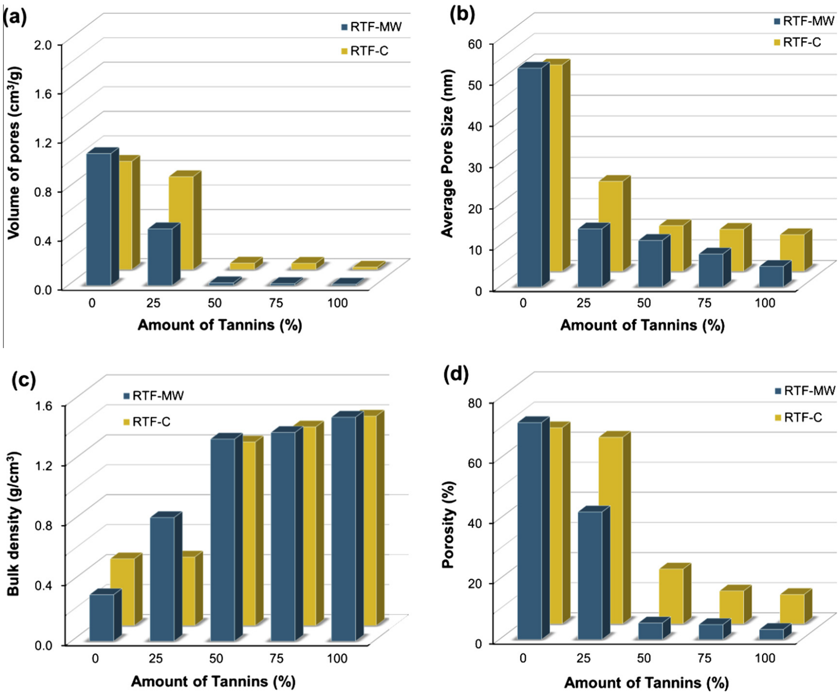

Fig. 1. Porous properties of xerogels prepared using different heating methods.

Table 1
Elemental analysis of RTF-C xerogels.

Sample	Elemental analysis (wt.%, dry basis)				
	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
RTF-0%-C	63.4	4.8	31.8	0.0	0.0
RTF-25%-C	61.7	4.9	33.4	0.0	0.0
RTF-50%-C	60.2	5.4	34.3	0.1	0.0
RTF-75%-C	56.4	5.6	37.9	0.1	0.0
RTF-100%-C	54.3	5.4	40.1	0.2	0.0

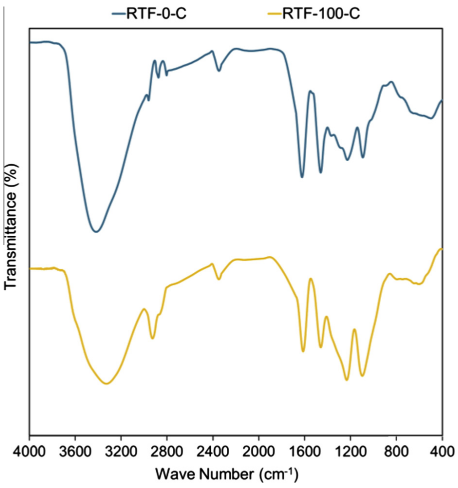

Fig. 2. FT-IR spectra of samples RTF-0-C and RTF-100-C.

repulsive forces on the resorcinol and tannin anions [1]. As a result, during the sol–gel reaction, the structure formed more slowly and farther away from the surfactant anions, leading to a greater volume of pores of larger size than when no surfactant was used (see Figs. 1a, 3a and 1b, 3b, respectively). Thus, it seems that the addition of sodium dodecyl sulphate is a key factor for the synthesis of highly porous materials.

If the heating methods are compared, only the pore size follows the same trend in both the RTF-S-C and RTF-S-MW sets of samples (Fig. 3b). It can be seen that the size of the pores increased as an increasingly higher amount of tannin replaced the resorcinol. This trend may be related to the size of the tannin molecules, which is larger than that of the resorcinol molecules, resulting in larger clusters and therefore, larger voids between clusters, as shown in Fig. 4.

On the other hand, the specific pore volume, density and overall porosity exhibit opposite trends depending on the heating method (Fig. 3). This is probably due to the fact that microwave radiation increases the reaction rate and hence the gelation point is reached faster. Thus, a smaller number of large clusters were formed during the polymerization reaction, as shown in Fig. 5. The size of the clusters determines the size of the pores, which are larger in sample RTF-75-S-MW than in sample RTF-75-S-C (Fig. 3b). It should also

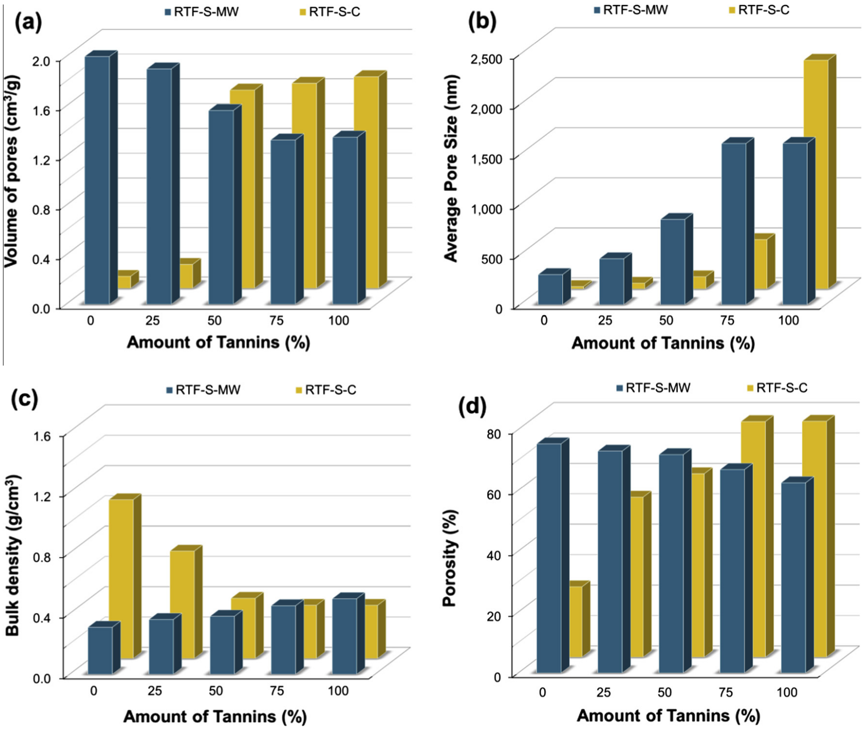

Fig. 3. Porous properties of xerogels prepared using different heating methods (for the RTF-S-MW and RTF-S-C samples).

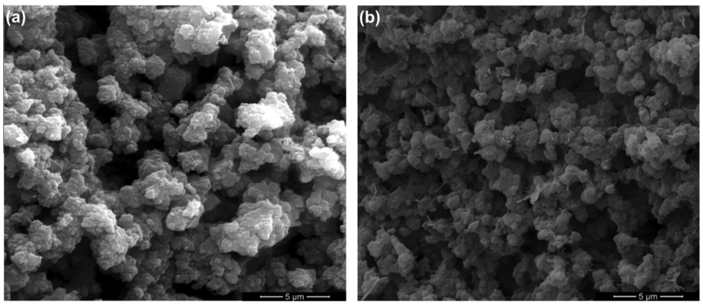

Fig. 4. SEM images of samples RTF-100-S-MW (a) and RTF-0-S-MW (b).

be noted that, generally, samples with small clusters exhibit greater densities. However, sample RTF-75-S-C has a low density value (Fig. 3c). In this case, drying by conventional heating led to a slight shrinkage and, as the materials were highly branched (Fig. 5a), the structure was able to withstand the surface tension created by the water content. Consequently, the structure did not collapse, resulting in a material with a larger volume of pores and greater porosity (Fig. 3a and d).

However, the differences between the RTF-S-MW samples are much smaller than those in the RTF-S-C series. In fact, the porosity decreased from 85% to 20% in the RTF-S-C samples series, whereas the decrease in porosity in the samples synthesized by microwave heating was only from 70% to 65%. Similarly, the density variations ranged from 0.3 to 1.0 g/cm^3 and only from 0.2 to 0.4 g/cm^3 for the RTF-S-C and RTF-S-MW series, respectively. Thus, the final porous properties of the xerogels obtained by adding tannin were less affected by MW heating than by conventional heating. This is because microwave causes the rotation of the permanent and induced dipoles of polar molecules, generating energy which is subsequently dissipated as heat [7]. Hence, the larger amount of OH groups in the tannin molecules favours the absorption of microwave energy and increases the temperature of the reaction medium. In light of this, tannin appears to be an excellent option as a reagent for the microwave-assisted synthesis of carbon xerogels.

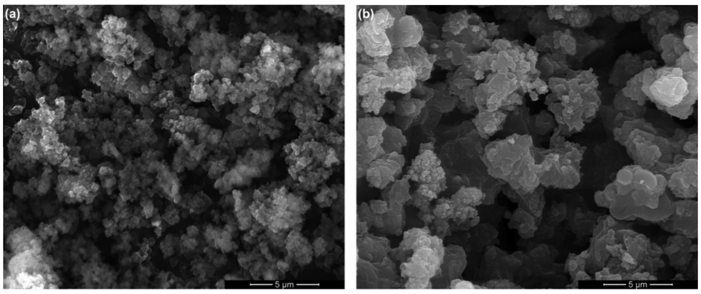

Fig. 5. SEM images of samples RTF-75-S-C (a) and RTF-75-S-MW (b).

Table 2
Porous properties of RTF xerogels synthesized via different routes.

Sample	Density (g/cm^3)	Porosity (%)	Volume of pores (cm^3/g)	Average pore size (nm)
RTF-100-S-MW	0.47	62	1.4	1613
RTF-100-S-C	0.31	77	1.7	2285
[17]	0.31	78	2.2	14000

Table 3
Elemental analysis of RTF-X-S-C xerogels.

