

Article

Carbon Aerogel-Supported Pt Catalysts for the Hydrogenolysis and Isomerization of *n*-Butane: Influence of the Carbonization Temperature of the Support and Pt Particle Size

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Received: 18 July 2012; in revised form: 3 September 2012 / Accepted: 24 September 2012 / Published: 12 October 2012

Abstract: Carbon aerogels prepared at different carbonization temperatures and with varying mesopore volumes were used as supports for Pt catalysts to study the *n*-C₄H₁₀/H₂ reaction. Mean Pt particle size depended on the mesopore volume of the support, showing a linear decrease when the mesopore volume increased. The turnover frequency (TOF) for hydrogenolysis was much higher than for isomerization in catalysts supported on carbon aerogels obtained at 900–950 °C. However, both TOF values were similar in catalysts supported on the carbon aerogel obtained at 500 °C. TOF for hydrogenolysis and isomerization were related to the mean Pt particle size in catalysts supported on carbon aerogels obtained at 900–950 °C. In addition, both reactions showed a compensation effect between the activation energy and pre-exponential factor, indicating that they have the same intermediate, *i.e.*, the chemisorbed dehydrogenated alkane.

Keywords: carbon aerogels; Pt catalysts; *n*-butane hydrogenolysis; *n*-butane isomerization

1. Introduction

Alkane hydrogenolysis consists of the breakage of C-C bonds with the uptake of hydrogen. It is always exothermic, because each hydrogenolysis reaction involves the rupture of a C-C bond and the formation of two C-H bonds. Alkane hydrogenolysis over supported metal catalysts is of theoretical

interest, because many hydrogenolysis reactions are structure sensitive, as well as having industrial applications in alkane reforming [1–3].

The type of metal influences the catalyst activity and hydrogenolysis depth, *i.e.*, the number of C-C bonds broken per collision of a reactant molecule with the catalyst surface. For instance, Pt is not as active as other metals in groups 8, 9, and 10 of the Periodic Table, but it is highly selective for single hydrogenolysis, breaking a single C-C bond per collision with the metal surface.

Alkane isomerization can also take place under hydrogenolysis conditions, although Pt catalysts are generally more active in hydrogenolysis than in the isomerization reaction. Both reactions depend on the metal catalyst and support.

Carbon aerogels can be used as supports for metal catalysts among other applications because they can be prepared with high purity and homogeneity, and with controlled micro and mesoporosity [4]. In addition, carbon aerogels can be synthesized in a large variety of forms such as monoliths, microspheres, powders and thin films. These materials are produced by the carbonization of organic aerogels prepared by the sol-gel polymerization of phenolic compounds with formaldehyde [5], using either basic or acid catalysts, and dried with supercritical CO₂.

In the present work, carbon aerogels obtained at different carbonization temperatures and with varying mesopore volumes were used as supports for Pt catalysts to study the influence of support characteristics on Pt particle size and activity in the *n*-C₄H₁₀/H₂ reaction. An activated carbon was also used as Pt catalyst support for the purposes of comparison.

