Activated-carbon-heterogenized $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ for the selective hydrogenation of 1-heptyne

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The complex $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ has been heterogenized on two different activated carbons and tested as a catalyst for the semihydrogenation of 1-heptyne. The results are compared with those previously reported with the γ-Al_2O_3-supported complex. An important effect of the support porosity has been found. The location of the complex in the narrow pores induces shape selectivity. The effect of the support in concentrating the substrate close to the active species has been observed. A very active and selective catalyst has been prepared using an essentially microporous carbon.

KEY WORDS: 1-heptyne hydrogenation; metal complexes; heterogeneous catalysis; activated carbon.

1. Introduction

The homogeneous semihydrogenation of alkynes has special interest from an academic and industrial point of view. Many products obtained through this kind of reaction are useful in the synthesis of natural products, such as compounds presenting biological activity [1]. In these cases, avoiding overhydrogenation to single bonds is also recognized as a key feature. One of the most studied catalytic systems is the Lindlar catalyst ($Pd/CaCO_3$ modified with $Pb(OAc)_2$) developed several decades ago. Since then, other catalysts have been presented in the literature. Among them are metallic and bimetallic catalysts [1–5]. Other authors have investigated transition metal complexes, which have become increasingly important, not only as homogeneous catalysts [6–10] but also as supported ones as well [11–14]. They exhibit some outstanding characteristics such as activity and selectivity values higher than those obtained with the Lindlar catalyst and also with metal complexes used in homogeneous conditions, even working under mild operational conditions [12]. The supported complexes present obvious advantages inherent to heterogeneous catalysis: on the one hand they can be easily separated from the reaction media and, on the other hand, better tailoring is possible by control of the size and packing of the catalytically active particles.

In a previous paper [15] the catalytic activity of the $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ complex (Pd(TDA)) was studied for the semihydrogenation of 1-heptyne to 1-heptene under mild conditions, in the homogeneous and heterogeneous phase using alumina as the support. The results showed that by supporting this complex on γ-Al_2O_3 it is possible to obtain a heterogeneous catalyst that is more active and selective for the 1-heptyne hydrogenation to 1-heptene than the classic Lindlar catalyst. Under the same operational conditions, the γ-Al_2O_3-supported Pd(TDA) complex is also more active and selective than the same complex in the homogeneous phase. As determined by Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS), the active species is the complex itself, which is stable under the reaction conditions.

Activated carbons have also been used as the support for Pd(TDA) to prepare catalysts for the cyclohexene hydrogenation [16–18]. The carbon-supported catalysts were more active and sulfur resistant than the γ-Al_2O_3-supported catalysts. The obtained results showed, as well, that complex leaching does not take place under the reaction conditions [18], nor after a treatment of 100 h in pure toluene under the usual operational conditions for 100 h [16].

Considering the hydrogenation of 1-heptyne, the location of the active phase (the complex) in the porous network of the support could increase the selectivity to the planar double bond end of the 1-heptene molecule, which can also be enhanced by a certain shape of the pores. In this sense, activated carbons have the advantage of slit-shaped pores.

On this basis, the palladium complex Pd(TDA) has been anchored on two activated carbon supports with differences in pore size distribution. The aim of this

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work is to analyze the catalytic activity and selectivity of these catalysts for the selective hydrogenation of 1-heptyne to 1-heptene under mild conditions. The obtained results are compared with those of the alumina-supported Pd(TDA) complex catalyst.

2. Experimental

2.1. Supports

Two pelletized commercial carbons (RX-3 and GF-45, from NORIT) were used as the supports. For comparative purposes, γ-Al_2O_3 (Ketjen CK 300), pellets of 3 mm in length and 1.5 mm in diameter were also used as support after calcination in air at 773 K for 3 h.