Sample	Elemental Analysis (wt.%, dry basis)				
	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
RTF-0-S-C	58.5	5.8	31.2	0.0	4.4
RTF-25-S-C	58.6	6.3	31.1	0.1	3.9
RTF-50-S-C	56.6	6.5	32.5	0.1	4.2
RTF-75-S-C	55.1	6.6	34.1	0.1	4.1
RTF-100-S-C	53.7	6.6	35.8	0.2	3.7

The results of the present work are also in good agreement with those reported by Amaral-Labat et al. [17]. These authors conventionally synthesized TF xerogels at different pH values using Pluronic F-127 as surfactant. The porous properties of a sample synthesized from a precursor solution with a pH value of 5 are shown in Table 2.

It can be deduced from the data in Table 2, that the RTF xerogels synthesized by adding sodium dodecyl sulphate as surfactant exhibit similar properties to those obtained using Pluronic F-127, although their average pore size is substantially lower. The xerogels synthesized by microwave heating underwent a slight shrinkage during drying, resulting in a slightly smaller pore size and a denser material (Fig. 3b and c). Nevertheless, microwave heating seems to be a very promising technology as xerogels with a well-developed porous structure are obtained by employing a natural reactant and an easy, fast and scalable synthesis process [7].

As for the chemical composition of the samples with and without surfactant, the elemental analysis data provided in Tables 1 and 3 show that the trends were similar in both cases. The 4 wt.% sulphur content and the slightly higher percentage of hydrogen and oxygen could have been due to the composition of the surfactant. The fact that the elemental analysis of the samples with and without surfactant showed the same trends suggests that no interaction occurred between the surfactant and the polymeric structure. These findings are confirmed by the infrared spectroscopy spectra in Fig. 6.

Sample RTF-100-S-C exhibits the same absorption bands as sample RTF-100-C and the surfactant. No additional bonds were formed, indicating that no reaction occurred between the polymeric structure and the surfactant. This will facilitate the removal of the surfactant during carbonization and ensure that the porous structure remains similar to that of the organic samples, although some possible shrinkage may occur due to the carbonization process itself.

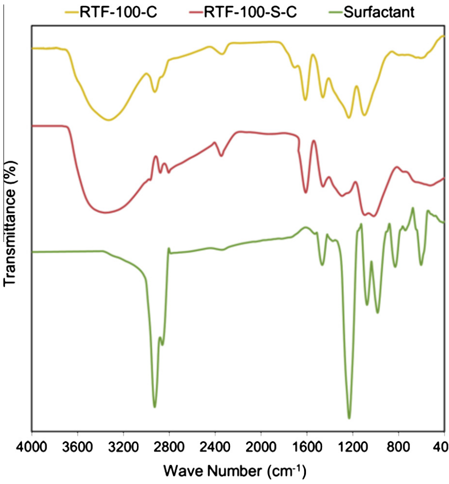

Fig. 6. FT-IR spectra of samples RTF-100-C, RTF-100-S-C and anionic surfactant (dodecyl sulphate).

4. Conclusions

Organic xerogels by conventional and microwave heating using tannin instead of resorcinol has been synthesized. Heating by microwave radiation during the three stages of the synthesis process (sol–gel reaction, curing and drying), a reduction in time of 95% was achieved, as expected by the results presented in a previous work [8]. It has been demonstrated that microwave-assisted synthesis of tannin–formaldehyde xerogels is a viable process which gives rise to materials with similar properties to those obtained by conventional heating [17]. However, to obtain tannin–formaldehyde xerogels with a well-developed porous structure it is necessary to use surfactants. The addition of 5 wt.% of sodium dodecyl sulphate yielded xerogels with 77% and 62% of porosity under conventional and microwave heating, respectively. Although microwave heating produces slightly less porosity, this method is preferable as it is viable at industrial scale, allowing carbon xerogels to be produced at a lower cost.

Accordingly, in the present work, the two main drawbacks that have so far prevented the production of carbon xerogels at industrial scale and its commercialization have been successfully addressed. However, there are still many efforts to be done in this field as the final porous properties of the gels depends largely on the synthesis conditions, as explain in previous work [3]. Hence, it would be interesting to optimize the process including all the variables (pH, ration of reagents, dilution, etc.) and their interrelation [3], in order to control the porous properties of tannin–formaldehyde carbon xerogels. The final step would be the substitution of formaldehyde by other monomer more environmental friendly, in order to obtain a real bio-xerogel material with tailored porosity.

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6.2. SÍNTESIS DE XEROGELES TANINO-FORMALDEHÍDO

Una vez evaluado el efecto de sustituir el resorcinol por taninos y corroborada la necesidad de añadir un surfactante a la mezcla precursora para obtener xerogeles tanino-formaldehído (TF) porosos, se estudió el efecto de modificar de forma simultánea el ratio másico T/F y la concentración del surfactante aniónico dodecilsulfato de sodio (SDS).

Objetivos

Los objetivos planteados para llevar a cabo este estudio fueron los siguientes:

- ✓ Evaluar estadísticamente las variaciones producidas sobre las propiedades porosas de los xerogeles de carbono, obtenidos a partir de mezclas precursoras tanino-formaldehído, al modificar el ratio másico T/F y la concentración de surfactante (SDS).

- ✓ Establecer el grado de sinergia entre el ratio másico T/F y la concentración de surfactante, y establecer su efecto sobre las propiedades químicas y porosas de los xerogeles de carbono sintetizados.

- ✓ Determinar si es posible diseñar a medida las propiedades porosas de los xerogeles TF mediante la selección adecuada de las condiciones de síntesis.

Selección del rango de estudio

La selección del rango de estudio para el ratio másico T/F y la concentración de surfactante se llevó a cabo considerando los siguientes aspectos:

- ➢ El valor del ratio másico T/F se varió entre 0.6 y 2.6. Estos valores se fijaron en base a la Publicación IX, incluida al final de la sección anterior, donde se utilizó un ratio másico de 1.2. El propósito de este nuevo estudio es evaluar el efecto de modificar la concentración de formaldehído, por lo que se seleccionó un valor inferior y uno superior al anteriormente indicado.

- El porcentaje en peso de la concentración del surfactante aniónico (SDS) se modificó entre 0 y 20%. El porcentaje máximo se seleccionó a medida que se desarrollaba el trabajo experimental, es decir, el porcentaje de surfactante se aumentó progresivamente hasta obtener materiales que apenas presentaban porosidad.

El efecto de variar de forma simultánea el ratio másico T/F y la concentración de surfactante sobre las propiedades porosas de los xerogeles de carbono se evaluó mediante el uso de la versión de prueba del software estadístico comercial Design-Expert (Stat-Ease, Inc.). La obtención de conclusiones válidas y objetivas se consiguió tras sintetizar y caracterizar un total de 16 xerogeles de carbono.

Conclusiones

Los detalles experimentales y los resultados obtenidos se describen y discuten en la Publicación X, incluida al final de esta sección, y cuyas principales conclusiones se detallan a continuación:

- La concentración del surfactante SDS tiene un efecto notable en las propiedades porosas de los xerogeles de carbono sintetizados. El surfactante forma micelas cuya superficie, en contacto con la mezcla precursora, está cargada negativamente. Estas cargas crean fuerzas de repulsión entre la micela y los grupos hidroxilo desprotonados de las moléculas flavonoides. Debido a estas fuerzas de repulsión, la formación de la estructura polimérica se retrasa, aumentado el tiempo necesario para que se produzca la reacción sol-gel. Un aumento del tiempo de reacción da lugar a la formación de una estructura con pocos nódulos de gran tamaño. Por tanto, el volumen y tamaño de los poros aumenta a medida que se incrementa la concentración de SDS.

- Las propiedades químicas de los xerogeles de carbono obtenidos a partir de mezclas tanino-formaldehído dependen en gran medida de la concentración de surfactante. El análisis elemental revela que, a medida que se incrementa la concentración de

SDS el contenido de azufre aumenta. Así mismo, los análisis de espectroscopía infrarroja indican que el azufre interacciona con la estructura polimérica incorporando nuevos grupos funcionales. Por tanto, la utilización de SDS no solo permite controlar la estructura porosa del material sino que también permite obtener materiales dopados con azufre.

- El ratio másico T/F influye significativamente en el volumen y tamaño de los poros, mientras que no ejerce un efecto significativo en la porosidad y densidad de los xerogeles de carbono sintetizados. Un exceso de formaldehído da lugar a la formación de mayor número de nódulos pero de menor tamaño y, por tanto, materiales con volumen y tamaño de poro más pequeño.

- El efecto del ratio másico T/F está interrelacionado con la concentración de SDS. Si la concentración del surfactante es elevada, el efecto de esta variable prevalece sobre el efecto del ratio másico T/F. Las micelas disminuyen la velocidad de reacción y se forman menos nódulos de mayor tamaño. Por tanto, para poder controlar las propiedades porosas de los xerogeles de carbono es esencial seleccionar adecuadamente la combinación T/F-SDS.

PUBLICACIÓN X

IMPROVEMENTS FOR TAILORING THE POROSITY OF TANNIN-BASED CARBON XEROGELS

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Advances in tailoring the porosity of tannin-based carbon xerogels

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ABSTRACT

Usually, carbon xerogels are obtained from resorcinol–formaldehyde organic gels. However, more cost-effective and eco-friendly carbon xerogels can be synthesised by using tannins instead of resorcinol, provided that a suitable surfactant is added to prevent the collapse of the structure. The use of tannin, a natural phenolic compound derived from wood, allows obtaining carbon xerogels with controlled porosity, as the porous properties of these materials can be tailored by an appropriate choice of the synthesis conditions. In this work, tannin–formaldehyde xerogels containing different amounts of surfactant and formaldehyde were synthesised in order to evaluate their effect on the porous structure and chemical composition. It was found that porosity and density depend greatly on the amount of surfactant. The lowest density and highest porosity values –0.34 g/cm^3 and 78%, respectively-were obtained by adding 10 wt.% of surfactant. It was also found that S-doped carbon xerogels can be easily synthesized due to the strong affinity between the carbon in the structure and the sulphur from the surfactant. Furthermore, statistical analysis showed that there is interdependence between the effect of formaldehyde and the surfactant, especially in the case of volume and pore size. Hence, the choice of the appropriate surfactant-formaldehyde concentration is essential for controlling the formation of the porous polymeric structure.

