Deep Eutectic Assisted Synthesis of Carbon Adsorbents Highly Suitable for Low-Pressure Separation of CO₂/CH₄ Gas Mixtures

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Broader context

Carbon dioxide (56%) and methane (18%) are the two main greenhouse gases emitted today. These gases are produced in many current industrial processes as well as those in prospective areas such as the purification of hydrogen produced from biomass. This is why there is an urgent demand to develop efficient strategies for the separation/storage of CO₂ and CH₄ via processes with minimal environmental impact and affordable costs material. Carbonaceous solid sorbents exhibiting enhanced sorbent capability and recyclability may offer an interesting alternative in economical terms. Thus, it is the core competence of material chemists to develop sustainable synthetic strategies capable to produce carbons with enhanced performance. Within this context, the use of ionic liquids and deep eutectic solvents is gaining increased interest because of the particular features demonstrated by these solvents in number of synthetic processes that allow to minimize the number of reagents used in a particular synthesis while provide an excellent control of both the compositional and structural properties of the resulting materials. Herein, the use of a DES-assisted synthesis provided carbons with an extraordinary capability for low-pressure CO₂ separation from both N₂ and CH₄ based on the molecular sieve effect played by their narrow microporosity.

Abstract

Ionic liquids and deep eutectic solvents (a new class of ionic liquids obtained by complexation of quaternary ammonium salts with hydrogen bond donors such as acids, amines, and alcohols among others) have been recently used as solvents and even as precursors in the synthesis of carbonaceous materials. Particularly interesting has been the use of long-alkyl-chain derivatives of ionic liquids that, playing the role of structure directing agents, were capable to design the mesopore structure of the resulting carbons. Meanwhile, deep eutectic solvents proved efficacy tailoring the structure comprised between large mesopores and small macropores but the control over the smaller ones (e.g. small mesopores and micropores) is yet a challenge as compared to ILs. Herein, we have used deep eutectic solvents composed of resorcinol, 4-hexylresorcinol and tetraethylammonium bromide for the synthesis of carbon monoliths with a tailor-made narrow microporosity. Behaving as molecular sieves, these carbons exhibited not only good capacities for CO₂ adsorption (up to 3 mmol/g) but also an outstanding - especially at low pressures - CO₂/CH₄ selectivity.

Introduction

Ionic liquids (ILs)¹ and deep eutectic solvents (DESs, a new class of IL obtained by complexation of quaternary ammonium salts with hydrogen bond donors such as acids, amines, and alcohols among others)² have been recently used as solvents³ and even as precursors⁴ in the synthesis of carbonaceous materials. For instance, nitrogen-doped carbons with nitrogen contents of up to 18 at. % have been obtained by the direct carbonization of some particular ILs of choice (e.g. nitrogen-rich ILs such as, for example, 1-ethyl-3-methylimidazolium – EMIm – or 3-methyl-1-butylpyridine – 3-MPB combined with dicyanamide – dca – or other anions containing nitrile groups – $[\text{C}(\text{CN})_3]^-$).^{5, 6, 7} Porous carbons (either non-doped or nitrogen-doped) with high surface areas can also be obtained using ILs as carbonaceous precursors and with or without the aid of traditional structure directing agents (SDAs).^{8, 9, 10, 11, 12, 13, 14} Particularly interesting is the use of ILs composed of a long-alkyl-chain derivative that, playing the role of a regular SDA, are capable to tailor the pore surface area of the resulting carbon.¹⁵

Meanwhile, DESs have proven efficacy for the preparation of hierarchical porous carbons (both non-doped and nitrogen-doped) via a spinodal-like decomposition process in which DESs components act not only as precursors but also as SDAs.^{9g} The use of DESs is attractive because, as compared to ILs, they are cheap and easy to prepare from a wide range of compounds such as regular carbonaceous precursors (e.g. resorcinol). The use of resorcinol is by no means trivial because it provides high carbonization yields (up to ca. 85 wt%). This feature besides the capability of recovering of the second component of DES that is not involved in carbon formation (e.g. choline chloride) make synthetic processes based on DESs especially attractive in terms of efficiency and sustainability. Nonetheless, it is worth noting that the success of DESs as SDAs in the synthesis of bimodal porous materials is just partial and while excellent control has been achieved to tailor the pores comprised within the 10 nm to several microns (e.g. 5-10 μm) range, control over the smaller ones (e.g. small mesopores and micropores) is yet a challenge as compared to ILs.¹⁵