The porosity of the supports was characterized by physical adsorption of N_2 (77 K) and CO_2 (273 K). Gas adsorption is useful to calculate specific surface area and pore volume. The use of both adsorptives (N_2 and CO_2) allows one to estimate the pore volume distribution of pores up to about 7.5 nm in diameter [19]. By applying the Dubinin–Raduskevich equation to the CO_2 adsorption isotherm at 273 K, the volume of micropores with a diameter less than 0.7 nm (V_{micro}) can be obtained. On the other hand, the volume of supermicropores (V_{sm}), diameter ranging from 0.7 to 2 nm, is obtained by subtraction of V_{micro} from the volume calculated by applying the Dubinin–Raduskevich method to the N_2 adsorption isotherm at 77 K [19]. The volume of mesopores with diameter between 2 and 7.5 nm was calculated from the N_2 adsorption isotherm at 77 K. In this respect, the volume of gas adsorbed between 0.2 and 0.7 relative pressure corresponds to the mesopore range of porosity. The wider porosity, macropores (V_{macro}) and part of the mesopores (with diameter from 7.5 to 50 nm), was determined by mercury porosimetry, using a Carlo Erba 2000 porosimeter. This equipment reaches a maximum pressure of 196 MPa, which allows one to estimate the volume of pores with a diameter greater than 7.5 nm. The addition of the mesopore volumes determined from the N_2 adsorption isotherm and by mercury porosimetry gives the total mesopore volume (V_{meso}) [19]. Finally, with the BET equation applied to the N_2 adsorption isotherm at 77 K it is possible to evaluate the specific surface area.

2.2. Catalysts

The complex synthesis and preparation of the catalysts were fully described in a previous publication [16]. In summary, the complex was synthesized by reaction of $PdCl_2$ with tridecylamine in toluene in glass equipment under a purified Ar atmosphere ($T = 338$ K). The final purification of the complex was made by column chromatography. The heterogenization of the Pd complex was carried out by means of the incipient wetness technique [16]. A solution of the palladium complex in toluene was used to obtain a catalyst containing 0.3 wt% Pd.

The pure and the heterogenized complex were characterized by XPS. Determinations were carried out using a Shimadzu ESCA 750 electron spectrometer coupled to a Shimadzu ESCAPAC 760 data system. A detailed description of the conditions and procedures has been published elsewhere [17].

2.3. Catalytic determinations

Catalytic performance was determined for the selective hydrogenation of 1-heptyne to 1-heptene using a 2% (v/v) solution of 1-heptyne in toluene with an H_2 pressure of 150 kPa. The reaction was carried out at $T = 303$ K in a batch stainless steel stirred tank reactor ($V = 100$ ml; stirring velocity = 600 r.p.m.). Both the reactor and the stirrer were polytetrafluoroethylene (PTFE) coated in order to avoid possible contamination of the reaction media with metal cations. The weight of the supported complex catalyst was 0.075 g in every case.

The possibility of diffusional limitations in the catalytic tests was investigated following procedures described in the literature [20,21]. Experiments were carried out at different stirring velocities in the range 180–1400 r.p.m. The constancy of the activity and selectivity above 500 r.p.m. ensured that external diffusional limitations were absent at the rotary speed selected. On the other hand, to ensure that the catalytic results were not influenced by intraparticle mass transfer limitations, the heterogenized complex catalyst was crushed up to a quarter of the original size. Then, several runs using the crushed complex catalyst were carried out. In every case, the conversion and selectivity values obtained were the same as those corresponding to the catalyst that was not crushed. Hence, it may be concluded that internal diffusional limitations were absent under the operational conditions of this work.

Reactants and products were analyzed by gas chromatography using a FID detector and a CP Sill 88 capillary column. All runs were carried out in triplicate; the relative experimental error was about 3%.

3. Results and discussion

Table 1 presents the BET surface area and the pore volumes (V_{micro}, V_{sm}, V_{meso} and V_{macro}) calculated as described in section 2. The activated carbons are mainly microporous solids with a large proportion of pore volume in the range of micro- and supermicropores. Comparing the two activated carbons, GF-45 has a wider pore size distribution and presents a larger supermicro- and mesoporous contribution, the so-called transport pores. γ-Al_2O_3 is a mesoporous solid with a poor contribution of micro-, supermicro- and macropores.