1. Introduction

Carbon gels are porous materials that are obtained by drying and carbonizing organic polymer-based gels (Elkhatat and Al-Muhtaseb, 2011). The great advantage of these materials is that, depending on the preparation method and the nature, concentration and chemical composition of the precursors, the porous structure can be controlled (Matos et al., 2006; Rey-Raap et al., 2014). Hence, their final properties can be tailored to fit the requirement of a specific application. The versatility of carbon xerogels is the reason why these materials are perfect candidates for various applications such as adsorption (Job et al., 2005), hydrogen storage (Zubizarreta et al., 2009), electrode material for supercapacitors or batteries (Braghiroli et al., 2015b; Roberts et al., 2014), catalyst support (Yang et al., 2014), thermal insulators (Tannert et al., 2015), etc.

The most common method of synthesising organic gels is by means of the polymerisation of resorcinol with formaldehyde in the presence of a solvent (Elkhatat and Al-Muhtaseb, 2011). The organic gel obtained can be dried under supercritical conditions, by freeze-drying process or by evaporation, which give rise to aerogels, cryogels and xerogels, respectively (Rey-Raap et al., 2014). The preparation of aerogels and cryogels involves cumbersome solvent exchange processes and complex drying stages (Al-Muhtaseb and Ritter, 2003). Thus, evaporative drying is the quickest and simplest method and therefore, yields the most cost-competitive materials.

Although resorcinol and formaldehyde are the most commonly employed reagents, they are costly and harmful to the environment. Consequently, studies with less expensive and greener precursors have been undertaken over the last few decades (Rey-Raap et al., 2015; Szczurek et al., 2014). All the hydroxylated benzenes tested to date contain reactive hydroxyl groups which make them similar to resorcinol in the way they react with aldehydes (Arbenz and Averous, 2014; Lochab et al., 2014). Of all the possible reagents, the use of tannin, a natural counterpart to resorcinol, for the synthesis of carbon gels has attracted a great deal of interest in recent years due to the characteristics of this reagent, which is "eco-friendly", cheap and non-toxic (Braghiroli et al., 2015a; García et al., 2014).

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As in the synthesis of resorcinol–formaldehyde carbon xerogels, the concentrations of all the reagents employed to polymerize tannin with formaldehyde (i.e. tannin, formaldehyde, solvent and catalyst), play an important role in tailoring the final properties of these porous materials (Amaral-Labat et al., 2013b; Rey-Raap et al., 2014). These concentrations have been reported in the literature to be related to the pH, the percentage of solids and the weight ratio of tannin to formaldehyde (Amaral-Labat et al., 2013b; Szczurek et al., 2014). The pH has been one of the most studied variables as it has a great influence on the final properties of tannin–formaldehyde carbon gels over the entire range of porosity (Amaral-Labat et al., 2013a,b, 2015; Szczurek et al., 2011a,b). Other studies focused on the influence of the pH and percentage of solids, have reported that a decrease in pH and percentage of solids leads to an increase in macroporosity, while mesoporosity reaches its maximum value with an increase in the percentage of solids (Amaral-Labat et al., 2013b). It should be pointed out that most of the studies reported to date were performed on aerogels and cryogels (Amaral-Labat et al., 2013b; Szczurek et al., 2011a,b), since the synthesis of carbon xerogels with tannin as precursor can only be achieved if surfactants are added (Amaral-Labat et al., 2013a, 2015). In a study on the synthesis of tannin-based xerogels, Amaral-Labat et al. (2015) reported the effect that modifying the concentration of Pluronic F-127 from 5 to 20 wt.% has on the final porous properties. These authors found that xerogels turned from macroporous to mesoporous materials as the amount of surfactant was increased. However, triblock copolymer surfactants such as Pluronic require both an increase in temperature and the addition of an organic solvent to dissolve and, hence, an extra step is required in the synthesis process (Amaral-Labat et al., 2013a, 2015). However, a recently published work has demonstrated that tannin-based xerogels can be synthesized by using sodium dodecyl sulphate (Rey-Raap et al., 2015). The use of this latter surfactant is expected to give rise to S-doped materials. The introduction of heteroatoms during the synthesis process is of great importance. For instance, the production of S-doped carbon materials can enhance the properties of the started carbons and improve its suitability in some applications concerning sorption and energy storage/conversion devices (Kiciński et al., 2014).

Despite the importance of the concentration of formaldehyde for tailoring the porous properties, the effect of modifying the tannin to formaldehyde weight ratio from 0.5 to 0.6 has been evaluated, to the best of our knowledge, in only one study (Szczurek et al., 2011a), that focuses on carbon cryogels. Yet it is essential to appreciate the importance of the concentration of formaldehyde for the polymerization reaction in order to control porous properties of carbon xerogels.

The aim of the present work is to move a step closer towards the synthesis of tailored porous carbon xerogels by a more cost-effective and environment-friendly route. To achieve this goal, tannin–formaldehyde carbon xerogels were synthesised using different amounts of formaldehyde and surfactant. The surfactant employed in the present study does not require the addition of any organic solvent as it can be easily dissolved in water. All the carbon xerogels synthesised were characterised from the point of view of their chemical and porous structure in order to determine the effect of formaldehyde and surfactant on the final porous properties of the xerogels.

2. Experimental

2.1. Raw materials

Commercial wattle tannin extracted from Acacia Mearnsii (De Wild) bark was used for the present study. This raw material was kindly supplied by SilvaChimica (San Michele Mondovi, Italy) under the name of Fintan OP. The industrial extraction process of tannins has been explained in detail elsewhere (Braghiroli et al., 2014). Briefly, fresh bark was subjected to leaching in a sodium bisulphite aqueous solution at 70 °C. The resulting solutions were concentrated and then spray-dried to yield a light-brown powder containing 80–82 wt.% of phenolic flavonoid materials, 4–6 wt.% of water, 1 wt.% of amino acids and other components such as monomeric and oligomeric carbohydrates consisting of broken pieces of hemicellulose. The light-brown powder thus obtained is referred to as tannin (T).

Formaldehyde (37 wt.% in water, stabilised by 10–15 wt.% of methanol), was supplied by Roth. The sodium dodecyl sulfate and sodium hydroxide were purchased from Sigma–Aldrich and from Carlo Erba, respectively.

2.2. Preparation of the carbon xerogels

Organic gels were synthesised by the polycondensation of tannin (T) and formaldehyde (F) using deionised water as solvent, sodium hydroxide as catalyst, and sodium dodecyl sulfate (SDS) as surfactant (all the relevant data related to the reagents employed in this study can be found in the Supporting information). Tannin was first dissolved in deionized water in open glass beakers under magnetic stirring at room temperature. Once the tannin had dissolved, formaldehyde was introduced into the solution. Finally, sodium dodecyl sulfate was added and the resulting mixture was stirred until a homogeneous brown solution was obtained. All the gels were synthesised from 20 mL of precursor solution with a pH value fixed at 5.5 by adding sodium hydroxide. The tannin/formaldehyde weight ratio varied between 0.6 and 2.6 whereas the percentage of solids remained fixed at 25 wt.% for all the samples. The concentration of sodium dodecyl sulfate varied between 0 and 20 wt.%.

Each precursor solution was poured into a sealed glass tube, with an inner diameter value of 1.4 cm, which was then placed in a ventilated oven at 85 °C for 72 h to undergo gelation and curing. Afterwards, the tube was opened and introduced again into the oven at 85 °C for 48 h for the organic gel to completely dry by evaporation of the solvent. Once dry, each xerogel was carbonised at 900 °C under nitrogen in a horizontal tubular furnace. The residence time was 2 h and the heating rate was set at 5 °C/min. The resultant carbon xerogels were labelled ‘TF’ followed by the tannin–formaldehyde weight ratio and the percentage of surfactant added, e.g. TF—1.2–10%.

2.3. Sample characterisation

The porous properties of the carbon xerogels were characterised by means of mercury porosimetry (Autopore IV, Micromeritics). Measurements were performed between 0.0035 and 414 MPa, and Washburn’s equation was applied to the corresponding data to obtain the specific pore volume and average pore size (see Supporting information for more details). Skeletal and bulk densities were determined by helium (Accupyc II 1340, Micromeritics) and envelope (Geopyc 1360 Envelope Density Analyzer, Micromeritics) pycnometry, respectively. The overall porosity was determined from the bulk and skeletal densities. The morphology of the carbon structure was observed using a Quanta FEG 600 scanning electron microscope and the chemical structure was investigated using an Infrared Affinity-1 spectrometer (Shimadzu, Japan) by applying an average of 20 scans at a maximum resolution of 4 cm^{-1} over a range of 4000–400 cm^{-1}. For this purpose, pellets were prepared by pressing 1 mg of sample ground together with 100 mg of dry potassium bromide. The chemical composition of the samples was determined by elemental analysis (C, H, O, N, S), using a Vario EL Cube microanalyzer (Elementar).