Herein, we describe the use of DESs composed of resorcinol, 4-hexylresorcinol and tetraethylammonium bromide in the synthesis of carbon monoliths exhibiting a hierarchical porous structure. DESs played a multiple role in the synthetic process; the liquid medium ensuring reagents homogenization, the structure-directing agent responsible of the achievement of the hierarchical structure, and the precursor of the solid sorbent obtained after carbonization. DESs formation was studied by ^1H NMR spectroscopy and differential scanning calorimetry (DSC). Carbons were obtained by polycondensation of resorcinol and 4-hexylresorcinol with formaldehyde and subsequent carbonization. ^{13}C NMR and FTIR spectroscopies provided an estimation of the degree of polycondensation. The hierarchical

structure of carbons was studied by scanning electron microscopy (SEM). Whether the use of DESs composed of a long-alkyl-chain derivative such as 4-hexylresorcinol was capable to provide any modification on the textural properties of the resulting carbons was studied by nitrogen (N_2) and carbon dioxide (CO_2) adsorption isotherms. The adsorption equilibrium isotherms revealed a significant CO_2 sorption capability. Measurements at 273, 298 and 323 K provided the isosteric heats of adsorption for CO_2 . The selective adsorption of CO_2 not only versus N_2 but also versus CH_4 could make these carbons good candidates for separation purposes.

Experimental

Preparation of Deep Eutectic Solvents (DESs): DESs were obtained upon thermal treatment (at 90 °C overnight) of the physical mixture of the individual components: resorcinol (R), 4-hexylresorcinol (H) and tetraethylammonium bromide (T) in different molar ratios (1.00:1:1, 1.25:1:1, 1.50:1:1, 1.75:1:1 and 2.00:2:1 for DES100, DES125, DES150, DES175 and DES200, respectively).

Preparation of Carbons:

DES100, DES125, DES150, DES175 and DES200 were mixed with aqueous solutions of formaldehyde (37 wt %) for a (R+H):F molar ratio of 2.24. Polycondensations were catalysed by addition of three different aqueous solutions of Na_2CO_3 (140, 180 or 220 mg/mL) so that up to fifteen different samples were obtained. Nonetheless, it is worth mentioning that only eight of them exhibited a homogeneous structure (see below). Tables 1 and S1 provide details of the experimental conditions used for preparation of homogeneous and non-homogeneous samples, respectively. The DESs content in dilution ranged from 55 to 60 wt %. After stirring for 5 min, the resulting mixtures were aged for two hours at room temperature and, afterwards, thermally treated (first 6 h at 60 °C and then, 7 days at 90 °C) in closed containers to avoid evaporation. The resulting gels were washed three times in water (35 mL) for tetraethylammonium bromide recovery. The washed gels were thermally treated under N_2 atmosphere to 210 °C for 4 h and then, to 800 °C for another 4 hours (the heating ramp was 1.0 °C/min).

Samples characterization: DSC traces were obtained using a TA Instruments Model DSC Q-100 system. The samples were run under nitrogen atmosphere in an aluminium pan in a sealed furnace, stabilized for 5 min at 20 °C, and then cooled to -90 °C before heating at a rate of 5 °C/min. 1H NMR spectra were recorded in a Bruker spectrometer DRX-500. DESs were placed in capillary tubes, using deuterated chloroform ($CDCl_3$) as an external reference (the deuterium signal was used for locking and shimming the sample). FTIR spectra were recorded in a

BrukerModel IFS60v. Solid-state ^{13}C -CPMAS-NMR spectra recorded in a Bruker AV-400-WB spectrometer, using a standard cross-polarization pulse sequence. The morphology of the resulting carbons was studied by scanning electron microscopy (SEM, using a FE-SEM Nova Model NanoSEM 230 system). Mercury porosimetry analyses were carried out in a Micromeritics Autopore II 9220.

Nitrogen adsorption/desorption isotherms at $-196\text{ }^{\circ}\text{C}$ were carried out in an ASAP 2020 from Micromeritics on samples previously outgassed under dynamic vacuum (ca. 10^{-5} torr) at 100°C for 6 hours. The Brunauer-Emmett-Teller (BET) theory was used to calculate the specific surface areas. Gas adsorption/desorption isotherms of selected gases (N_2 , CO_2 and CH_4) were performed at various temperatures in a Micromeritics Tristar 3020 instrument in the pressure range of 0.1-900 torr. The analyzer is equipped with a pressure transducer of capacity 1000 mmHg (accuracy within 0.15 % of reading). The outgassing conditions before the adsorption measurements were as indicated above. Strict analysis conditions were programmed during the gas adsorption measurements to assure equilibrium data in all gases, while each isotherm was performed by duplicate to guarantee the accuracy of the experiments (error was below 0.1%) and to obtain reproducible data. During the analysis, the adsorption temperature was maintained using a circulating-oil bath at a constant-temperature. Gases were all supplied by Air Products with an ultrahigh purity (i.e., 99.9992%). The isosteric heat of adsorption were determined from the set of equilibrium isotherms using the Clausius–Clapeyron equation. The Henry's constants were obtained by fitting the adsorption data to a Virial-type expression:¹⁶