2. Results and Discussion

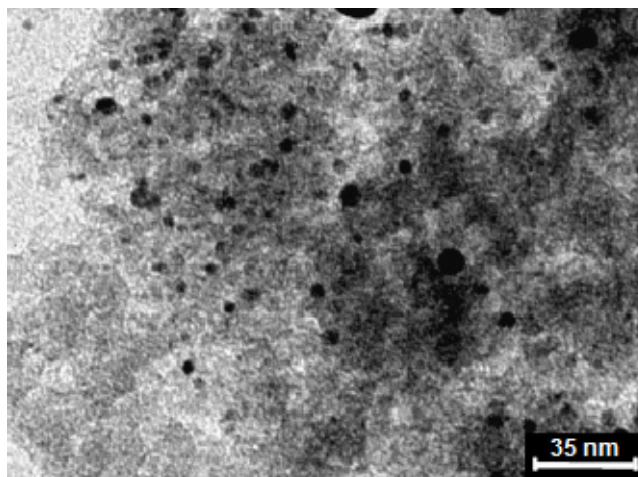
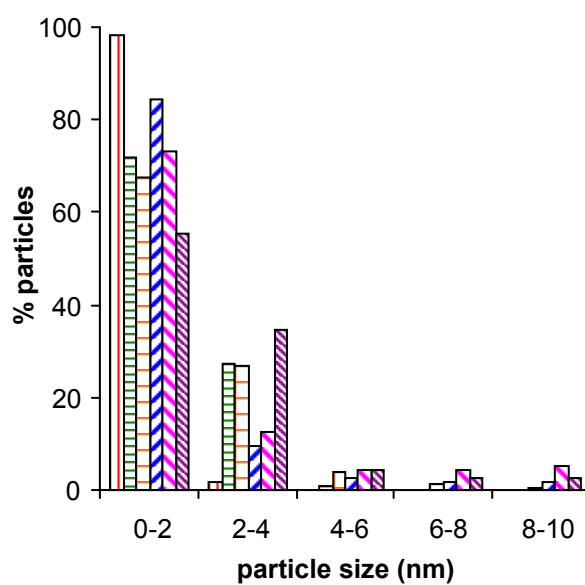
Table 1 compiles the surface area, $V_{\text{micropores}}$ ($\varnothing < 2$ nm) and $V_{\text{mesopores}}$ ($2 < \varnothing < 50$ nm) of the supports. These surface characteristics were discussed in details elsewhere [6–8].

Table 1. Surface area and porosity of the supports.

Supports	S_{BET} (m ² /g)	$V_{\text{micropores}}$ (cm ³ /g)	$V_{\text{mesopores}}$ (cm ³ /g)
CA1	618	0.26	0.86
CA2	700	0.29	0.61
CA3	592	0.26	0.03
P3-900	588	0.23	0.30
POX-900	519	0.23	0.31
POX-500	514	0.21	0.29
BV46	1153 ^a	0.40	n.d. ^b

^a From immersion calorimetry into benzene at 30 °C; ^b n.d: not determined.

A TEM micrograph of catalyst P3-900-2Pt after its reduction pre-treatment is given in Figure 1, as an example, and shows that Pt particles are well dispersed on the support. Figure 2 depicts the PSDs of catalysts supported on carbon aerogels. Distributions are narrow, with around more than 80% of particles being <4 nm in size.

Figure 1. TEM picture of catalyst P3-900Pt.**Figure 2.** Particle size distribution of catalysts CA1Pt, CA2Pt, CA3Pt, P3-900Pt, POX-900Pt, POX-500Pt.

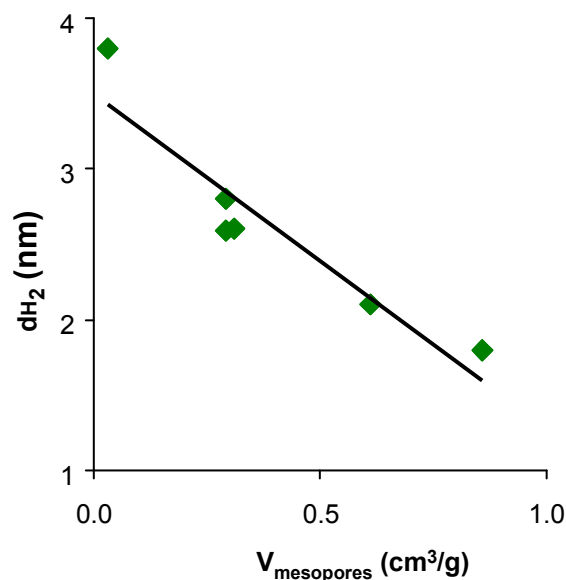
Mean Pt particle size (d) and its dispersion (D) from H_2 chemisorption at 25 °C and from TEM are compiled in Table 2. For the same catalyst, d_{H_2} and d_{TEM} values are similar or very close.

