Carbon supports for the catalytic dehydrogenation of liquid organic hydrides as hydrogen storage and delivery system

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Abstract

The use of liquid organic hydrides as hydrogen carriers is a promising storage and delivery system due to the advantages of using liquid-based infrastructures and its economic feasibility compared to other conventional systems. The reversible dehydrogenation/hydrogenation of liquid organic hydrides is a key point for the development of highly performance reactors. In this study different carbon materials have been investigated as platinum supports, including carbon nanofibers, carbon black, carbon xerogel, activated carbon and ordered mesoporous carbon. To individuate the effect of the carbon support on the catalytic activity, platinum particles were synthesized by a microemulsion procedure. The analysis of the hydrogen evolution curves indicate that the support BET surface area plays a very important role on the initial catalytic activity, obtaining a maximum rate of $220 \text{ mmol g}_{\text{Pt}}^{-1} \text{ min}^{-1}$ when using an ordered mesoporous carbon with a surface area of $930 \text{ m}^2 \text{ g}^{-1}$. Nevertheless, the analysis of catalytic activity at prolonged duration indicates a better behavior towards deactivation for supports characterized by wide pores and low graphitization degree like carbon black or carbon xerogel, despite their lower initial dehydrogenation rate ($100\text{-}140 \text{ mmol g}_{\text{Pt}}^{-1} \text{ min}^{-1}$). The ultimate use in the dehydrogenation reactor as well as the operation conditions will define the best catalyst structure from the point of view of the carbon support.

Keywords: hydrogen storage, decalin dehydrogenation, carbon nanofibers, carbon black, carbon xerogel, activated carbon, ordered mesoporous carbon.

1 Introduction

There is a growing interest in increasing the energy density in both volumetric and gravimetric basis of hydrogen storage systems. The storage and delivery of hydrogen still continues to represent an important technical barrier towards hydrogen-based energy structures, especially when considering on-board storage in the automotive sector. The reversible dehydrogenation/hydrogenation of liquid organic hydrides (LOH) was already proposed three decades ago for its technical and economic feasibility [1]. As liquids have significant engineering and safety advantages over solids or gases, LOH represents a potential system to store and deliver hydrogen in a non-gaseous infrastructure concept [2-4]. Moreover, hydrogen released from LOH is CO and CO₂ free, so it can be directly fed to fuel cells with a high purity.

Some liquid carriers have been developed and studied for the storage and delivery of hydrogen with adequate theoretical hydrogen content and dehydrogenation enthalpy, such as N-ethyl carbazole [5], although the most studied liquid organic pairs (alkane/arene) are, in increasing order of hydrogen capacity: methylcyclohexane/toluene, cyclohexane/benzene and decalin/naphthalene [6]. Whatever the LOH, the rapid, stable and cost-efficient evolution of hydrogen through the catalytic dehydrogenation of the cycloalkane to the aromatic compound is the main concern. Platinum based catalysts were studied in the early 2000s by Hodoshima and coworkers [7-9] and Kariya and coworkers [10, 11] to be used under reactive distillation conditions. These catalysts present a high activity and selectivity towards the complete dehydrogenation of the alkanes. When a second metal (Ni, W, Ir, Re, etc.) is added to platinum, an enhancement of activity has been observed due to the promotion of C-H cleavage and/or desorption of aromatic compounds [3, 6, 8, 10]. Nickel based catalysts (Pt-free) have also been successfully applied [12, 13] but, despite their lower cost, platinum is generally preferred to avoid the cracking reaction and coke deposition at high temperatures

that lead to deactivation of nickel catalysts, as well as to favor the selectivity towards hydrogen and aromatic compounds without compromising the reversibility of the process.

Apart from the catalytic phase, the support also plays a key role. Two main types of supports have been studied for LOH: alumina [12, 14-16] and carbon [17- 21]. The role of catalytic supports is to provide a high surface area to disperse the metal particles, stabilize these particles against deactivation phenomena and provide an adequate porosity for the transfer of reactants and products. The use of carbon seems to be favorable in comparison with alumina to accomplish high activity, selectivity and stability [10, 22, 23], which has been attributed to the effect of hydrogen spillover [24]. The porosity of the support has also been observed to influence the evolution rate. Either its surface area or its pore volume favors the dehydrogenation of cyclohexanes on Pt supported on activated carbon [21], although the influence of support properties is not yet clear. The aim of this work is to analyze and compare for the first time carbon supports with very different properties in terms of porosity and morphology. More precisely they include ordered mesoporous carbon, carbon xerogel, carbon nanofibers, carbon black and activated carbon. In order to minimize the effect of the support on the characteristics of platinum nanoparticles, a microemulsion procedure will be used to control Pt particle size independently of support features and the activity towards the dehydrogenation of decalin will be studied.