$$\ln(P/V) = A_0 + A_1V + A_2V^2$$

where P is the pressure, V is the adsorbed amount, T is the temperature, and A_i are the Virial coefficients required to adequately describe the isotherms. From these results, the Henry's constant (k_H) can be calculated as:

$$k_H = \exp(-A_0)$$

The Henry's Law selectivity for gas component i over j at a given temperature was calculated using the equation $S_{ij} = K_{Hi}/K_{Hj}$. The selectivity was also measured under equilibrium conditions at 25°C and 1 atm.

IAST was used to predict binary mixture adsorption from the experimental pure-gas isotherms.¹⁷ The integration required by IAST was achieved by fitting the single-component gas isotherms to the Jensen equation.¹⁸ Typical conditions of flue gases in postcombustion processes (e.g. CO_2/N_2 mixtures of 15/85) and natural gas fields (e.g. CO_2/CH_4 mixtures of 15/85 and 30/70) were used in the binary mixtures predictions. Equimolecular mixtures (e.g. 50/50) of both CO_2/N_2 and CO_2/CH_4 were also analyzed

Results and Discussion

DES125, DES150 and DES200 were all based on ternary mixtures of resorcinol, 4-hexylresorcinol and tetraethylammonium bromide in three different molar ratios (1.25:1:1, 1.50:1:1 and 2.00:2:1, respectively). DESs were obtained by thermally treating (at 90 °C) the physical mixture of the components. Neither T_m nor T_c were displayed in the DSC trace of RHT221-DES (Figure 1), a common feature observed for non-easily crystallizable ILs and DESs. The viscosity of RHT221-DES was higher than that of RHT111-DES, as correspond to DESs having higher glass transition temperatures (T_g).¹⁹ The formation of RHT complexes was also confirmed by the upfield chemical shift of the signals ascribed to resorcinol, 4-hexylresorcinol and tetraethylammonium bromide in the ^1H NMR spectra of the mixtures (see Figure S1 and Table 2).²⁰

Polycondensation of DES125, DES150 and DES200 proceeded following a synthetic mechanism that was analogue to that described recently for hierarchical carbons obtained from resorcinol-based DESs.^{9g} Briefly, the resorcinol and 4-hexylresorcinol that form part of the DES were co-condensed by addition of an aqueous solution of formaldehyde and Na_2CO_3 . It is worth noting that most of typical DES features are preserved upon dilution to 55-60 wt % (Table 2) but the availability of some resorcinol and 4-hexylresorcinol molecules to initiate polycondensation is also favoured.^{4g} It is generally assumed that the process evolves by the formation of a rich-polymer phase (via polycondensation) that is accompanied by the segregation of the non-condensed matter (creating a poor-polymer phase or depleted-polymer phase), the elimination of which (either before carbonization by washing or during carbonization by thermal decomposition) results in the formation of the bicontinuous porous carbon structure after thermal treatment.²¹ This is the typical mechanism of spinodal-like decomposition processes. In this work, we found that the achievement of homogeneous bicontinuous structures depended on both the molar ratio between resorcinol and 4-hexylresorcinol and the concentration of catalyst used for the polycondensation. Thus, our next experiments focused only on those samples that, after carbonization, exhibited homogeneous bicontinuous structures. Figure 2 shows the detailed morphology of the selected carbons. It is obvious that non-homogenous structures lacked of interest because of the impossibility to synthesize them in a reproducible fashion (Figures S2 and S3). In those samples that exhibited a bicontinuous structure, the occurrence of tetraethylammonium bromide segregation during polycondensation was corroborated by washing (up to three times) the resulting gels with abundant water (35 mL each) for clearance of non-condensed reagents. The weight of the residue corresponded well with the theoretical amount of tetraethylammonium bromide that was forming part of DES before polycondensation.