Table 2. Mean particle size (d) and dispersion (D) from H_2 chemisorption at 25 °C and TEM, and surface to total Pt ratio (Pt_{XPS}/Pt_{total}).

Catalyst	d_{H_2} (nm)	d_{TEM} (nm)	D_{H_2} (%)	D_{TEM} (%)	Pt_{XPS}/Pt_{total}
CA1Pt	1.8	1.3	60	83	1.0
CA2Pt	2.1	1.6	51	68	0.6
CA3Pt	3.8	2.9	28	37	0.3
P3-900Pt	2.6	2.7	42	40	0.8
POX-900Pt	2.6	2.6	42	42	0.8
POX-500Pt	2.8	2.7	39	40	n.d
BV46Pt	4.0	n.d	27	n.d	n.d

Figure 3 shows that the mean Pt particle size linearly decreases when the mesopore volume of the support increases, indicating the importance of this type of pores to obtain a high Pt dispersion.

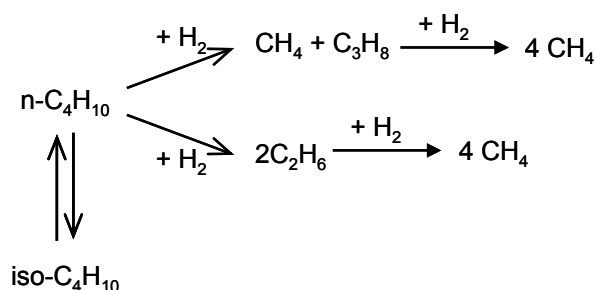
Figure 3. Relationship between mean Pt particle size and mesopore volume of the support.



The $\text{Pt}_{4f7/2}$ core level deconvoluted spectra of catalysts showed two peaks [6], at binding energies of 71.6 eV and 73.0 eV, which are assigned to Pt(0) and Pt(II), respectively [6,9,10]. Table 2 shows the $\text{Pt}_{\text{XPS}}/\text{Pt}_{\text{total}}$ ratio, which is equal to the unity for the catalyst with the highest metal dispersion (CA1Pt) and takes the lowest value for the catalyst with the lowest dispersion (CA3Pt). This is due to the decrease in surface Pt atoms *versus* total Pt atoms when Pt particle size increases.

The $n\text{-C}_4\text{H}_{10}/\text{H}_2$ reaction catalyzed by Pt yields the hydrogenolysis products (propane, ethane and methane) simultaneously with iso-butane according to the following Scheme:

Scheme 1. Simultaneous hydrogenolysis and isomerization of *n*-butane.



Given that *n*-butane has only four carbon atoms, the formation of cyclic isomerization products is unlikely, and the only isomerization product is iso-butane. The reaction is produced in the presence of H_2 , which regulates the concentration of surface intermediates with different degrees of dissociation [1]. Hydrogenolysis of *n*-butane can take place through a terminal C-C bond cleavage, yielding CH_4 and C_3H_8 , or by a central C-C bond cleavage, yielding C_2H_6 . In the first case, the propane produced can

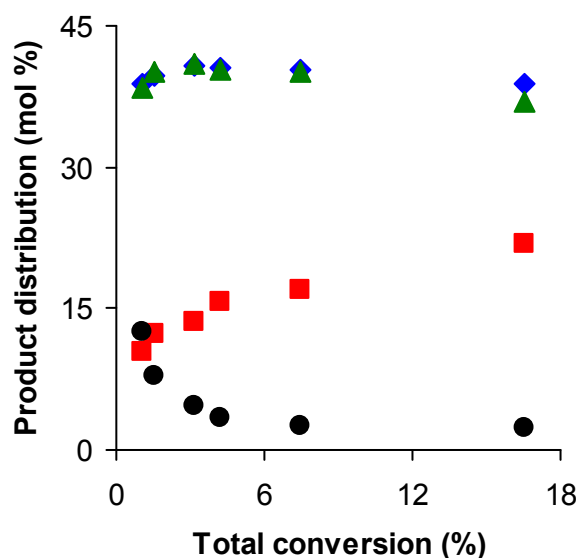
undergo hydrogenolysis, yielding ethane and methane, and the ethane produced can be further degraded to methane.