2 Experimental

2.1. Carbon supports and Pt/C catalysts

Carbon supports in this study include, in increasing order of specific surface area: carbon nanofibers (CNF), carbon black (CB), carbon xerogels (CXG), activated carbon (AC) and ordered mesoporous carbon (OMC). CB Vulcan XC-72R was supplied by Cabot Corp. and AC CP97 was supplied by Engelhard Italiana SpA., whereas CNF, CXG and OMC were in-house synthesized as follows.

CNF were synthesized by the catalytic decomposition of methane on a nickel-based catalyst ($\text{NiCuAl}_2\text{O}_3$) at 600 °C. For this, the in-house prepared catalyst precursor was reduced in hydrogen at 550 °C for 1 h. The growth of CNF took place at 600 °C by feeding pure methane to the reactor ($10 \text{ L g}^{-1} \text{ h}^{-1}$) for 10 h. The methane conversion to carbon was monitored by gas chromatography. Further details can be found elsewhere [25].

CXG were synthesized by the pyrolysis at 800°C of an organic gel obtained by the polycondensation of resorcinol and formaldehyde in stoichiometric ratio (2 mol of formaldehyde per mol of resorcinol). The gelation and curing process took place at an initial pH of 6.0 and using sodium carbonate as catalyst (0.04 mol.% with respect to total content of resorcinol+formadehyde). The procedure includes three steps: 24 h at room temperature, 24 h at 50 °C and 120 h at 85 °C. Subsequently, remaining water is exchanged with acetone and the gel is dried under subcritical conditions before its pyrolysis. Pyrolysis took place at 800°C under a nitrogen atmosphere for 3 h. Further details can be found elsewhere [26].

OMC were obtained by the carbonization of a silica template impregnated by a furanic resin and followed by the removal of silica. Furan resin (Hüttenes-Albertus) was used as carbon precursor and SBA-15 silica was used as cast. To initiate the polymerization of the resin, nitric acid (65 wt.%, Panreac) was used and subsequently the silica was impregnated. Impregnated silica was cured at 108 °C for 24 h and then carbonized at 700 °C for 2 h. The

removal of the silica was carried out by washing with HF (40wt.%, Fluka) for 24 h, thoroughly washed with water and dried overnight at 108°C. Further details can be found elsewhere [27].

Platinum catalysts supported on the different supports were synthesized using a microemulsion procedure [28-31]. The choice of a microemulsion method was prompted by the need of minimizing the influence of the support on the platinum catalytic particle size. Catalytic activity is strongly influenced by the surface structure of metal particles, this is, the density of highly active catalytic sites. In the case of monometallic catalysts the density of active sites strongly depends on the particle size for small nanoparticles (< 5 nm) [19]. In order to obtain similar particle sizes independently of support features, reverse micelles were used for the confinement of Pt crystallites growth by the use of a surfactant (polyethylene glycol dodecyl ether). The microemulsion composition was 16.5 vol.% surfactant and 0.77 vol.% of aqueous solution (for a water to surfactant molar ratio of 1) including the platinum precursor (H_2PtCl_6 , Sigma-Aldrich) in a concentration of 0.05 M, using n-heptane (Panreac) as hydrophobic phase. The carbon support was then dispersed in the microemulsion under sonication for one hour. The reduction agent, sodium borohydride (Sigma-Aldrich) was slowly added in excess to the dispersion under vigorous stirring and left overnight for the complete reduction. The catalyst was then filtered and thoroughly washed with ethanol and water and subsequently dried at 60°C overnight.