The polycondensation of 4-hexylresorcinol with resorcinol merited investigation. This was by no means a trivial issue considering that, in 4-hexylresorcinol, one of the positions of the aromatic ring that is favoured for nucleophilic substitution is blocked by the presence of the hexyl group. Actually, polycondensation of DESs without resorcinol (e.g. just composed of 4-hexylresorcinol and tetraethylammonium bromide) never became a gel because the polycondensation of the two nucleophilic positions that remain available resulted in the formation of linear chains rather than crosslinked networks. It is therefore that cross-linked networks could only be achieved upon an efficient co-condensation between resorcinol and 4-hexylresorcinol. The lack of 4-hexylresorcinol in the waters used for washing the gels (see above) was a first indication about the occurrence of co-condensation between resorcinol and 4-hexylresorcinol. To further assess such occurrence, FTIR and solid-state ^{13}C -NMR spectroscopy were performed in two representative gels that resulted from polycondensation of RHT-DES125 and RHT-DES200 with formaldehyde using 220 mg/mL and 180 mg/mL Na_2CO_3 as catalyst, respectively. In the FTIR spectra, the bands at 1604 cm^{-1} came from aromatic ring stretches, whereas medium to weak absorption bands at 1239 and 1088 cm^{-1} corresponded to the C-O stretch and deformation of benzyl ether groups (methylene ether groups), respectively (Figure 3). The broad band at 3388 cm^{-1} included the aromatic OH groups of resorcinol and 4-hexylresorcinol while the bands at 2925 and 1465 cm^{-1} were assigned to methylene groups (associated with the CH_2 stretching and bending vibrations).²² Methylene ether and methylene groups are typically indicative of the number of bridges established upon polycondensation. This is not the situation in our case because of the contribution of methylene groups of 4-hexylresorcinol to the overall intensity of the bands at 2925 and 1465 cm^{-1} . Actually, more intense signals were provided by polycondensation between resorcinol and 4-hexylresorcinol than between resorcinol itself whereas the opposite situation would be the expected one if only methylene bridges were contributing to these signals (i.e. it is worth noting that the hexyl moiety of 4-hexylresorcinol is blocking one of the two positions of the aromatic ring in which condensation is favoured so that the neat methylene bridges must be lower than for the self-condensation of resorcinol).

These two gels were also studied by solid-state ^{13}C -NMR spectroscopy. In terms of polycondensation, the most interesting signals were those centred at about 53, 31 and 23 ppm, which are typically assigned to methylene ether (e.g., $\text{CH}_2\text{-O-CH}_2$ at 53 ppm) and methylene (e.g., CH_2 at 31 and 23 ppm) bridges (Figure 4). Different types of CH_2 bridges can be distinguished depending on the chemical shift.²³ Thus, the most common 4-4' methylene bridge has been typically assigned to signals at 30-38 ppm, and the less common 2-4' methylene bridges to signals at 22-30 ppm. The relative intensity of these signals was higher

(ca. 2.5-fold) than that of samples obtained upon self-condensation of resorcinol but it is worth noting that, in the current case, not only methylene bridges but also hexyl groups provided by 4-hexylresorcinol appear within this range of chemical shifts. Actually, signals at 14 and 7 ppm also provided evidence of the presence of hexyl groups. Thus, the clear assessment of the degree of polycondensation from the overall intensity of these signals was difficult to establish. More useful were the signals at 122 and 131 ppm, the former corresponding to aromatic carbons bearing CH₂ groups in all *ortho* positions relative to the two phenolic OHs and the latter to non-substituted aromatic carbons in *meta* positions. The relative intensity of these signals was similar to that of samples obtained upon self-condensation of resorcinol so it seems that all the available nucleophilic positions of both precursors participated in the polycondensation and this was only impeded in the position occupied by hexyl groups. The good extension in which resorcinol and 4-hexylresorcinol co-condensed was corroborated by the excellent carbon conversions (e.g. 75-85 %, see Table 1) that were obtained after carbonization of washed gels at 800°C in N₂ atmosphere, in range to those found for self-condensation of resorcinol.