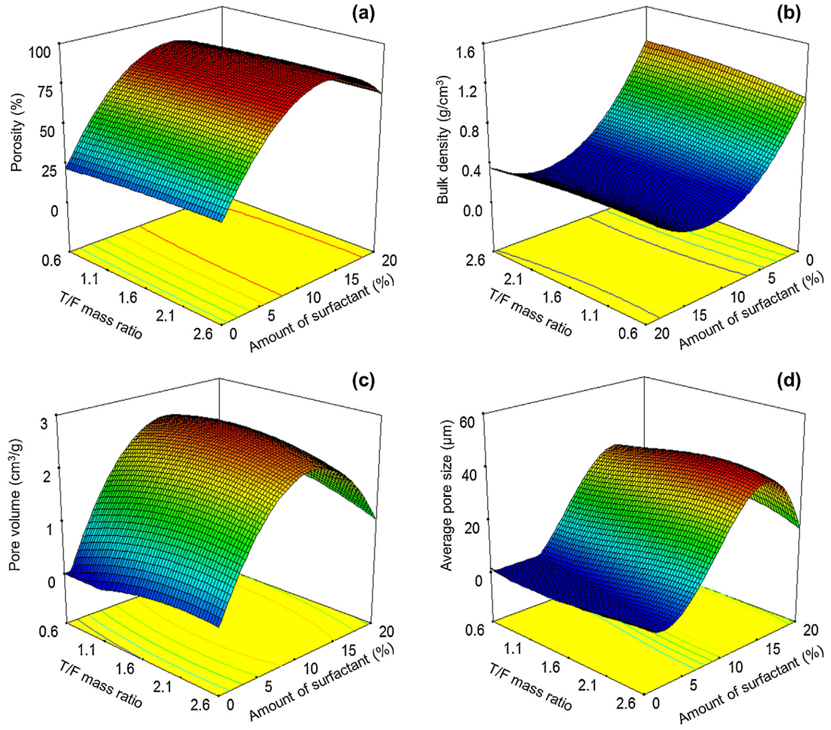

Fig. 1. Three-dimensional surfaces representing the effect of the T/F weight ratio and percentage of surfactant on the porosity (a), bulk density (b), pore volume (c) and average pore size (d) of tannin-based carbon xerogels.

2.4. Statistical analysis

Response surface methodology was applied to the porous characterisation data in order to assess the significance of each of the variables studied (amount of anionic surfactant (SDS) and tannin/formaldehyde (T/F) weight ratio) and of any possible synergy between them. Significance was determined by applying an analysis of variance (ANOVA) to each of the four porous properties selected as responses: porosity, bulk density, pore volume and average pore size. The implementation of ANOVA allows the interaction between variables and their effect on the main porous properties to be evaluated with a minimum number of experiments. If the *p*-values obtained from the ANOVA were smaller than 0.05, the corresponding variable would be assumed to have a significant effect on the response. An optimal design covering all the possible SDS-T/F combinations together with repeated experimental runs were employed to obtain a statistical model that adequately fitted the experimental results. The design matrix was generated by using a Design-Expert 9.0 Trial version from Stat-Ease Inc.

3. Results and discussion

3.1. Statistical analysis

Response surface methodology was applied to the four variables selected as responses: porosity, bulk density, pore volume and average pore size. Porosity and bulk density were adjusted to a quadratic function, whereas pore volume and average pore size were fitted to a cubic function. The *R*-squared values for porosity, bulk density, pore volume and average pore size were 0.90, 0.93, 0.89 and 0.96, respectively, indicating that the calculated results are in good agreement with those obtained experimentally. Moreover, the data obtained by employing a least square technique indicate that the model applied to each response is significant (the ANOVA data for each response variable are shown in Tables S1, S2, S3 and S4 in the Supporting information). The linear and quadratic terms for the amount of surfactant have a significant effect on porosity and density, whereas the volume and the average size of the pores depend on linear, quadratic and cubic terms of the amount of surfactant, and also on the T/F weight ratio and the interaction between the SDS and T/F weight ratio. Fig. 1 shows the three-dimensional surface plots constructed on the basis of model equations that represent the response surface curves of the independent variables (T/F weight ratio and percentage of surfactant) versus the dependent variables: porosity (Fig. 1a), bulk density (Fig. 1b), pore volume (Fig. 1c) and average pore size (Fig. 1d). From the ANOVA analysis it can be inferred that the four variables studied are highly dependent on the percentage of surfactant, while the T/F weight ratio significantly affects only on the volume and average size of the pores.

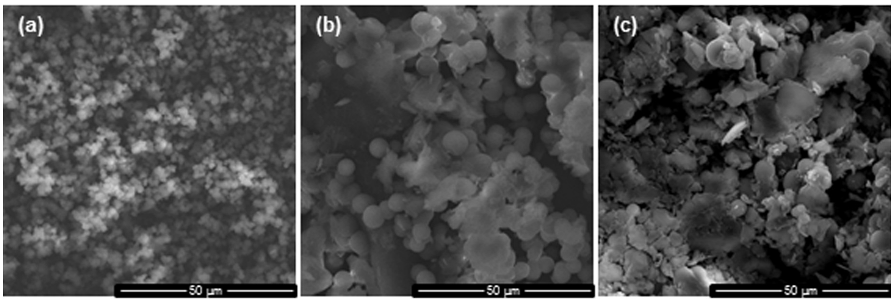

Fig. 2. SEM images of organic TF xerogels with 5 wt.% (a), 10 wt.% (b) and 20 wt.% (c) of surfactant.

3.2. *Effect of the surfactant*

In Fig. 1a and b, clear differences can be observed when the percentage of surfactant is modified. By adding 10 wt.% of surfactant, all the carbon xerogels exhibit the lowest density and highest porosity values, 0.34 g/cm^3 and 78%, respectively. An increase in the percentage of surfactant to above 10 wt.% causes a slight decrease in porosity from 78% to 70%. Conversely, a decrease to below 10 wt.% leads to materials with a poorly developed porous structure, with an average porosity of less than 20% if no surfactant is added.

The effect of the anionic surfactant (SDS) on the final porous structure of TF carbon xerogels can be attributed to the polymerisation of the tannin and formaldehyde. Since reactive hydroxyl groups give tannin a reactivity towards formaldehyde similar to resorcinol (Amaral-Labat et al., 2013a; Arbenz and Averous, 2014), it is possible to deduce a mechanism for the reaction based on the well-known polymerisation reaction between resorcinol and formaldehyde. Hence, the first step in the polymerisation of tannin and formaldehyde can be assume to be the formation of tannin anions via hydrogen abstraction (Rey-Raap et al., 2014). Formaldehyde is then added to them to form hydroxymethyl derivatives which are linked to each other by methylene and ether bonds. As the reaction proceeds, the number of bonds between the rings increases, leading to the formation of the polymer backbone and, in turn, three-dimensional cross-linked polymer clusters (Rey-Raap et al., 2014). However, two points must be borne in mind when using tannin as precursor for the synthesis of carbon gels (Rey-Raap et al., 2015): (i) the larger amount of OH groups in tannin molecules compared to those of resorcinol will probably leave a larger number of unreacted OH groups and (ii) as the large size and lack of flexibility of tannin molecules cause steric hindrance, the addition of formaldehyde will be less effective than if resorcinol is used. As a result, a poorly branched structure, whose mechanical strength will not be able to counteract the capillary forces created during drying, is formed. Hence, the material shrinks, leading to the collapse of the polymeric structure and to a poorly developed porosity. The addition of sodium dodecyl sulfate (anionic surfactant) prevents shrinkage due to the repulsive forces among the tannin anions generated during the polymerisation reaction and, as a result, the structure of the xerogel forms further away from the SDS micelles (Matos et al., 2006). Furthermore, due to these repulsive forces, the formation of methylene and ether bonds is retarded and, consequently, a longer time is required for the completion of the sol–gel reaction. The time required for the accomplishment of the sol–gel reaction is directly related to the growth and formation of clusters: longer times lead to the formation of a small number of large clusters. The differences in cluster size are clearly shown in Fig. 2a and b, where SEM images of samples with 5 wt.% and 10 wt.% of surfactant are displayed. An increase in the concentration of surfactant from 5 wt.% to 10 wt.% gives rise to structures with larger clusters and, as a result, with a greater porosity (Fig. 1a). On the other hand, an excessive amount of surfactant leads to the formation of a poorly cross-linked polymeric structure and to a more heterogeneous material (Fig. 2c) with a broader pore size distribution, as shown in Fig. S2 in the Supporting information.

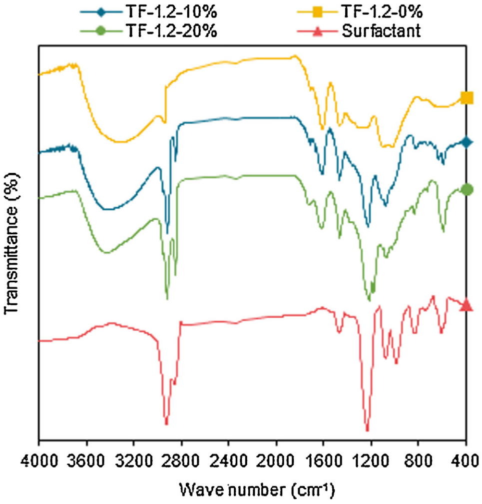

Fig. 3. FT-IR spectra of SDS anionic surfactant and organic TF xerogels with 5 wt.%, 10 wt.% and 20 wt.% of surfactant.

The elemental analysis data in Table S5 in the Supporting information clearly show that the anionic surfactant is prevalent in the organic samples, since the sulphur content increases from 0 to 7–9 wt.% (on dry basis) when the amount of surfactant is increased from 0 to 20 wt.%. The infrared spectroscopy spectra of the organic xerogels in Fig. 3 indicate that the surfactant interacts with the polymeric structure, as a result of which new functionalities are incorporated into the final material.