2.2. Characterization techniques

The pore texture of carbon supports was characterized by the analysis of nitrogen adsorption-desorption isotherms, performed at -196 °C. The instrument used was a Micromeritics ASAP 2020. The analysis of the isotherms provided BET specific surface area, S_{BET} , micropores volume calculated by the t-plot method and the total pore volume from the

adsorbed nitrogen at saturation. Barret-Joyner-Halenda (BJH) equation was applied to the desorption isotherm to obtain the pore size distribution and the mean pore size for the supports.

X-ray diffraction (XRD) analyses were carried out using a Bruker AXS D8Advance diffractometer, in a θ - θ configuration and with a $\text{CuK}\alpha$ radiation. Platinum crystal sizes were calculated applying the Scherrer's equation to the Pt reflections correcting for the contribution of every peak and using the Rietveld refinement method.

Thermogravimetric analyses (TGA) were performed using a Setaram Setsys Evolution thermogravimetric analyser. The experiments were carried out in air at atmospheric pressure from room temperature to 950 °C with a heating rate of 5 °C min⁻¹. The residual weight after carbon complete oxidation obtained for the supports and the catalysts separately were used to calculate the noble metal content.

2.3. Dehydrogenation catalytic activity

The catalysts were tested a batch-type experimental set-up as reported elsewhere [17]. It must be considered as an experimental equipment to test the different catalyst formulations in the decalin dehydrogenation reaction under reactive distillation conditions, i.e. under boiling and refluxing conditions [7, 10, 32]. The void volume of the reactor is 90 cm³.

In a standard experiment, 0.25 g of catalyst is scattered at the bottom of the reactor vessel forming a thin layer of powder. Then, 0.667 ml of decalin (Sigma-Aldrich, reagent grade) is added to the catalyst layer dropwise to ensure the catalyst is completely wetted with decalin. The experimental set-up is swept with nitrogen for 20 minutes to remove air. In parallel, a mixture of solid salts (NaNO_3 and KNO_3 1:1) is heated to the reaction temperature, 260 °C. The decalin to catalyst ratio and temperature values (2.7 ml g⁻¹ and 260°C, respectively) were chosen to maximize the rate constant and minimize the retardation constant according

to a previous work with activated carbon supported catalysts [17]. When the reaction temperature of the molten salt bath is reached and stable, the reactor vessel is introduced in the bath and the hydrogen released during the reaction is monitored by the volume of water displaced in a buret.

3 Results

3.1. Carbon supports and Pt/C catalysts characterization

The five carbon supports studied in this work, as described in the experimental section, are: carbon nanofibers (CNF), carbon black (CB), carbon xerogel (CXG), activated carbon (AC) and ordered mesoporous carbon (OMC). They present substantial differences within them from both morphological and structural point of views. AC is a highly porous form of carbon, comprised of stacked and cross-linked microcrystalline graphite interspersed with non-graphitic aromatic carbon structures, containing heteroatoms all crumpled into a randomly-oriented three-dimensional structure. AC is generally obtained by the pyrolysis of carbonaceous precursor materials (either natural like wood, or synthetic like waste tyres) followed by an activation process to develop porosity. This type of carbon has been widely used as support for the LOH dehydrogenation due to its high surface area [7-10, 13, 17, 24]. CXG and CB are characterized by the random aggregation of primary carbon spherules, with sizes in the interval of 10-20 nm for CXG and of 30-40 nm for CB. Nonetheless, CXG and CB are the result of really different synthesis processes, as CXG results from the pyrolysis of an organic gel which is first dried under subcritical conditions [33, 34] and CB results from the incomplete combustion of petroleum derived products. Finally, OMC and CNF are comprised by ordered filamentous carbon structures. OMC results from the replica of a silica-based cast, of controllable and well-defined cylindrical cavities with diameters of around 5-6 nm and ordered orientation in bundles [35]. Whereas, CNF results from graphitic carbon deposition on a transition metal catalyst in whisker-like mode, with filament diameters from 20 nm to 80 nm and randomly entangled in a three dimensional network.