The textural properties of the set of eight different carbons that exhibited a homogeneous structure were first explored by nitrogen adsorption/desorption isotherms at 77 K. The N₂ uptake was negligible for every of the synthesized carbon (Table 3). Meanwhile, the CO₂ adsorption isotherms at 273 K revealed a remarkable CO₂ adsorption capacity with uptakes of up to 3.0 mmol/g at 760 mmHg (Figure 5, Table 3). The application of the Dubini-Raduskevich and Stoeckli-Ballerini equations to the CO₂ adsorption isotherms allowed the calculation of the micropore volume (W₀) and the average micropore size (L), respectively (Table 3). The latter provided an average micropore diameter for every sample of ca. 0.6 nm. The restricted diffusion of N₂ at 77 K through micropores of such a small dimensions explains the negligible N₂ uptake described above.²⁴ Interestingly, CO₂ adsorption/desorption isotherms were fully reversible – after sample refreshing under vacuum at 50 °C for 4h – with no significant changes in the uptake after subsequent cycles, which indicates that the narrow micropores of these carbons are interconnected forming a molecular sieve network.

It is generally assumed that the CO₂-uptake capacity is dictated by many factors such as surface area, pore functionality and pore size, among the principal ones. Considering the non-doped nature of our carbons, the selective adsorption of CO₂ adsorption was ascribed to the small pore dimensions of these carbons that, behaving as gas molecular sieves, anticipated the preferred adsorption of gases having small kinetic diameters (e.g. 0.33 nm for CO₂) over those having large ones (e.g. 0.36 nm for N₂ or 0.38 nm for CH₄). The potential performance of these carbons for gas separation purposes was evaluated for two representative samples (C125-220

and C200-180). In particular, we investigated the adsorption capacity of strategic gases (e.g. N₂, CO₂ and CH₄) at 900 mmHg and at temperatures near ambient conditions (Figure 6). Thus, both C125-220 and C200-180 exhibited an adsorption capacity for CO₂ of 2.2 mmol/g at 298 K that, in both samples, decreased to 0.39 mmol/g for N₂ (Table 4). For CH₄ and at 298 K, C125-220 and C200-180 exhibited adsorption capacities of 0.20 and 0.55 mmol/g, respectively (Table 4). These numbers suggested a more pronounced size exclusion effect in the former than in the latter sample, despite significant differences between them were not previously revealed by the textural characterization based on N₂ adsorption at 77K and CO₂ adsorption at 273K.

A better understanding of the adsorption properties can be provided by the calculation of the isosteric heats of adsorption (Q_{st}). In our case, Q_{st} was calculated by applying the Clausius–Clapeyron equation to the adsorption isotherms obtained at 273, 298 and 323 K (Figure 7). C125-220 and C200-180 exhibited Q_{st} values for CO₂ of around 35 and 41 kJ/mol at zero coverage, respectively, that decreased monotonically to ca. 30 kJ/mol along with the adsorbed CO₂ (e.g. for 20 cm³/g and above) (Figure S4 and Table 4). The moderate Q_{st} values found for these carbons were ascribed to the non-specific interactions that govern gas affinity to non-functionalized carbons²⁵ and confirmed the above-mentioned low-energy requirements for regeneration and reutilization in subsequent cycles.²⁶

The calculation of the Q_{st} values of both C125-220 and C200-180 for CH₄ was not possible because of the inverse adsorption dependence with the temperature observed for this gas - that is, the increase in the adsorption capacity upon the rise of temperature - .This is due to the prevalence of kinetic vs thermodynamic effects, and indicated that the decrease of the gas-solid affinity was compensated by the improved diffusion of gases through the narrow micropores of both C125-220 and C200-180. This pronounced molecular sieving effect explained the selective adsorption of gases with small (e.g. CO₂) versus large (e.g. N₂ or CH₄) kinetic diameters.

It is well known that high CO₂-uptake capacity at 1 bar does not necessarily lead to a large selectivity for CO₂ over other components of a gas mixture, particularly for low-pressure postcombustion applications where the flue gas usually contains less than 15% in CO₂. For this reason, the adsorption selectivity was evaluated in the Henry law regime that accounts for the low partial pressure region, representative of flue-gas streams characteristic of post-combustion and natural gas fields. Besides the screening of the gas adsorption selectivity at low partial pressures, the Henry's law constant, k_H , can also provide a preliminary assessment of gas-solid interactions because it is related to the gas-adsorbent affinity at infinite dilution.²⁷ For instance, C200-180 exhibited k_H values for the three gases studied in this work that

increased in the order $\text{CO}_2 > \text{CH}_4 > \text{N}_2$. This was not the tendency exhibited by C125-220 in which the smallest k_H value found for methane again revealed a particularly pronounced size exclusion effect most likely due to the particularly narrow pore apertures of this carbon (see discussion above). The CO_2/N_2 selectivities calculated for both carbons from their respective k_H values were in the range of or slightly above those previously reported for typical adsorbents (non-doped carbons and carbon monoliths, zeolites or MOFs, among others).²⁸ More remarkable was the CO_2/CH_4 selectivity that, in the particular case of C125-220, reached unprecedented values as compared to most of sorbents reported to date (Table 5).²⁹