Table 1
BET surface area and pore volumes of the supports

Sample	S_{BET} ($m^2 g^{-1}$)	V_{micro} ($ml g^{-1}$)	V_{sm} ($ml g^{-1}$)	V_{meso} ($ml g^{-1}$)	V_{macro} ($ml g^{-1}$)
RX-3	1411	0.356	0.333	0.098	0.430
GF-45	1718	0.345	0.498	0.449	0.400
γ-Al_2O_3	180	0.048	0.030	0.487	0.094

Table 2
Pd $3d_{5/2}$, N $1s_{1/2}$ and Cl $2p$ peak binding energies for the pure palladium complex and the same complex supported on activated carbons RX-3 and GF-45 and on γ-Al_2O_3, before and after catalytic evaluation

Sample	State	Binding energy (eV)		
		Pd $3d_{5/2}$	N $1s_{1/2}$	Cl $2p$
Pure Pd(TDA)	Fresh	338.2	401.9	198.3
Pd(TDA)/RX-3	Fresh	338.4	401.9	198.2
	Used	338.3	402.0	198.3
Pd(TDA)/GF-45	Fresh	338.2	401.9	198.0
	Used	338.3	401.8	198.1
Pd(TDA)/γ-Al_2O_3	Fresh	338.3	401.7	198.2
	Used	338.2	402.0	198.1

Table 2 includes the binding energies (BEs) corresponding to Pd $3d_{5/2}$, N $1s_{1/2}$ and Cl $2p$ for the pure palladium complex and the complex supported on carbons RX-3 and GF-45 and on alumina, before and after catalytic evaluation. It can be observed that the binding energies in the pure complex and in the complex supported on carbon and on alumina, before and after catalytic use, were almost the same. Pd $3d_{5/2}$ peak corresponds to palladium (II) [22]. The position of the N $1s_{1/2}$ and Cl $2p$ peaks corresponds, in every case, to nitrogen in an amine and to chlorine as chloride species, respectively [22], in accordance with the theoretical electronic state that could be expected for the complex under study.

Figure 1 shows the course of reaction (concentration (wt%) of reactants and products vs. time) for the palladium complex supported on both carbons and alumina. The reaction profile of 1-heptyne selective hydrogenation follows the typical behavior of a consecutive reaction. In all cases 1-heptyne was initially converted to 1-heptene. No substances other than 1-heptyne, 1-heptene and heptane were detected in the reactant solutions in any of the experiments carried out. Previous results [15], comparing the behavior of the Pd(TDA) complex in the homogeneous phase and supported in the mesoporous γ-Al_2O_3, allow one to conclude that the support exerts a positive effect in the total conversion and in the selectivity to the semihydrogenated product. Now the effect of support properties will be analyzed.

As can be observed in figure 1, activated-carbon-supported Pd(TDA) catalysts reach a slightly higher