The porous structure of these carbon materials is very different as a consequence of their diverse structures. Fig. 1(a) shows the nitrogen physisorption isotherms for the mentioned carbon materials. Three distinct behaviors can be observed with respect to nitrogen adsorption

at intermediate partial pressure: CB and CNF present a low adsorption capacity, CXG presents an intermediate adsorption capacity and OMC and AC are the materials with the highest capacity. This is also advised in Table 1, where the BET surface area increases in the order $\text{CNF} < \text{CB} < \text{CXG} < \text{AC} < \text{OMC}$, covering a wide interval of values from $140 \text{ m}^2 \text{ g}^{-1}$ to $931 \text{ m}^2 \text{ g}^{-1}$. However, the porosity and density of these samples does not follow the same trend according to the adsorption at high relative pressure and as revealed by the pore volume values of Table 1. The pore volume increases in the order $\text{CB} < \text{CNF} < \text{OMC} < \text{AC} < \text{CXG}$, from $0.37 \text{ cm}^3 \text{ g}^{-1}$ to $0.80 \text{ cm}^3 \text{ g}^{-1}$. Another important differentiating feature is the pore size distribution. The adsorption at low relative pressure indicates a higher microporosity for the samples with the highest surface areas. The pores of these materials present the size distribution shown in Fig. 1(b) as calculated applying BJH model to the desorption curves. CXG, CB and CNF are characterized by wide pore size distributions centered at around 30 nm, indicating a high mesoporosity. Indeed, average pore sizes calculated from the desorption isotherm and applying the mentioned BJH model are 9.6 nm for CB, 16.8 nm for CXG and 18.3 nm for CNF (Table 1). On the other hand, OMC and AC present much narrower pore size distributions, centered at 3.1 nm and 4.9 nm respectively, in other words, wide pores and wide size distributions characterize the group CXG, CB and CNF, whereas narrow pores characterize the porosity of AC and OMC.

Another aspect regarding carbon materials properties is the structural ordering of carbon. Differential thermogravimetric (DTG) analyses were carried out to study the oxidation of carbon in air. The peaks obtained (not shown) correspond to the carbon oxidation, being the temperature at which this occurs (Table 1) and indicator of the resistance of carbon and, in turn, of the ordering degree. OMC and CB present the lowest oxidation temperature, starting early at 300°C with a peak at 400°C . The presence of two peaks for CB (399°C and 446°C) and three peaks for OMC (401°C , 409°C and 431°C) in the DTG profile indicate possible

different structures of carbon that oxidize at slightly different temperatures. The other three carbon materials present similar profiles within them, that oxidize at higher temperatures, CXG (560 °C), AC (580 °C) and CNF (621 °C), indicating a carbonaceous structure more similar to that of graphitic carbons as the oxidation temperature increases.

Fig. 2 shows the XRD profiles for the platinum catalysts supported on the different carbon materials. Reflections ascribed to platinum, carbon and, in the case of CNF, nickel, are found. The presence of Ni traces (< 1%) was observed to have no significant influence on the catalytic dehydrogenation of cycloalkanes when using only CNF [18]. Moreover, nickel contribution to catalytic surface area must be considered negligible in comparison to Pt because Ni crystal size (*ca.* 40 nm) is an order of magnitude bigger than Pt (3 nm), so the possible synergistic effect has not been considered in this work. The Pt peak broadening was used to calculate metal crystal sizes according to the Scherrer's equation and considering the weighed contribution of all reflections, and they are summarized in Table 2. With the exception of Pt/CXG, the catalysts show similar crystal sizes around 3 nm. The synthesis of Pt particles deposited on the carbon supports has been carried out following a water-in-oil microemulsion procedure, as described in the experimental section. This synthesis technique is advantageous since a narrow metal particle size distribution can be obtained, the particle size can be controlled, and there is no expected effect of the support on the formation of the particles [28]. Moreover, platinum particles are preferentially adsorbed on the external surface of the support as the diffusion of micelles containing the metal precursor is hindered in the micropores. This represents an advantage for their behavior as catalysts since platinum particles sunk in micropores are considerably less active than particles deposited on wide pores. However, the higher particle size encountered for Pt/CXG may be caused by a carbon surface less prompt to the electrostatic adsorption of dispersed Pt crystallites, which results in bigger particles during the reduction process despite the use of a surfactant.

From TGA experiments performed to the supports and the catalysts we calculated the Pt uptake considering the residual weight after oxidation. The platinum loading differs among catalysts from 1.8 wt.% for Pt/OMC to 4.7 wt.% for Pt/CB (Table 2), below the nominal 5 wt.% objective. Future work will focus on minimizing Pt particle size and optimizing Pt uptake for the best support. Nonetheless, the catalytic activity for the LOH dehydrogenation is more sensitive to the Pt particle size than to the Pt uptake [19].