We further investigated the selectivity of these carbons by the application of the Ideal Adsorbed Solution Theory (IAST) to the experimental adsorption isotherms of CO_2 , CH_4 and N_2 obtained for the single components. IAST has been used for the accurate prediction of multicomponent adsorption mixtures on a wide range of porous materials having homogenous energetic adsorption sites.^{29a, 30} In our case, we applied IAST to CO_2/N_2 mixtures representative of synthetic flue gases in postcombustion processes (e.g. with a v/v gas composition of 15/85) and to CO_2/CH_4 mixtures characteristic of natural gas upgrading processes (e.g. with v/v gas compositions of 15/85 and 30/70). As a general trend, the selectivities calculated by the IAST equation for binary mixtures (Table 6) were slightly below those obtained from the single component gas data, but increased along with the mole fraction of CO_2 in the mixtures. The IAST selectivities exhibited a similar trend than those calculated from Henry's constants. Moreover, CO_2/N_2 selectivities predicted from IAST were within the range of those reported for activated carbons and some MOFs, while more remarkable selectivities were found for CO_2/CH_4 mixtures.³¹ Nonetheless, it is worth noting that IAST selectivities were always lower than those obtained from Henry's law, which revealed our carbons as particularly suitable for CO_2/CH_4 separation processes carried out at low pressures.

Conclusions

We have described the synthesis of DESs composed of resorcinol and 4-hexylresorcinol (as hydrogen donors) and tetraethyl ammonium chloride (as hydrogen acceptor) that played a capital role in the preparation of hierarchical porous (bimodal, with micro- and macropores) carbon monoliths. For instance, DES provided a suitable liquid medium for 4-hexylresorcinol dissolution that was not possible otherwise (e.g. using aqueous solutions). The dissolution of 4-hexylresorcinol was by no means a trivial issue because the particularly narrow microporosity of the resulting carbons was only achieved in presence of this precursor. The excellent carbon conversions (e.g. above 70%) and the low cost of the precursors made this synthetic process quite attractive – in economical terms – for practical applications. In particular, we explored

the gas adsorption features and separation capability for CO₂/N₂ and CO₂/CH₄ mixtures of two representative carbons. Both carbons exhibited moderate heats of adsorption for CO₂, thus avoiding the energy penalties that are typically required for regeneration of functionalized adsorbents. For the same reason, the CO₂ adsorption capacities were just good (up to 3 mmol/g). However, the particularly narrow microporosity of one of the studied samples provided an outstanding CO₂/CH₄ selectivity, especially at low pressures. Overall, these features - integrating a remarkable performance at low cost - open interesting perspectives for the application of the carbons herein described as sorbents in separation technologies for CO₂ low-pressure postcombustion processes and natural gas upgrading.

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Table 1: Details on reagent concentrations used for carbon preparation. The carbon conversions obtained after polycondensation and carbonization are included. Samples are named as, for instance, C125-220 where C stand for carbons, 125 for the molar ratio of resorcinol used for DES preparation and 220 for the concentration of the catalyst solution used for polycondensation. The digits used to name the samples are in bold.

Sample	R + H + T in DES ^a (mols)	F ^a (mols)	(R + H)/F molar ratio	Na ₂ CO ₃ (mg/mL)	Na ₂ CO ₃ (μL)	Conversion (%)
C125-220	1.25 + 1 + 1	5.0	2.24	220	35	77,60
C125-180	1.25 + 1 + 1	5.0	2.24	180	35	73,41
C150-180	1.50 + 1 + 1	5.6	2.24	180	40	89,71
C150-140	1.50 + 1 + 1	5.6	2.24	140	40	90,72
C175-180	1.75 + 1 + 1	6.2	2.24	180	44	84,73
C175-140	1.75 + 1 + 1	6.2	2.24	140	44	84,95
C200-180	2.00 + 1 + 1	6.7	2.24	180	47	82,24
C200-140	2.00 + 1 + 1	6.7	2.24	140	47	86,23

^a R stands for resorcinol, H for 4-hexylresorcinol, T for tetraethyl ammonium chloride and F for formaldehyde

Table 2: ^1H -NMR spectroscopy data of D_2O dilutions of (a) DES125 (55 wt % DES) and (b) DES200 (60 wt % DES) used for polycondensation with formaldehyde and Na_2CO_3 . The chemical shifts of resorcinol (R), 4-hexylresorcinol (H) and tetraethyl ammonium chloride (T) are included for comparison.