Sample TF—1.2–0% presents a more intense band at around 3300 cm^{-1}, associated to O—H stretching vibrations, than samples TF—1.2–10% and TF—1.2–20%, and a more intense band at ca. 1600 cm^{-1} attributed to the characteristic modes of aromatic rings (Lochab et al., 2014). This is probably due to the incorporation of the carbonaceous chains of the surfactant that gives rise to materials

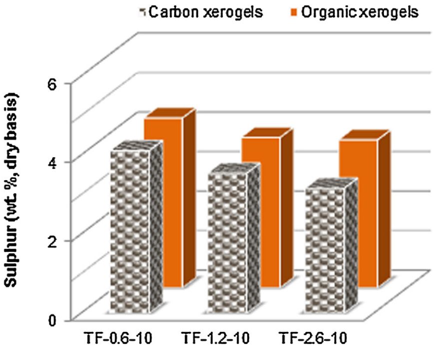

Fig. 4. Sulphur content in organic and carbon xerogels.

with a lower concentration of OH groups and to a lower aromatic ring content. On the other hand, the incorporation of SDS induces a higher concentration of aliphatic C—H, as a result of which samples TF—1.2–10% and TF—1.2–20% display more intense bands at 2900–2800 cm^{-1} and 1400–1500 cm^{-1} than the pristine organic xerogel (Viana et al., 2012). Also, samples with surfactant present a new type of surface group corresponding to the sulphur content and as a consequence, an absorption band at ca. 1230 cm^{-1} attributed to the SO_2 asymmetric vibrations appears (Viana et al., 2012). This functional group is probably also responsible for the presence of the peaks at wavenumbers lower than 1100 cm^{-1}. Some authors point out that the values corresponding to these peaks may vary according to the way in which the molecules are packed (Viana et al., 2012).

The data obtained from the infrared spectroscopy spectra are in good agreement with the results of the elemental analysis of the carbon xerogels in Fig. 4. The results obtained are in agreement with the idea that not all the surfactant is released as volatile matter during carbonisation, probably due to the strong affinity between sulphur and carbon. These results are of great interest, as not only are cheaper and more environmentally-friendly materials obtained, but also S-doped materials, which are useful for a wide range of applications (Kiciński et al., 2014).

3.3. *Effect of formaldehyde*

The T/F weight ratio hardly affects the density and porosity of the carbon xerogels within the range studied (Fig. 1a and b). However, the volume and average size of the pores differ greatly when the T/F weight ratio is modified. In general, as with RF carbon xerogels, an increase in the concentration of formaldehyde shifts the chemical equilibrium towards the products, favouring the addition reaction. This suggests that clusters form and grow faster, resulting in TF structures with a large number of small clusters, as illustrated in Fig. 5. However, in TF carbon xerogels, there is also interdependence between the effect of the formaldehyde and that of the surfactant, as shown by the data from the statistical analysis mentioned above, on the basis of which different porous structures can be tailored depending on the SDS-T/F combination employed to prepare the precursor solution.

Formaldehyde not only accelerates the formation and growth of clusters but also creates more interconnections between the clusters (Rey-Raap et al., 2014), leading to highly branched structures. Hence, when the concentration of surfactant is low (below 10 wt.%), carbon xerogels synthesised with a large amount of formaldehyde

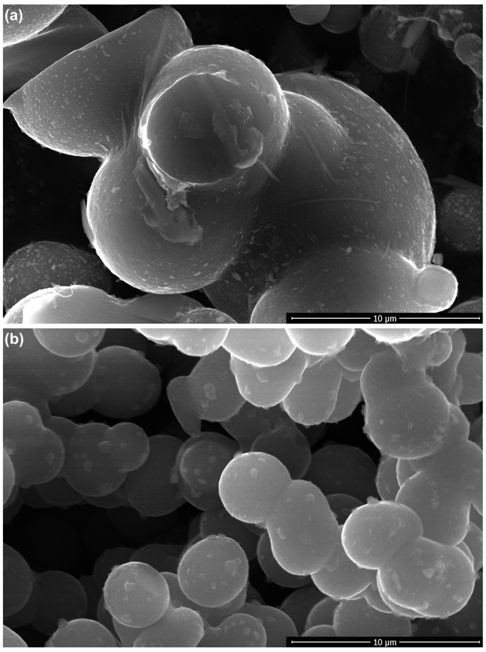

Fig. 5. SEM images of carbon xerogels with 10 wt.% of SDS and a T/F weight ratio of 2.6 (a) and 1.2 (b).

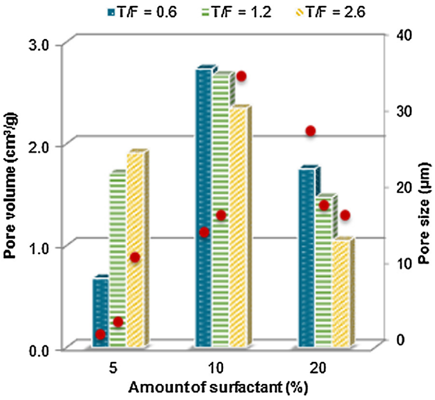

Fig. 6. Pore volume (columns) and average pore size (dots) of carbon xerogels synthesized from precursor solutions with different T/F weight ratios and surfactant concentrations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

have a lower volume of pores of smaller size, as shown in Fig. 6. As can be seen, the pore sizes range from 0.8 to 11 μm.

Due to the synergy between the formaldehyde and surfactant, the effect of formaldehyde can be reversed by increasing the concentration of surfactant to above 10 wt.%. This is probably because the higher number of micelles slows down the reaction rate, causing the formation of a smaller number of clusters but of larger size, and also because of the more heterogeneous material (Fig. 2). This effect, combined with the fact that a smaller concentration of formaldehyde gives rise to weaker structures, results in materials with a mechanical strength that is not able to counteract the capillary forces created during drying and hence the materials shrink. As a result, materials with a lower volume of pores of smaller average size are obtained (Fig. 6).

The samples with 10 wt.% of surfactant deserve special mention because in their case, an increase in the T/F weight ratio results in a large increase in average pore size, whereas the pore volume decreases slightly, as shown in Fig. 6. This behaviour is opposite to that generally found for carbon xerogels where structures with smaller pores also have lower pore volumes (Rey-Raap et al., 2014). In the present study, an increase in the T/F weight ratio leads to the formation of a small number of large clusters (Fig. 5) and therefore to pores of a larger size (Fig. 6). However, as the concentration of formaldehyde is lower, the structure is less branched and a certain degree of shrinkage takes place during drying, resulting in a slight decrease in pore volume.

In general, when the amount of surfactant increases, porosity passes through a maximum, while when the T/F weight ratio is modified, the porosity increases or decreases depending on the amount of surfactant added, due to the high interdependence between these two variables. From these results, it can be seen that the right choice of SDS-T/F combination is essential for controlling the formation of the polymeric structure and for tailoring the porous properties of tannin-based carbon xerogels so that they fit the requirements of a specific application.

As an example to demonstrate the importance of being able to control the porous properties, the thermal conductivity of the organic TF xerogels synthesised by adding 10 wt.% of surfactant and different concentrations of formaldehyde (TF—2.6–10%, TF—1.2–10% and TF—0.6–10%) was measured, taking into account that materials are considered insulating if their thermal conductivity value is typically lower than 50 mW/m/K. As mentioned above, Fig. 6 shows that as the amount of formaldehyde increases, the average pore size decreases, whereas the pore volume increases. These porous properties have a great effect on the thermal conductivity of the materials. Sample TF—2.6–10% exhibits a thermal conductivity of 65 mW/m/K, corresponding to a poor insulating material, whilst sample TF—1.2–10% and TF—0.6–10% present values of 51 and 39 mW/mK, respectively. In short, modification of the formaldehyde concentration gives rise to materials with porous properties that lead to different insulation capacities. Accordingly, in order to use carbon xerogels as insulating materials the appropriate process conditions should be chosen.

4. Conclusions

In the present work, highly porous tannin-based carbon xerogels have been successfully synthesised. An appropriate selection of the amount of surfactant and formaldehyde allows controlling the formation of the polymeric structure and thus, the porous properties. Materials synthesised are more cost-effective and environmentally "greener" than the commonly used resorcinol–formaldehyde xerogels, due to the use of tannin, a natural compound industrially obtained from wood. Moreover, tannin-based xerogels can be compared to resorcinol–formaldehyde xerogels with respect to porosity and density. However, these "greener" materials have higher volume of large pores due to the nature of tannin molecules and the need to use surfactants. Hence, tannin-based carbon xerogels synthesised have certain limitations for those applications requiring narrow mesopores, but are totally useful in those applications in which larger pore sizes are required. Furthermore, an additional advantage is that the surfactant used in the present work allows sulphur to remain trapped inside the structure, which can be used as a basis for obtaining S-doped carbons.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.indcrop.2015.12.001.

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6.3. CONCLUSIONES

Los resultados obtenidos a lo largo de este capítulo demuestran que el resorcinol, uno de los reactivos más utilizados en la síntesis de xerogeles de carbono, puede ser sustituido por otro compuesto más económico y respetuoso con el medio ambiente como son los taninos. La sustitución del resorcinol por taninos es una línea de investigación con un gran interés comercial ya que disminuye considerablemente los costes del producto. No obstante, cabe destacar que los materiales obtenidos son, en su mayoría, materiales exclusivamente macroporosos. Si se quieren diseñar las propiedades a medida de una aplicación, como ocurre en el caso de los xerogeles resorcinol-formaldehído, es necesario seguir trabajando en esta línea de investigación. El siguiente aspecto que se debería estudiar para mejorar las prestaciones de estos xerogeles de carbono, es la evaluación del efecto sobre las propiedades de estos materiales al modificar de forma simultánea la concentración del resto de los reactivos (tanino, formaldehído, agua y catalizador), fijando un rango de estudio más amplio. Por otro lado, las propiedades químicas y porosas de los xerogeles de carbono, preparados a partir de mezclas tanino-formaldehído durante la realización de esta Tesis Doctoral, coinciden con las propiedades requeridas en el campo de las baterías de ion-litio determinadas en el Capítulo 5 de la presente memoria: baja área superficial y elevado contenido en nitrógeno y oxígeno. Por tanto, la utilización de estos materiales como material de electrodo en baterías es un aspecto a considerar como otra posible línea de investigación futura.