3.2. Hydrogen evolution from decalin dehydrogenation

Fig. 3(a) shows the hydrogen evolution from the dehydrogenation reaction of decalin for the whole duration of the experiments (120 minutes). The dehydrogenation of decalin ($C_{10}H_{18}$) through tetralin ($C_{10}H_{12}$) to result in naphthalene ($C_{10}H_8$) follows the Eq. 1:

All catalysts experience an initial rapid evolution of hydrogen followed by a progressive decrease in activity that, in some cases, can lead to complete deactivation as observed for Pt/OMC, Pt/AC and Pt/CNF. These three catalysts present a horizontal profile from a certain time on. This dramatic decay of activity was not observed before for AC and CNF supported Pt catalysts [17, 18], possibly due to the lower reaction temperature. In the case of Pt/OMC and Pt/AC, since narrower pores characterize the supports, the deactivation may be caused by the adsorption of aromatic compounds like tetralin or naphthalene or organic derivative compounds on the surface, which hinder the accessibility of decalin to the catalytic active sites [18]. In the case of Pt/CNF other cause different from this mechanism of pore plugging must account for the blocking of active sites since CNF present wider pores than AC and OMC (Fig 1(b)). On the other hand it results of interest that both CB and CXG based catalysts do not present other significant deactivation than that predicted by the Langmuir-Hinshelwood model for the test duration. This suggests that for the high hydrogen evolution

rate at continuous operation, the removal of aromatic products from the carbonaceous matrix is critical for highly porous substrates like OMC and AC and do not represent a significant drawback for mesoporous carbons like CB and CXG.

Another aspect of interest is the analysis of catalytic behavior at low decalin conversion. Fig 3(b) shows the hydrogen evolution profiles for the initial part of the curves. Applying the Langmuir-Hinshelwood desorption equation (Eq.2) to these H₂ evolution curves, and assuming a low decalin conversion according to a previous work [17], we have calculated the rate constant, k , and the retardation constant, K , and they are summarized in Table 2.

$$v = \frac{k}{1 + K [\text{naphthalene}]} \quad (2)$$

where v is the hydrogen evolution rate. There is a clear effect of the carbon support on the catalytic dehydrogenation reaction that leads to an almost two-fold higher activity when using highly porous supports (OMC, AC) in comparison with those supports with low surface area (CB, CNF). Despite the lower pore size for OMC and AC, the porous structure and the surface area of the carbon support are important features known to influence the Pt distribution and mass transfer in catalysis [36]. The catalyst with the lowest rate constant is Pt/CXG, *i.e.* the catalyst characterized by the highest Pt particle size (5.3 nm). Indeed, the Pt theoretical surface areas (TSA) were estimated considering spherical morphology and particle sizes obtained from XRD analyses. Accordingly, the almost two-fold lower TSA of Pt/CXG (53 m² g⁻¹) compared to the other catalysts (90-108 m² g⁻¹) explains its lowest initial activity. To individuate the effects of Pt dispersion and any other effect (such as metal-support interaction, diffusivity through the catalytic structure, etc.), the rate constant normalized by the theoretical surface of Pt was accordingly calculated (k_s , mmol m_{Pt}⁻² min⁻¹), which indicates the velocity of hydrogen formation per unit of catalytic site surface (Table 2). Fig. 4 shows the effect of the support BET surface area on this surface normalized rate constant, k_s . It can

be observed that the rate constant increases linearly with S_{BET} and independently of other properties of the support. This suggests that the surface of the support plays a very important role in the dehydrogenation reaction for comparable values of Pt surface area. Presumably the homogeneous distribution of Pt particles on the support, which is favored by the support surface area, is of key importance towards a high evolution rate of hydrogen. The higher the support surface area, the higher the average distance among Pt nanoparticles, favoring the access of reactants/desorption of products to/from the catalytic sites. It must be pointed out that higher catalytic activity may be achieved by decreasing the Pt particle size, and in turn increasing the Pt surface area, according to a previous work [18], so the activity values presented in this work (*ca.* 220 mmol g_{Pt}⁻¹ min⁻¹) are not optimized.