Product distributions obtained at 320 °C are compiled in Table 3, and Figure 4 depicts, as an example, the variation of product distributions with total conversion for catalyst POX-900Pt. Results show that the percentages of methane and propane produced are practically the same in all cases. Hence, it can be assumed that the methane obtained in the reaction is produced by terminal C-C bond cleavage and that there is no multiple hydrogenolysis of butane as with other catalysts, e.g., Ni [3,11].

Table 3. Conversion (%) and product distribution (mol%) in the hydrogenolysis (H) and isomerization (I) reactions at 320 °C.

Catalyst	Conversion (%)		C ₁	C ₂	C ₃	i-C ₄
	H	I				
CA1Pt	6.2	0.4	40	17	40	3
CA2Pt	6.7	0.4	40	17	40	3
CA3Pt	6.0	0.7	40	16	39	5
P3-900Pt	7.3	0.3	41	17	40	2
POX-900Pt	7.1	0.4	40	17	40	3
POX-500Pt	0.3	0.3	30	9	30	31
BV46Pt	0.8	0.3	35	18	30	17

Figure 4. Relationship between product distribution and total conversion for catalyst POX-900Pt. ♦ C₁, ■ C₂, ▲ C₃, ● i-C₄.



TOF values at 320 °C are compiled in Table 4. TOF_H is much higher than TOF_I, by around one order of magnitude, for Pt catalysts supported on carbon aerogels obtained at 900–950 °C. These results are in agreement with reports for Pt(100) and Pt(111) single crystals and polycrystalline Pt foil [12] and for Pt catalysts supported on zeolite [13]. In contrast, Pt catalysts prepared with support

carbonized at 500 °C (POX-500) and the activated carbon BV46 exhibit much lower TOF_H values *versus* the other catalysts, which are of the same order of magnitude to TOF_I values.

Table 4. Turnover frequency (TOF) at 320 °C, apparent activation energy (E_a) and pre-exponential factor (Ln A) for hydrogenolysis (H) and isomerization (I) reactions.

Catalyst	$\text{TOF}_\text{H} \cdot 10^3 \text{ s}^{-1}$	$\text{TOF}_\text{I} \cdot 10^3 \text{ s}^{-1}$	Temp. range °C	$E_\text{a}(\text{H})$ kJ/mol	Ln A(H)	$E_\text{a}(\text{I})$ kJ/mol	Ln A(I)
CA1Pt	37.5	2.5	260–340	131	27	42	7
CA2Pt	51.2	3.1	270–320	138	29	30	4
CA3Pt	74.3	8.2	280–320	150	31	55	10
P3-900Pt	67.4	3.0	280–380	143	30	32	4
POX-900Pt	61.6	3.3	280–350	147	31	31	4
POX-500Pt	3.2	3.1	280–390	153	31	72	13
BV46Pt	8.1	2.6	300–400	129	27	125	24

Importantly, the TOF_H of POX-500Pt is around 20-fold lower than that of POX-900Pt, despite the similar surface area and pore texture of the supports (Table 1) and the similar mean Pt particle size of the catalysts (Table 2). A major difference between the carbon aerogels carbonized at 500 and 900 °C was the greater degree of aromatization of the carbon structure in the latter. Thus, the full width at the half maximum of the $\text{C}_{1\text{s}}$ graphite XP peak at 284.6 eV decreases as the heat treatment increases from 500 to 1500 °C due to the loss of oxygen atoms and to a certain ordering of the aromatic structure of the graphene layers of the carbon aerogel [7].