Sample	δ (ppm)														
	Resorcinol(R)				4-Hexylresorcinol(H)									Tetraethyl ammonium bromide(T)	
	HO	H-C5	H-C4	H-C2	HO	H-C12	H-C11-C9	H-C8	H-C7	H-C6	H-C5	H-C2	H-C2	H-C1	
R	--	7.0 (1H)	6.4 (2H)	6.3 (1H)											
H	--					0.9 (3H)	1.3 (6H)	1.5 (2H)	2.5 (2H)	6.3 (1H)	6.9 (1H)	6.3 (1H)			
T	--												1.2 (12H)	3.2 (8H)	
DES125 (july2)	8.0-7.6 (2.5H=2×1.25)	6.8-6.4 (5H=4×1.25)			8.0-7.6 (2H)	0.7 (3H)	1.1 (6H)	1.1 (2H)	2.4 (2H)	6.8-6.4 (3H)			0.7 (12H)	2.4 (8H)	
DES200 (july10)	8.0-7.6 (4H=2×2.0)	6.7-6.3 (8H=4×2.0)			8.0-7.6 (2H)	0.6 (3H)	1.0 (6H)	1.3 (2H)	2.3 (2H)	6.7-6.3 (3H)			0.5 (12H)	2.3 (8H)	
DES125 - 24.78%	--	6.8-6.2 (5H=4×1.25)			--	0.7 (3H)	1.1 (6H)	1.3 (2H)	2.3 (2H)	6.8-6.2 (3H)			0.7 (12H)	2.5 (8H)	
DES200 - 26.15%	--	6.8-6.2 (8H=4×2.0)			--	0.7 (3H)	1.10 (6H)	1.30 (2H)	2.26 (2H)	6.8-6.2 (3H)			0.61 (12H)	2.34 (8H)	

Table 3: Data obtained from N₂ (at 77 K, grey columns) and CO₂ (at 273 K, white columns) adsorption/desorption isotherms.

Sample	S_{BET} (m ² /g)	$V_{\text{total pores}}$ (cm ³ /g)	W_0 (cm ³ /g)	L (nm)	E_0 (kJ/mol)	CO ₂ -uptake (mmol/g)
C125-220	0,1	0,000	0.215	0.57	30.2	2.8
C125-180	2	0,003	0.210	0.58	30.1	2.8
C150-180	2	0,009	0.194	0.59	29.8	2.6
C150-140	4	0,007	0.215	0.56	30.7	2.9
C175-180	7	0,011	0.227	0.61	29.2	3.0
C175-140	2	0,004	0.224	0.59	29.8	3.0
C200-180	4	0,006	0.224	0.59	29.6	3.0
C200-140	2	0,003	0.225	0.61	29.1	3.0

Table 4: Data describing CO₂ Adsorption Capacity for C125-220 and C200-180 at different temperatures.

	C125-220	C200-180
CO ₂ -adsorption capacity at 273K (mmol/g)	2.8	3.0
CO ₂ -adsorption capacity at 298 K (mmol/g)	2.2	2.2
CO ₂ -adsorption capacity at 323 K (mmol/g)	1.5	1.5
Isosteric Heat (kJ/mol)	35.5 ^a – 30.0 ^b	41.1 ^a – 30.0 ^b
CH ₄ -adsorption capacity at 273K (mmol/g)	0.11	0.44
CH ₄ -adsorption capacity at 298 K (mmol/g)	0.20	0.55
CH ₄ -adsorption capacity at 323 K (mmol/g)	0.17	0.45

^a Measured at zero coverage ^b Measured for coverages of 20 cm³/g and above

Table 5: CO₂/N₂ and CO₂/CH₄ selectivities of C125-220 and C200-180 at ambient (obtained under equilibrium conditions) and at low (obtained from Henry constants) pressures. Data collected from different works are included for comparison. Measurements were typically carry out at 1.2 bar and 298K. Otherwise, the samples were selected so that the experimental conditions were similar to those mentioned above (see table foot note).