Regarding the retardation constant, the values encountered were similar to those found in previous works under similar reaction temperature and decalin to catalyst ratio [17]. Although Pt/OMC presents the highest initial activity, its retardation constant indicates a deactivation mechanism more influenced by the presence of aromatic products (naphthalene) than that using other carbon supports like AC, CB or CNF. Nonetheless, the most important deactivation mechanism is not the production of naphthalene, but the sudden decrease of activity at prolonged times as stated in Fig. 3(a). Catalysts based on supports with intermediate porosity (CB and CXG) resulted less affected by this deactivation phenomena and continued active after 2 hours, even overcoming the evolved amount of hydrogen from the catalyst with the highest initial activity, Pt/OMC, after 25 minutes. This deactivation phenomenon must be further studied and has to be taken into consideration for the appropriate design of the catalyst structure according to the expected operation conditions in the dehydrogenation reactor (temperature, residence contact time, dehydrogenation/reactivation cycles frequency and conditions, etc.).

4 Conclusions

Platinum nanoparticles were deposited on carbon supports characterized by different porosity and structure. These carbon supports included carbon nanofibers, carbon black, carbon xerogel, activated carbon and ordered mesoporous carbon. They present BET surface areas from $140 \text{ m}^2 \text{ g}^{-1}$ to $930 \text{ m}^2 \text{ g}^{-1}$. Although not optimal, obtaining similar Pt particle sizes by using a microemulsion procedure has allowed the comparison of different porous structures in the decalin dehydrogenation reaction. From the analysis of catalytic activity, the BET surface area of the carbon support seems to play a more significant role than any other characteristic on the initial rate of hydrogen evolution. In terms of initial activity towards the evolution of hydrogen, ordered mesoporous carbon represents the best choice to disperse Pt particles and maximize the rate constant. Nonetheless, the loss of activity for prolonged operation is avoided by using carbon supports with wider pores like carbon blacks. Consequently, the adequate choice of the catalytic structure is a function of the operating conditions at the dehydrogenation reactor: for continuous operation, a high stability is mandatory, so carbon blacks or carbon xerogels may be preferred as support due to their low retardation constant; for operation with a high frequency of reactivation steps (*i.e.* reactivation of the catalyst by removal of adsorbed species), ordered mesoporous carbons would be the best choice due to their high rate constant.

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Figure captions

Figure 1. (a) Nitrogen physisorption isotherms for the different carbon supports; (b) Pore size distributions obtained from BJH model to the desorption isotherms.

Figure 2. XRD patterns obtained for the Pt catalysts supported on the different carbon materials.

Figure 3. (a) Hydrogen evolution from the dehydrogenation of decalin at prolonged duration (b) Detail of initial hydrogen evolution curves.

Figure 4. Influence of support BET surface area on the surface normalized initial rate constant.

Table 1. Characterization of carbon materials.

Sample	Support S _{BET} (m ² g ⁻¹)	External surface area, t-plot (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Micropore volume, t-plot (cm ³ g ⁻¹)	Pore size, BJH (nm)	DTG oxidation temperature (°C)
OMC	931	49	0.64	0.54	3.1	401-431
AC	743	308	0.67	0.25	4.9	580
CXG	482	178	0.80	0.17	16.8	560
CB	212	148	0.37	0.03	9.6	399-446
CNF	140	149	0.59	0	18.3	621

Table 2. Rate data of decalin dehydrogenation in batch-type reactor at 260°C.

Sample	Pt crystal size (nm)	Pt loading (wt. %)	Pt theoretical surface area (m ² g ⁻¹)	Rate constant, k (mmol g _{Pt} ⁻¹ min ⁻¹)	Rate constant, k_s (mmol m _{Pt} ⁻² min ⁻¹)	Retardation constant, K (ml mmol ⁻¹)
Pt/OMC	3.1	1.8	90	219.1	2.42	3.6
Pt/AC	2.9	2.7	97	214.8	2.22	2.3
Pt/CXG	5.3	4.6	53	96.0	1.81	3.9
Pt/CB	3.0	4.7	93	140.4	1.50	2.1
Pt/CNF	2.6	3.7	108	123.2	1.14	2.9

Figure 1

Figure 2

Figure 3

Figure 4