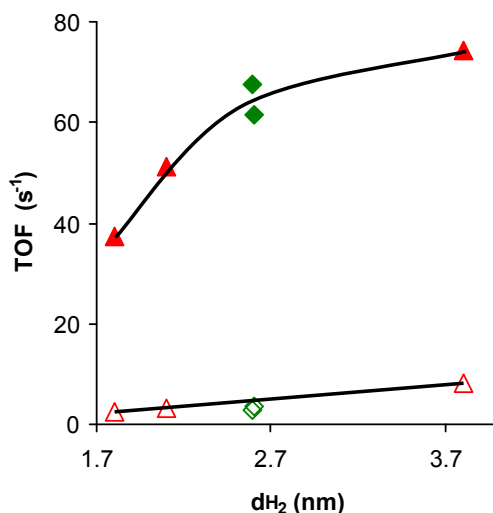
According to this finding, the higher the aromatization degree of the carbon aerogel, the higher is the TOF_H of supported Pt catalyst. One explanation may be an electronic transfer between the support and Pt particles that would facilitate the cracking of the chemisorbed alkane (see below). A further possible explanation for the difference in TOF_H and TOF_I values is that Pt particles supported on carbon aerogels obtained at 900–950 °C develop preferentially low-index Pt surfaces. Thus, it has been shown [12] that the more open Pt(100) surfaces are more active for the hydrogenolysis of *n*-butane than the close-packed Pt(111) surfaces, by one order of magnitude.

The TOF_H and TOF_I values of catalyst BV46Pt are of the same order of magnitude as published findings for other Pt catalysts supported on activated carbons [1]. The difference in aromatization degree between carbon aerogels obtained at high temperature and activated carbons may also account for this behavior.

The relationships of TOF_H and TOF_I with mean Pt particle size are depicted in Figure 5 for catalysts supported on carbon aerogels prepared at 900–950 °C. TOF_H shows a large increase with d_{H_2} up to around 2.7 nm in size, being more moderate this increase for higher sizes up to around 4 nm. However, TOF_I shows a linear increase throughout the studied d_{H_2} range although less markedly in comparison to TOF_H . Hydrogenolysis in the above catalysts appears to be sensitive to the catalyst structure, at least up to a mean Pt particle size of 2.7 nm. However, TOF_I showed a lesser variation in the studied particle size range, and the sensitivity of this reaction to the catalyst structure is less clear. These results differ from findings for Pt catalysts supported on activated carbons [1], which showed that TOF_H linearly increased with smaller mean Pt particle size and that TOF_I was not sensitive to variations in Pt particle

size within the range studied (2.1–13.5 nm). This could be attributable to the above commented differences in surface chemistry between carbon aerogels and activated carbons.

Figure 5. Relationship of TOF_H , closed symbols and TOF_I , open symbols at 320 °C with the mean Pt particle size for catalysts supported on carbon aerogels obtained at 900 °C, ● and 950 °C, ▲.



Arrhenius plots were used to calculate the apparent activation energy for hydrogenolysis $E_a(\text{H})$ and isomerization $E_a(\text{I})$ and the corresponding pre-exponential factors ($\ln A$). Figure 6 shows a typical example of such plots for catalyst POX-900Pt. The numbers for the experimental points indicate the order in which they were determined and there is a good agreement for data obtained in increasing and decreasing temperature cycles. This is a good indication of the fact that in the experimental procedure followed the Pt surface is clean in each activity measurement and that there is no deactivation of the catalyst.

Figure 6. Arrhenius plot for catalyst POX-900Pt: □, hydrogenolysis; △, isomerization.

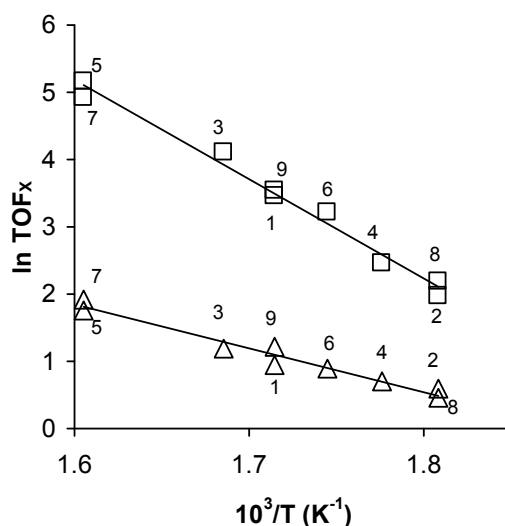
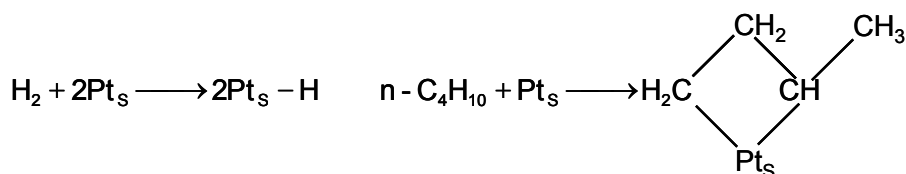