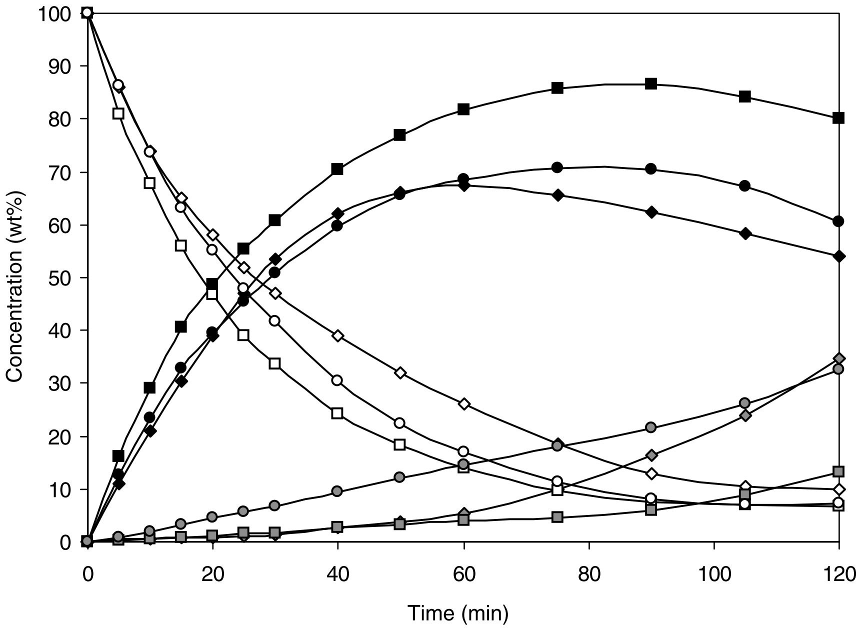

Figure 1. Course of reaction for the palladium complex anchored on different supports; $P = 150$ kPa, $T = 303$ K. RX-3: (□) 1-heptyne, (■) 1-heptene, (■) heptane; GF-45: (○) 1-heptyne, (●) 1-heptene, (●) heptane; γ-Al_2O_3: (◇) 1-heptyne, (◆) 1-heptene, (◆) heptane.

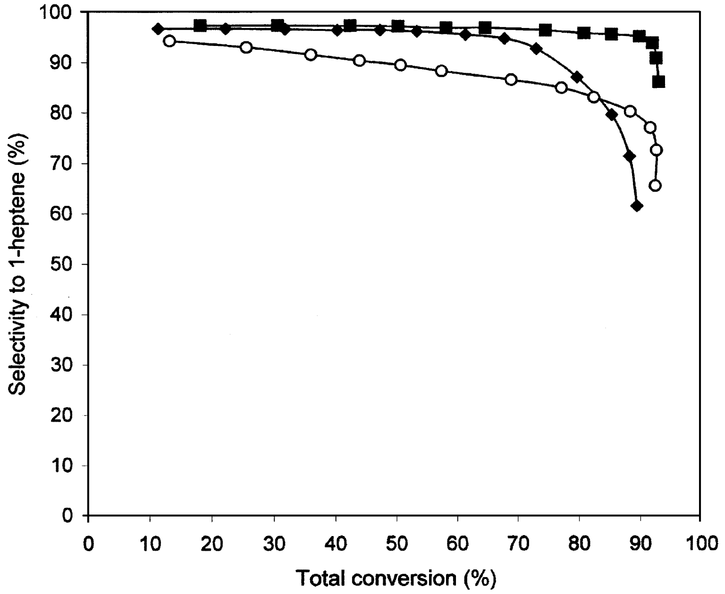

Figure 2. Selectivity to 1-heptene as a function of the 1-heptyne total conversion for [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] supported on RX-3 (■), GF-45 (○) and γ-Al_2O_3 (◆).

1-heptyne conversion than the γ-Al_2O_3-supported one and, at high conversion levels, the differences between the catalytic behavior of the three catalysts under study are more important.

In the case of Pd(TDA)/GF-45, heptane production became significant almost at the beginning of the reaction. However, in the case of Pd(TDA)/RX-3 and Pd(TDA)/γ-Al_2O_3 the production of heptane is much slower. The 1-heptene curves show a maximum at a certain time (between 50 and 90 min, depending on the sample), which means that from this time the conversion of 1-heptene to heptane becomes more important. After 120 min reaction time, the 1-heptene to heptane mass ratio was about 6.0/1 for Pd(TDA)/RX-3, 1.9/1 for Pd(TDA)/GF-45 and 1.6/1 for Pd(TDA)/γ-Al_2O_3. Hence, the palladium complex supported on RX-3 presents a higher selectivity to semihydrogenation than the same complex supported on GF-45 and on alumina. At the maximum conversion of 1-heptene the ratio is even higher.