CAPÍTULO 7

CONCLUSIONES GENERALES

Las publicaciones recopiladas en esta memoria muestran los resultados derivados del estudio del diseño de xerogeles de carbono *a la carta* mediante su síntesis inducida por microondas. Las conclusiones más relevantes de dicho estudio se presentan a continuación:

- La selección adecuada de los parámetros del dispositivo microondas en función de la cantidad de muestra que se va a sintetizar es fundamental para conseguir materiales porosos bien desarrollados.

- La variación simultánea de la concentración de los reactivos principales en las mezclas precursoras de los xerogeles de carbono permiten un mayor control sobre las propiedades porosas de estos materiales, que el conseguido cuando se modifica cada concentración por separado.

- La introducción de agentes aditivos en las mezclas precursoras permite obtener xerogeles de carbono con propiedades diferentes a las obtenidas modificando la concentración de los reactivos principales, demostrando una vez más la gran versatilidad de los xerogeles de carbono.

- El tratamiento de los resultados a través de técnicas estadísticas permite determinar las condiciones de síntesis que darán lugar a un xerogel de carbono con las propiedades requeridas por una aplicación determinada.

- Todas las publicaciones recogidas en el Capítulo 4 de la presente memoria demuestran que la síntesis inducida por microondas de xerogeles de carbono permite obtener materiales con propiedades que abarcan todo el rango de porosidad. Es decir, se han podido sintetizar xerogeles de carbono microporosos, micro-mesoporosos y micro-macroporos, con diferentes grados de porosidad.

- El uso de materiales de electrodo en baterías de ion-litio, preparados a partir de un mismo xerogel de carbono pero con dos disolventes distintos, N-metil pirrolidina (NMP) y agua, da lugar a capacidades electroquímicas muy similares. Esto pone de manifiesto la posibilidad de sustituir por agua un compuesto dañino para el ser humano, NMP, sin que ello suponga una pérdida en el rendimiento electroquímico de las baterías de ion-litio. De este modo, se demuestra que es posible preparar los electrodos empleando un método más económico y respetuoso con el medio ambiente.

- Se ha demostrado que existe una relación directa entre el área superficial externa de los xerogeles de carbono y las capacidades electroquímicas de las baterías de ion-litio. Esta relación es de gran utilidad ya que, hasta la fecha, no se habían establecido qué propiedades debían tener los xerogeles de carbono para conseguir incrementar la capacidad electroquímica de las baterías de ion-litio. Por tanto, el trabajo llevado a cabo durante la realización de esta Tesis Doctoral sirve como como punto de partida para posteriores estudios sobre el uso de los xerogeles de carbono como material de electrodo en baterías de ion-litio.

- En la presente Tesis Doctoral, además de evaluar la aplicabilidad de los xerogeles de carbono, se ha apostado por la utilización de los xerogeles orgánicos, ya que así se elimina la etapa de carbonización y se disminuye considerablemente el coste de producción. Los resultados del estudio sobre la utilización de los xerogeles orgánicos como materiales aislante térmico demuestran que estos materiales presentan un gran potencial en este campo de aplicación, ya que se han obtenido valores de conductividad térmica similares al del poliestireno expandido, uno de los materiales más utilizados como aislante térmico.

- Las publicaciones recogidas en el Capítulo 5 de la presente memoria demuestran la gran versatilidad de los xerogeles, ya sean en su estado orgánico o carbonizado, incrementando así el potencial comercial de estos materiales.

- Se ha demostrado que la síntesis de xerogeles de carbono a partir de taninos se puede llevar a cabo mediante calentamiento con microondas. Además, la sustitución del resorcinol por este compuesto natural reduce considerablemente los costes del producto.

- La síntesis de xerogeles de carbono a partir de mezcla precursoras tanino-formaldehído requiere el uso de surfactantes. La adición de dodecilsulfato de sodio ha permitido obtener materiales dopados con azufre, sin la necesidad de realizar ninguna etapa de dopaje complementaria.

GENERAL CONCLUSIONS

The publications compiled in the present report show the results derived from the study of the design of bespoke carbon xerogels by means of microwave-induced synthesis. The main conclusions of this study are presented below:

- An adequate adjustment of the parameters that control the microwave device depending on the amount of sample to be synthesized is essential for obtaining well-developed porous materials.
- The simultaneous variation of the concentrations of the main reagents in the precursor solutions allows greater control over the porous properties of the carbon xerogels than could be achieved if each concentration were modified separately
- The introduction of additives into the precursor solution allows the synthesis of carbon xerogels with different properties to those obtained by varying the concentration of the main reagents.
- Treatment of the results by statistical techniques allows the synthesis conditions that give rise to carbon xerogels with the properties required for a particular application to be determined.
- All the publications listed in Chapter 4 show that the microwave-induced synthesis of carbon xerogel allows materials with properties that span the full range of porosity to be obtained. In other words, it was possible to synthesize microporous,

micro-mesoporous and micro-macropores carbon xerogels with different degrees of porosity.

- Electrode materials for use in lithium ion batteries, made from the same carbon xerogel but using two different solvents, N-methyl pyrrolidine (NMP) and water, showed very similar electrochemical capacities. Therefore, the NMP, a compound harmful to humans, can be successfully replaced by water, without any detriment to the electrochemical performance of lithium ion batteries. This proves that it is possible to prepare electrodes using a method that is more economical and respectful of the environment.

- It has been shown that there is a direct relationship between the external surface area of the carbon xerogels and the electrochemical capacity of lithium ion batteries. This relationship is important, since to date, the properties that carbon xerogels must have in order to increase the electrochemical capacity of lithium ion batteries have not been established. Therefore, this work could serve as a starting point for further studies on the use of carbon xerogels as electrode material in lithium ion batteries.

- This PhD thesis not only evaluates the applicability of carbon xerogels, but also considers the use of organic xerogels. By employing organic xerogels the carbonization step is eliminated and the production cost is greatly decreased. The study of the use of organic xerogels as thermal insulation materials shows that these materials have great potential in this field of application, since thermal conductivity values similar to those of expanded polystyrene, the most widely used thermal insulating material, were obtained.

- The publications listed in Chapter 5 demonstrate the versatility of xerogels, whether in their organic or carbonaceous state, which enhances the commercial potential of these materials.

- It has been shown that the synthesis of carbon xerogels from tannins can be achieved by applying microwave heating. Furthermore, replacement of resorcinol by this natural compound significantly reduces the product costs.

- The synthesis of carbon xerogels from tannin-formaldehyde precursor solutions requires the use of surfactants. By adding sodium dodecyl sulfate, S-doped materials can be obtained without the need for carrying out any additional doping step.

CAPÍTULO 8

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ANEXO I

PROCEDIMIENTOS EXPERIMENTALES

La presente Tesis Doctoral versa sobre la síntesis de xerogeles de carbono inducida por microondas con el propósito de obtener materiales porosos con propiedades diseñadas a medida de los requisitos establecidos en diversos campos de aplicación. Para llevar a cabo el trabajo, se prepararon diversos materiales y se analizaron mediante técnicas de caracterización físico-química. Así mismo, para poder evaluar el potencial de los xerogeles orgánicos como material para aislamiento térmico se realizaron medidas de conductividad térmica, mientras que para evaluar el potencial de los xerogeles de carbono como material de electrodo para baterías de ion-litio se realizaron ensayos electroquímicos.

A.1 PREPARACIÓN DE LAS MEZCLAS PRECURSORAS

A.1.1 MECLAS RESORCINOL-FORMALDEHÍDO

La síntesis de los xerogeles orgánicos resorcinol-formaldehído (RF) comienza con la mezcla de los reactivos: resorcinol (R), formaldehído (F), agua e hidróxido de sodio. El resorcinol se mezcla con el agua mediante agitación magnética hasta su completa disolución. Una vez disuelto el resorcinol, se añade el formaldehído y se mide el pH inicial de la mezcla que generalmente se sitúa en un valor próximo a 3. Finalmente se ajusta el pH utilizando dos disoluciones de hidróxido de sodio con diferentes concentraciones: 0.1 y 5 molar. La concentración de cada uno de los reactivos depende de los valores fijados para cada una de las variables estudiadas en este trabajo: volumen de mezcla, pH, ratio molar entre el resorcinol y el formaldehído y grado de dilución. Este último parámetro se define como los moles totales de agua añadida directamente y el agua y metanol contenidos en la disolución de formaldehido, en función de los moles de resorcinol y formaldehido puro.

A.1.2 INTRODUCCIÓN DE ADITIVOS

En el caso de introducir aditivos en la mezcla precursora, el agua utilizada como disolvente se divide en dos partes iguales. Una de ellas se utiliza para disolver el resorcinol y la otra para disolver el aditivo. Una vez disueltos ambos compuestos se añade el formaldehído y se ajusta el pH mediante las disoluciones de hidróxido de sodio. El cálculo de las concentraciones de los reactivos principales se realiza siguiendo la metodología descrita en el apartado anterior, mientras que los distintos porcentajes de aditivo, fijados para llevar a cabo el estudio, se calculan en base a los gramos totales de la mezcla precursora.

A.1.3 SUSTITUCIÓN DEL RESORCINOL

La síntesis de los xerogeles orgánicos tanino-formaldehído (TF) comienza con la mezcla de los reactivos: tanino (T), formaldehído (F), agua, dodecilsulfato sódico (SDS) e hidróxido de sodio. Los taninos se disuelven en agua mediante agitación magnética. Una vez disueltos, se añade el surfactante SDS y el formaldehído. Finalmente se ajusta el pH utilizando hidróxido de sodio en polvo. Todos los xerogeles TF se sintetizaron a partir de 20 ml de mezcla precursora fijando el pH en un valor de 5.5. La concentración de los reactivos depende de los valores fijados para cada una de las variables estudiadas en este trabajo: ratio másico entre los taninos y el formaldehído y cantidad de surfactante.