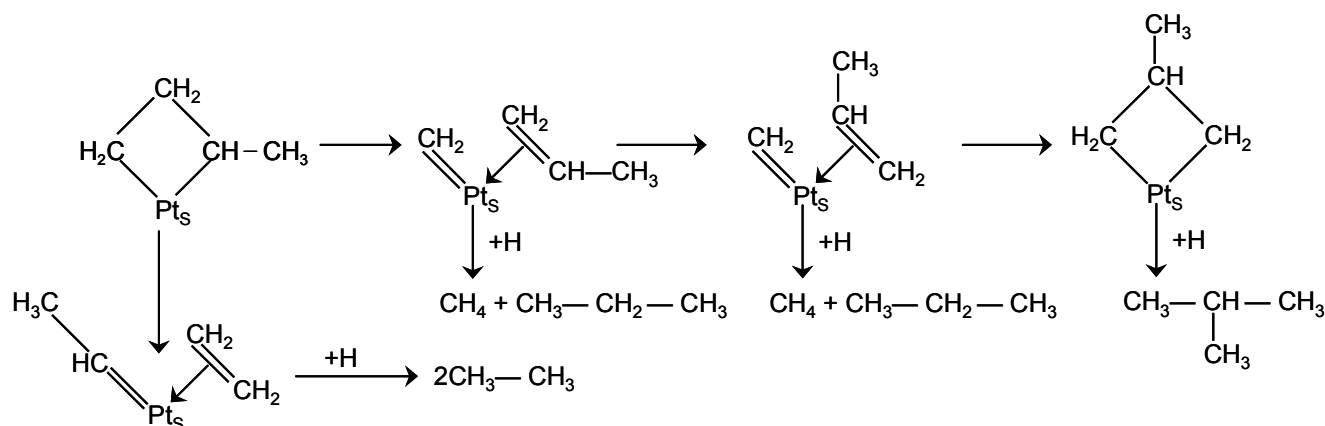
Table 4 shows the apparent activation energies and corresponding pre-exponential factors obtained in the temperature range indicated in that Table. $E_a(\text{H})$ was higher than $E_a(\text{I})$ for all catalysts supported on carbon aerogels, whereas both activation energies were equal for catalyst BV46Pt in agreement with findings for Pt catalysts supported on activated carbons [1].

Several models have been proposed for hydrogenolysis reactions over metal catalysts [3], but the following general reaction mechanism, that would also explain the isomerization, is widely accepted.

Step 1. Dissociative dihydrogen chemisorption and dehydrogenative chemisorption of the alkane.



where Pt_s is a surface Pt atom. The formation of this 1,3 diasorbed dehydrogenated alkane intermediate has been postulated for the hydrogenolysis of saturated hydrocarbons on Pt [1].