The selectivity to 1-heptene, displayed in figure 2 as a function of the 1-heptyne total conversion, also demonstrates the better catalytic behavior of Pd(TDA)/RX-3. The selectivity for Pd(TDA)/RX-3 remained constant and very high up to a total conversion of about 92%; meanwhile for Pd(TDA)/γ-Al_2O_3 it began to decrease at a total conversion of 68%. For Pd(TDA)/GF-45 there is a continuous decrease in the selectivity from the start of the reaction; at the final total conversion of 93% the selectivity decreased markedly to 65%.

Finally, from the results presented in figures 1 and 2, it can be concluded that the palladium complex supported on carbon RX-3 presents a final total conversion and selectivity for the 1-heptyne hydrogenation to 1-heptene higher than Pd(TDA)/γ-Al_2O_3 and Pd(TDA)/GF-45.

The higher selectivity to 1-heptene could be a consequence of a shape selectivity induced by the porous supports. This may be because the 1-heptene molecule has a planar end, unlike of the more voluminous end of the fully saturated heptane. If the active species is located in a narrow zone, the formation of heptane will be hindered. On the other hand, if the porosity of the support enhances a higher concentration of 1-heptene in the neighborhood of the metal complex, the consecutive hydrogenation of 1-heptene to heptane will be favored. In relation to these possibilities, a deeper analysis of the porosity of the supports and the heterogenized catalysts used in this work would help in the interpretation of the catalytic results obtained.

In a previous study [16] a considerable decrease in the supermicropore volume of the activated carbon supports, after metal complex impregnation, was observed; the mesopore volume, however, remained almost unchanged. From those results, it was concluded that the metal complex is adsorbed in the supermicropore porosity range. The suppression of this range of pore volume upon impregnation for samples Pd(TDA)/RX-3 and Pd(TDA)/GF-45 is, in absolute terms, 0.333 and 0.257 ml g^{-1}, respectively. In the case of Pd(TDA)/RX-3 this represents a complete suppression of the supermicropore volume (table 1), while for Pd(TDA)/GF-45 there is still a relatively large remaining supermicropore volume (of 0.241 ml g^{-1}). Considering that in both cases the amount of complex introduced is the same, the mentioned data reveal some differences in the structure of the supermicroporosity of both carbon materials. Because in carbon RX-3 the supermicroporosity is completely blocked, it can be suggested that in this carbon, the supermicroporosity is, in general terms, narrower. Also, the much larger mesopore contribution in activated carbon GF-45 should be considered.

As a summary, the higher 1-heptyne conversions on heterogenized Pd(TDA) compared with the homogeneous-phase reaction may be attributed to the higher concentration of reactants on the support surface produced by their adsorption. The unsaturated and saturated hydrocarbon adsorption is favored on activated carbons in comparison with γ-Al_2O_3. The hydrogenation of 1-heptene from the beginning of the reaction on Pd(TDA)/GF-45 is probably due to the presence of some complex in pores of a particular size (larger supermicropores). This fact favors a high concentration of the alkene close to the active site, thus causing olefin hydrogenation to occur. With Pd(TDA)/RX-3, however, the formation of the alkane is strongly impeded due to the location of the complex in the narrow porosity and because of that the catalyst is also selective at a high total conversion.

4. Conclusions

The results reported in this paper show the effect of the activated carbon support properties on the activity and selectivity to 1-heptene in the 1-heptyne semihydrogenation reaction.

The support has a positive effect on 1-heptyne conversion as a consequence of the substrate concentration, with respect to the bulk solution, in the neighborhood of the active species. The support porosity may enhance the selectivity to the alkene if the complex is located on the narrow porosity that induces shape selectivity due to the slit-shaped pores. In activated carbons with wider pore size distribution, a negative effect in selectivity appears when the complex is anchored on larger pores.

With carbon RX-3, an essentially microporous carbon (with about 50% of the porosity in the supermicropore range), the heterogenized Pd(TDA) complex is a very active and highly selective catalyst for the semihydrogenation of 1-heptyne.

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