A.2 SÍNTESIS DE XEROGELES ORGÁNICOS

Una vez obtenida una mezcla homogénea, esta se introduce en el horno microondas a 85ºC durante el tiempo fijado para llevar a cabo la etapa de reacción sol-gel y curado (2000, 6000 o 10000 segundos). Tras obtener el gel orgánico húmedo, éste se seca en mismo dispositivo microondas a 85ºC hasta conseguir una pérdida de masa entre el 50 y el 60%. La etapa de secado tiene una duración de 1-2 horas en función de las propiedades del xerogel sintetizado.

A.3 PROCESO DE CARBONIZACIÓN

Los xerogeles de carbono se obtienen a partir de la carbonización de los xerogeles orgánicos. Este proceso se lleva a cabo en un horno tubular horizontal a 700ºC durante 2 horas en atmósfera de nitrógeno. El caudal de gas utilizado se fijó en 150 ml/min y la velocidad de calentamiento en 50ºC/min.

A.4 TÉCNICAS DE CARACTERIZACIÓN FÍSICO-QUÍMICA

Los materiales obtenidos a lo largo del presente trabajo se caracterizaron con el objetivo de conocer sus propiedades porosas, químicas y estructurales. Previo a cada análisis, todas las muestras fueron desgasificadas a vacío (0.1 mbar) a una temperatura de 120ºC durante 12 horas. La cantidad de muestra utilizada en cada análisis no solo dependió del tipo de análisis sino también de la tipología de la muestra. A continuación se describen brevemente las distintas técnicas empleadas.

A.4.1 ADSORCIÓN FÍSICA DE GASES

La adsorción física de gases es una de las técnicas más empleadas en la caracterización de materiales porosos. Este análisis consiste en poner la muestra en contacto con un gas a temperatura constante, 77K en el caso de las isotermas de adsorción-desorción de nitrógeno, y determinar la cantidad de gas adsorbido (V_{ads}) por el material en un rango de presiones relativas (p/p^o) entre 0 y 0.99. Las curvas de adsorción obtenidas se clasifican en función de su forma siguiendo las normas establecidas por la IUPAC [*Sing, K. S. W. Pure and Applied Chemistry, 57, 603, 1985*]. La forma de la isoterma ofrece información rápida y visual sobre el tipo de material que se está caracterizando. Además, esta técnica permite determinar el área superficial específica, el volumen de poros y la distribución de tamaño de los poros.

Los datos obtenidos de las isotermas de adsorción-desorción de nitrógeno permiten conocer diferentes áreas superficiales. A lo largo de este trabajo se han tenido en cuenta dos de ellas: área superficial BET (S_{BET}) y área superficial externa (S_{EXT}). El área superficial BET se calcula mediante la aplicación del método BET [*Sing, K. S. W. Pure and Applied Chemistry, 57, 603, 1985*], mientras que el área externa se calcula empleando el método t-plot [*Lecloux, A.*

and J. P. Pirard. Journal of Colloid and Interface Science, 70, 265-281, 1979]. El volumen de poros determinado a partir de los datos de las isotermas obtenidas corresponde al volumen de microporos y se calcula mediante la ecuación de Dubinin-Radushkevich (DR), por lo que a este volumen se le conoce como volumen de Dubinin (V_{DUB}) [*Dubinin, M. M. Carbon, 27, 457-467, 1989*]. La distribución del tamaño de los poros, dentro del rango detectable mediante adsorción física de gases, se obtiene aplicando el método DFT (por sus siglas en inglés, Density Functional Theory). El equipo de adsorción utilizado es un analizador Tristar 3020 de la empresa Micromeritics.

Uno de las limitaciones que presenta esta técnica es que solo permite evaluar las propiedades porosas en el rango de los microporos y parte de la mesoporosidad. Por tanto, es necesaria la utilización de técnicas complementarias para poder determinar un rango más amplio, desde los microporos más estrechos hasta los macroporos de gran tamaño. La microporosidad que no es accesible mediante isotermas de adsorción-desorción de nitrógeno puede evaluarse utilizando CO_2 a una temperatura de 273K en lugar de nitrógeno a 77K. Este tipo de isotermas no se han empleado durante la realización de este trabajo y, por tanto, no se van a detallar los aspectos más relevantes de esta técnica. Por otro lado, las propiedades porosas de materiales con macroporos y mesoporos pueden determinarse mediante porosimetría de mercurio.

A.4.2 POROSIMETRIA DE MERCURIO

Una de las técnicas más utilizada para determinar las propiedades porosas de un material, clasificadas dentro del rango de la macroporosidad y una gran parte de la mesoporosidad, es la porosimetría de mercurio. Esta técnica consiste en introducir mercurio en un volumen conocido, en el cual se encuentra la muestra. Dado que el mercurio no es capaz de mojar la superficie del material de forma natural, a lo largo del análisis se aplica presión y se incrementa poco a poco, desde 0 a 228 MPa. A partir del volumen de mercurio introducido, se puede determinar el volumen de poros, la distribución del tamaño de los poros, la densidad aparente y el porcentaje de porosidad. Para poder determinar estas propiedades es necesario fijar los valores correspondientes a la tensión superficial del mercurio y el ángulo de contacto que se forma debido a esta tensión superficial. En este trabajo se ha utilizado un valor de tensión superficial de 485 mN/m y un ángulo de contacto de 130º.

La porosimetría de mercurio requiere llevar a cabo ciertas consideraciones matemáticas. La más generaliza es la utilización de la ecuación de Wahsburn [*Washburn, E. W. Physical Review, 17, 273-283, 1921*], que relaciona la presión ejercida con el tamaño de poro, considerando que los poros son cilíndricos y no están interconectados. Los datos obtenidos del análisis junto a la ecuación de Wahsburn, permiten obtener la relación entre el volumen que penetra en la estructura del material y el tamaño de los poros. A partir de estos datos se puede calcular tanto el volumen de mesoporos (V_{meso}) como de macroporos (V_{macro}). El volumen de mesoporos considera el volumen en un rango de tamaño de poros entre 5.5 nm (límite de detección del equipo) y 50 nm, y el volumen de macroporos se calcula para tamaños de poro superiores a 50 nm. El equipo empleado es el porosimetro de mercurio AutoPore IV de la empresa Micromeritics.

Cabe destacar que, debido a la presión ejercida por el mercurio y en función de la naturaleza del material, puede producirse la rotura de la muestra durante el análisis. Para comprobar que este fenómeno no ocurre en las muestras analizadas en el presente trabajo, se ha empleado otra técnica que permite conocer la densidad aparente y comparar los valores obtenidos con los obtenidos mediante porosimetría de mercurio.

A.4.3 ANÁLISIS DE DENSIDAD APARENTE

La densidad aparente de los materiales se determina mediante el uso del equipo Geopyc 1360 de la empresa Micromeritics. La técnica consiste en medir el desplazamiento de volumen que produce la muestra cuando se introduce en una cámara que contiene un fluido formado por pequeñas esferas rígidas y de alto grado de fluencia. Conocida la masa de la muestra, es posible calcular la densidad aparente dividiendo el valor de la masa de material introducido por el volumen obtenido mediante esta técnica. Si además, se conoce la densidad real del de la muestra, se puede determinar también el porcentaje de porosidad y volumen específico de poros.

A.4.4 PICNOMETRÍA DE HELIO

El picnómetro de helio se utiliza para determinar la densidad real de un sólido. Este análisis consiste en poner la muestra en un recipiente previamente calibrado con helio. Mediante la calibración se determina la relación entre el volumen que ocupa el helio y la presión a la que está sometido. De modo que cuando se introduce el material, por diferencia, se puede determinar el volumen ocupado por la muestra. Por tanto, conocida la masa de la muestra, es posible calcular la densidad, dividiendo el valor de la masa de material introducido por el volumen obtenido mediante el uso del picnómetro. El equipo utilizado es un picnómetro de helio AccuPyc II 1340 de la empresa Micromeritics.

A.4.5 ANÁLISIS ELEMENTAL

El análisis elemental es una técnica instrumental utilizada para obtener el contenido total (% en peso) de carbono (C), hidrógeno (H), nitrógeno (N) y azufre (S). La técnica de análisis se basa en la combustión completa e instantánea de una muestra mediante la aplicación de un tratamiento térmico a alta temperatura, aproximadamente 1200ºC, en una atmósfera de oxígeno puro. Los productos de la combustión (CO_2, H_2O, N_2 y SO_2) se transportan mediante el gas portador (mezcla de helio y argón) hasta un tubo de reducción. Tras la reducción, el N_2 pasa directamente al detector mientras que el resto de los elementos quedan retenidos para, posteriormente, ser analizados uno a uno. El equipo utilizado para analizar las muestras de este trabajo fue un microanalizador elemental Vario Cube de la empresa Elementar.

A.4.6 ESPECTROSCOPIA INFRARROJA

La espectroscopia infrarroja permite determinar la naturaleza de la muestra mediante la detección de los diferentes grupos funcionales. Esta técnica consiste en emitir una fuente de radiación infrarroja sobre la muestra a analizar. Parte de esta radiación es adsorbida por la muestra, mientras que la otra parte, la radiación transmitida, es la que registra el equipo y la transforma electrónicamente en un espectro. Cada banda de absorción observable en el espectro corresponde a una vibración determinada de alguno de los enlaces que forman la estructura molecular del material y, por tanto, pueden identificarse sus grupos funcionales.

Los espectros presentados en este trabajo se han obtenido mediante espectroscopia infrarroja con transformada de Fourier (FTIR) en un equipo Affinity-1S de la empresa Shimadzu. Para ello, la muestra se molió y se prensó junto a bromuro de potasio en polvo. Con esta mezcla se forma un pellet que contiene un 1% en peso de la muestra a analizar. En cada análisis se llevaron a cabo 20 barridos a máxima resolución (4 cm^{-1}) en un rango de longitudes de onda entre 4000 y 400 cm^{-1}.