Type of sample	Ref.	Equilibrium		Henry	
		α CO ₂ /N ₂	α CO ₂ /CH ₄	α CO ₂ /N ₂	α CO ₂ /CH ₄
Carbon C125-220	This work	6.2	10.8	30	4×10^4
Carbon C200-180	This work	5.9	4.0	25	11.3
Carbon N-doped	29a	8.4 ^a			
Carbon HCM-DAH-1	29b			28	
Carbon HCM-DAH-1-900-1				17	
Carbon HCM-DAH-1-900-3				13	
Carbon N-doped	29c	14			
Carbon BPL	29d			11.1 ^b	2.5 ^b
Zeolite 5				330 ^b	195 ^b
13X- Zeolite	29e	20 ^{a, c}	9 ^{a, c}		
H- β - Zeolite	29f			50.3 ^b	28.8 ^b
Na- β - Zeolite				25.6 ^b	12.8 ^b
MOF: Zirconium Phosphate	29g	4.9 ^a	17.3 ^a		
O-ZIF-8	29h			8.42	
N-ZIF-8				11.27	

H-ZIF-8				12.26	
A-ZIF-8				13.15	
ZIF-100	29i			25	5.9
ZIF-95				18	4.3
ZIF-68	29j	18	4.9		
ZIF-69		20	4.9		
ZIF-70		17	5.0		
ZIF-78		50	10.2		
ZIF-79		23	5.1		
ZIF-81		24	5.3		
ZIF-82		35	9.8		
ZIF-8	29k		14		
MOF: MIL-53(Al)	28c	10.1 ^b	3.8 ^b	6.3	2.3
MOF: MIL-100	29l				585 ^b
MOF: MIL-100c					31 ^b
MOP	29m	9-20 ^{a, c}			

^a Measured at 1 bar ^b Measured at 303K ^c Measured at 278K

Table 6: CO₂/N₂ and CO₂/CH₄ selectivities of C125-220 and C200-180 calculated from IAST simulations for different gas mixtures. Data collected from different works are included for comparison. Measurements were typically carry out at 1.2 bar and 298K. Otherwise, specific conditions are provided by subscripts (see table foot note).

Sample	Ref.	IAST predictions				
		α CO ₂ /N ₂ (15/85)	α CO ₂ /N ₂ (50/50)	α CO ₂ /CH ₄ (15/85)	α CO ₂ /CH ₄ (30/70)	α CO ₂ /CH ₄ (50/50)
Carbon C125-220	This work	4.0	13.3	7.2	14.8	
Carbon C200-180	This work	3.9	14.0	2.1	4.7	
Carbon N-doped	29a	5.7 ^a				
Carbon Nanotubes N-doped	31a					8 ^{a, d}
MOF	31b			10 ^a	9 ^a	
MOF	31c			18 ^{a, b} (296K)	15 ^{a, b} (296K)	12 ^{a, b} (296K)
PPN-6-SO₃H PPN-6-SO₃Li	29b	150 ^{a, c} 414 ^{a, c} (295K)				
MOF-5 Cu-BTC	31d			1.9 ^a 6.2 ^a	1.9 ^a 6.2 ^a	

Silicalite. MFI						2.6
C168 Schwarzite	31e					5.4
IRMOF-1						2.0
O-ZIF-8						9.64 ^a
N-ZIF-8						13.28 ^a
H-ZIF-8	29h					11.90 ^a
A-ZIF-8						14.38 ^a

^a Measured at 1 bar ^b Measured at 296K ^c Measured at 295K ^d Measured at 273K

Figure 1: DSC scans of DES111 (light blue), DES125 (dark blue), DES150 (green), DES175 (red) and DES200 (black).

Figure 2: SEM micrographs of carbons C125-220 and C200-180 showing a homogeneous bicontinuous structure. C125-180, C150-180, C150-140, C175-180, C175-140 and C200-140 also exhibited homogeneous bicontinuous structures similar to those depicted in this figure (micrographs not shown).

Figure 3: FTIR spectra of the gels resulting from polycondensation of RHT-DES125 (black) and RHT-DES200 (grey) with formaldehyde using 220 mg/mL and 180 mg/mL Na_2CO_3 as catalyst, respectively.

Figure 4: ^{13}C NMR spectra of gels resulting from polycondensation of RHT-DES125 (a) and RHT-DES200 (b) with formaldehyde using 220 mg/mL and 180 mg/mL Na_2CO_3 as catalyst, respectively.

Figure 6: CO₂ (blue), N₂ (red) and CH₄ (green) adsorption isotherms of C125-220 (a) and C200-180 (b) at 298 K.

Figure 7: CO₂ isotherms of C125-220 (a) and C200-180 (b) at 273 (red), 298 (blue) and 323 K (orange).

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