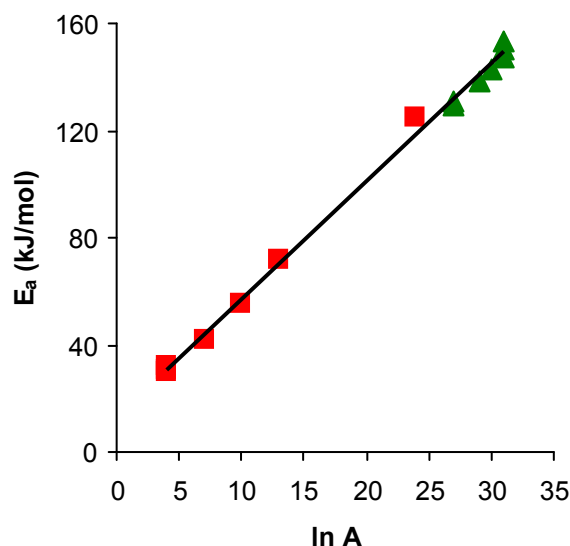
Steps 2 and 3. Fragmentation and rearrangement of the dehydrogenated species, and rehydrogenation and desorption of the product.

The plot of E_a against $\ln A$ for both the hydrogenolysis and isomerization reactions and for all catalysts is shown in Figure 7, and indicates a good compensation effect (correlation coefficient, $R^2 = 0.997$). This compensation effect has been observed for alkane hydrogenolysis over Pt catalysts [2,3] and other metals [14] and in other systems [15,16]. An interesting observation is that the isomerization reaction lies on the same compensation effect plot as the hydrogenolysis reaction. This means that both reactions have a common intermediate, *i.e.*, the dehydrogenated alkane formed in *Step 1*. Thus, rearrangement of the η^2 -propene intermediate in *Step 2* could yield isobutane.

The above hydrogenolysis mechanism may also explain the higher TOF_H value of Pt catalysts supported on carbon aerogels obtained at 900–950 °C in comparison to those obtained at 500 °C. The π -olefin complexes in *Step 2* are formed by a dative π -bond from the hydrocarbon to empty d-orbitals of Pt and a retrodonating π -bond from the filled d-orbitals to the empty π^* antibonding orbital of the olefin, and the two bonds reinforce each other by a synergic mechanism. Therefore, an increase in the aromatization degree of the support would increase the electronic density on the supported Pt particles,

leading to an increase of the retrodonating π -bond, and making easier the formation of the above π -olefin complexes, and therefore, the cracking of the chemisorbed dehydrogenated *n*-butane.

Figure 7. Relationship between E_a and $\ln A$ for the hydrogenolysis ($\blacktriangle$) and isomerization ($\blacksquare$) of *n*-butane.



3. Experimental Section

Supports used were the carbon aerogels CA1, CA2, CA3, P3-900, POX-500, and POX-900. Table 5 compiles the ingredients used in the preparation of the organic hydrogels.

Table 5. Organic aerogel recipes (Formaldehyde, 0.224 mol).

Sample	Resorcinol (mol)	Pyrocatechol (mol)	Catalyst precursor (mol)	Solvent (mL)
CA1	0.112	-	1.4×10^{-4} K ₂ CO ₃	H ₂ O (27)
CA2	0.112	-	1.4×10^{-4} K ₂ CO ₃	H ₂ O-MeOH ^a (24-3)
CA3	0.112	-	1.4×10^{-4} K ₂ CO ₃	H ₂ O-THF ^a (24-3)
P3	-	0.112	2.1×10^{-2} H ₃ BO ₃	H ₂ O (26.7)
POX	-	0.112	2.0×10^{-4} H ₂ C ₂ O ₄	H ₂ O (26.7)

^a MeOH and THF are methanol and tetrahydrofurane, respectively.

Subsequently, they were dried with supercritical CO₂ and carbonized in N₂ flow at 500 °C (POX-500), 900 °C (P3-900 and POX-900) and 950 °C (CA1, CA2 and CA3). Details of the preparation of all these samples were previously reported [6,7]. The activated carbon BV46 was also used as support. This sample was prepared from olive stones after carbonization in N₂ flow at 900 °C and steam activation at 850 °C to 46% burn-off [8]. Characterization of the supports was carried out by N₂ adsorption at −196 °C, mercury porosimetry and immersion calorimetry into benzene at 30 °C.