A.4.7 TERMOGRAVIMETRÍA

Los análisis termogravimétricos permiten medir los cambios de masa que ocurren en un material cuando se producen en él transformaciones químicas o físicas. La técnica consiste en someter el material a una o varias temperaturas durante un tiempo determinado en atmósfera gaseosa. De este modo se puede determinar la temperatura de descomposición del material, su estabilidad térmica, su reactividad frente al gas utilizado, su resistencia a la oxidación, etc. En este trabajo, los análisis termogravimétricos se llevaron a cabo en un analizador térmico SDT-Q600 de la empresa TA Instruments. Las pérdidas de peso se determinaron en una atmósfera de nitrógeno en un intervalo de temperatura entre 25 y 1000ºC. El caudal de gas utilizado se fijó en 20 ml/min y la velocidad de calentamiento en 10ºC/min.

A.4.8 MICROSCOPIA ELECTRÓNICA DE BARRIDO

El microscopio electrónico de barrido (SEM) es un instrumento capaz de ofrecer información sobre la superficie de la muestra. Su funcionamiento se basa en barrer un haz de electrones sobre la muestra. Debido a que la muestra es opaca a los electrones, cuando estos inciden sobre la superficie se generan dos tipos de electrones: electrones secundarios de baja energía ($E<50$ eV) y electrones retrodispersados. Los electrones secundarios de baja energía resultan de la emisión por parte de los átomos de la muestra más cercanos a la superficie, mientras que electrones retrodispersados son los electrones del propio haz incidente que al interaccionan con los átomos de la muestra rebotan, modificándose su trayectoria. Las señales producidas por los electrones son captadas por un detector que transforma la información en una imagen, de alta resolución, de la superficie de la muestra. Por lo que se obtienen datos directos acerca de la estructura morfológica de la muestra. En este trabajo, la morfología de la estructura de los materiales se examinó utilizando un microscopio electrónico de barrido Quanta-FEG 650 de la empresa FEI. Para ello, la muestra se fijó a una chincheta de aluminio utilizando cinta adhesiva conductora de doble cara. Los análisis se llevaron a cabo con un detector de electrones secundarios Everhart-Thornley y un voltaje de aceleración de 25 kV.

A.5 ENSAYOS DE CONDUCTIVIDAD TÉRMICA

La conductividad térmica de los materiales se determina mediante el uso de un analizador TPS 2200 de la empresa HotDisk. Este equipo se basa en el uso de un sensor plano transitoriamente climatizado que se coloca entre dos alícuotas de muestra de igual volumen. El sensor está compuesto por una espiral doble de níquel, intercalada entre dos capas de Kapton, que es un material aislante. El análisis consiste en hacer pasar una corriente eléctrica a través de una de las espirales de níquel provocando el calentamiento del sensor. Si la muestra a analizar es conductora, este calor se transmitirá a través de la estructura del material, detectándose en la otra espiral de níquel. Por lo que el equipo registra la resistencia ofrecida por el material a la transmisión del calor que emite el sensor.

A.6 ENSAYOS ELECTROQUÍMICOS

Para poder llevar a cabo los ensayos electroquímicos es necesario preparar previamente los electrodos y montar las celdas electroquímicas. Estos dispositivos son los que se van a caracterizar mediante ciclos de carga-descarga galvanostática.

A.6.1 MONTAJE DE LAS CELDAS ELECTROQUÍMICAS

Los ensayos electroquímicos se realizan utilizando celdas electroquímicas CR2032, comúnmente llamadas de tipo *botón*. Estas celdas están compuestas por un disco metálico de litio que actúa como ánodo y un electrodo carbonoso que actúa como cátodo. Ambos electrodos están separados por una membrana polimérica de polietileno mojada por 80 μl de una solución electrolito compuesta por 1M de $LiPF_6$ disuelto en una mezcla de carbonatos. El montaje de la celda se lleva a cabo en el interior de una caja seca para evitar la entrada de aire. El electrodo carbonoso se prepara mezclando el xerogel de carbono (material activo) con un disolvente y un aglutinante, de modo que el electrodo contenga un 92% (en peso) de material activo. La mezcla resultante se agita hasta obtener una tinta homogénea. Esta tinta se deposita mediante aerografía sobre discos de acero inoxidable de 15.5 mm de diámetro. Tras la deposición, el electrodo se seca quedando listo para su utilización en la celda electroquímica.

A.6.2 CICLOS DE CARGA-DESCARGA GALVANOSTÁTICA

La cronopotenciometría galvanostática, mediante la cual se obtienen los ciclos de carga-descarga, es una técnica electroquímica basada en la medición del potencial de un sistema en función del tiempo, cuando se aplica una intensidad de corriente constante. En este trabajo, las curvas de carga-descarga se obtuvieron fijando un índice de C5, es decir, se usó la intensidad de corriente necesaria para cargar la celda en 5 horas, teniendo en cuenta la capacidad teórica del grafito: 372 mAh/g. Los análisis se llevaron a cabo fijando una ventana de potencial entre 0.005 y 1.5 V (vs. Li^+/Li) usando un potenciostato Biologic VMP3 multicanal, situado dentro de una cámara aclimatada a 25ºC.

ANEXO II

OTRAS CONTRIBUCIONES

Artículos en revistas científicas

A continuación se listan una serie de publicaciones que, aunque guardan una estrecha relación con el tema principal de esta memoria, no se han incluido en los capítulos principales, puesto que el proceso experimental mostrado en dichas publicaciones ha sido abordado de forma paralela a la realización del presente trabajo.

- Bermúdez JM, Beneroso D, Rey-Raap N, Arenillas A, Menéndez JA. Energy consumption estimation in the scaling-up of microwave heating processes. Chemical Engineering and Processing: Process Intensification, 2015, 95, 1-8.

- Alonso-Buenaposada ID, Rey-Raap N, Calvo EG, Menéndez JA, Arenillas A. Effect of methanol content in commercial formaldehyde solutions on the porosity of RF carbon xerogels. Journal of Non-Crystalline Solids, 2015, 426, 13-8.

- Rey-Raap N, Calvo EG, Bermúdez JM, Cameán I, García AB, Menéndez JA, et al. An electrical conductivity translator for carbons. Measurement, 2014, 56, 215-8.

- Calvo EG, Rey-Raap N, Arenillas A, Menéndez JA. The effect of the carbon surface chemistry and electrolyte pH on the energy storage of supercapacitors. RSC Advances, 2014, 4, 32398-32404.
- Moreno ÁH, Arenillas A, Calvo EG, Rey-Raap N, Bermúdez JM, Menéndez JA. Xerogeles de carbono competitivos diseñados para aplicaciones específicas. Avances en Ciencia e Ingeniería, 2013, 4, 109-120.
- Rey-Raap N, Calvo EG, Arenillas A, Menéndez JA. High surface area carbon xerogels: microwave vs. conventional activation with KOH. Chemistry Today, 2012, 30, 30-2.

Participación en congresos

Los resultados obtenidos a lo largo del desarrollo de la presente Tesis Doctoral han dado lugar a una serie de trabajos presentados como comunicaciones orales o en panel en los siguientes congresos nacionales e internacionales:

Comunicaciones orales

- N. Rey-Raap, A. Szczurek, V. Fierro, J. A. Menéndez, A. Arenillas, A. Celzard. Sustitución del resorcinol por taninos: eliminando barreras en la producción de xerogeles de carbono. XIII Reunión del Grupo Español del Carbón, **GEC 2015**, Alicante, España, octubre 2015.
- Ana Arenillas; Ángel H. Moreno; Esther G. Calvo; Natalia Rey-Raap; J. Ángel Menéndez. Microwave-induced synthesis and curing of RF-polymers. 14th International Conference on Microwave and High Frequency Heating, **AMPERE 2013**, Nottingham, Reino Unido, septiembre 2013.

- Natalia Rey-Raap; J. Ángel Menéndez; Ana Arenillas; Peter Hall. Xerogeles de carbono con propiedades a medida para su utilización en sistemas electroquímicos. V Congreso Nacional de Pilas de Combustible, **CONAPPICE 2012**, Madrid, España, noviembre 2012.

Comunicaciones en panel

- Natalia Rey-Raap, Marie-Laure C. Piedboeuf, Ana Arenillas, J. Angel Menéndez, Alexandre F. Léonard, Nathalie Job. Comparison of organic and aqueous inks in the preparation of Li-ion battery anodes based on carbon xerogels with different meso- or macropore sizes. European Congress and Exhibition on Advanced Materials and Processes, **EUROMAT 2015**, Varsovia, Polonia, septiembre 2015.

- Natalia Rey-Raap; Ana Arenillas; J. Ángel Menéndez. Microwave-assisted synthesizes of tailored porous carbon xerogels by the combination of chemical variables. 10th International Symposium on the Characterization of Porous Solids, **COPS-X 2014**, Granada, España, mayo 2014.

- Natalia Rey-Raap; Ana Arenillas; J. Ángel Menéndez. Diseño de propiedades de xerogeles de carbono controlando las variables del proceso. XII Reunión del Grupo Español del Carbón, **GEC 2013**, Madrid, España, noviembre 2013.

- Esther G. Calvo; Natalia Rey-Raap; José M. Bermúdez; Ana Arenillas; Ángel H. Moreno. How the carbon surface and electrolyte pH affect to the capacity of the EDLC. International Carbon Conference, **CARBON 2013**, Rio de Janeiro, Brasil, julio 2013.

- Ana Arenillas; Esther G. Calvo; Natalia Rey-Raap; José M. Bermúdez; J. Ángel Menéndez. Measuring electrical conductivity on carbons. International Carbon Conference, **CARBON 2013**, Rio de Janeiro, Brasil, julio 2013.