Supported Pt catalysts were prepared by impregnation of the supports with an aqueous solution of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ to yield Pt catalysts with a metal loading of 2 wt.%, referred to by adding Pt to the name of the carbon aerogel. Exact total Pt content (Pt_{tot}) of supported catalysts was obtained by burning them off at 800 °C in air and weighing the residue. The supported catalysts were pre-treated in He flow, 60 cm^3/min , at 400 °C for 12 h before their characterization by H_2 chemisorption, transmission electron microscopy (TEM) or X-ray photoelectron spectroscopy (XPS) as explained in detail elsewhere [6]. Platinum dispersion, D , and its average particle size, d , were obtained from the H_2 uptake, assuming that one H atom was chemisorbed by one surface Pt atom and that $d_{\text{H}_2}(\text{nm}) = 1.08/D$. Particle size distributions (PSDs) were obtained analyzing different TEM micrographs from which the dispersion and average particle size were also calculated.

The $n\text{-C}_4\text{H}_{10}/\text{H}_2$ reaction was studied in a glass plug-flow microreactor, using 1 g of catalyst at a temperature between 260 and 390 °C depending on the supported catalyst in question, and following the experimental procedure described in reference [1]. Before the reaction, catalysts were pre-treated in the same reactor at 400 °C in He flow for 12 h. Subsequently, samples were cooled in He flow at the reaction temperature and the He flow was switched to an $n\text{-C}_4\text{H}_{10}/\text{H}_2$ flow, 60 cm^3/min , with a 1/10 molar ratio. Gases from the reactor were analyzed on-line by using a Varian model CP-3800 gas chromatograph with a Chromosorb 102 column. To reach steady-state conditions in the reactor, the reactant gases were flowed through the catalysts for 20 min before analyzing the reaction products; after the analysis only H_2 was flowed through the catalysts for 20 min in order to regenerate and clean the Pt surface; after this process the $\text{C}_4\text{H}_{10}/\text{H}_2$ mixture was again introduced into the reactor in order to study the reaction at different temperatures. The reactor was operated at atmospheric pressure, and the conversion was kept below around 16%.

Catalytic activity measurements for hydrogenolysis and isomerization are reported as the TOF, defined as the number of molecules reacting per surface metal atom per second, and calculated from Equation (1):

$$\text{TOF}_X = \frac{0.74 \times P_X \times F_{n\text{-C}_4\text{H}_{10}}}{W \times 2 \times Q_{\text{H}_2}} \quad (1)$$

where TOF_x is the turnover frequency for hydrogenolysis (TOF_H) or isomerization (TOF_I) in s^{-1} ; P_x is the proportion of n -butane undergoing hydrogenolysis (P_H) or converted to isobutane (P_I); $F_{n\text{-C}_4\text{H}_{10}}$ is the n -butane flow rate (cm^3/min); W is the weight of catalyst (g); Q_{H_2} is the dihydrogen uptake ($\mu\text{mol/g}$), multiplied by two because dihydrogen is dissociatively chemisorbed on two surface Pt atoms; and 0.74 is the conversion factor (cm^3/min to $\mu\text{mol/s}$).

4. Conclusions

Mean Pt particle size linearly decreased when the mesopore volume of the support increased within the range studied. Pt catalysts showed single hydrogenolysis. TOF_H was much higher than TOF_I in the catalysts prepared with carbon aerogels obtained at 900–950 °C. However, TOF_H was lower and similar to TOF_I in catalysts supported on carbon aerogels obtained at 500 °C and on the activated carbon. These results might be explained by the different degree of aromatization of the supports or by the development of Pt surfaces with different indexes.

Hydrogenolysis reaction with Pt catalysts supported on carbon aerogels obtained at 900–950 °C appeared to be structure sensitive, at least up to a Pt particle size of 2.7 nm. However, it was less clear whether the isomerization reaction with these catalysts was structure sensitive.

There was an evident compensation effect between the apparent activation energy and the pre-exponential factor, which was common to both hydrogenolysis and isomerization reactions, indicating that both reactions had the same intermediate.

Acknowledgments

Authors are grateful to MICINN and FEDER, project CTM2010-18889, for financial support.

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