Highly active catalyst from $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ on $NH_4ZSM\text{-}5$

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A palladium catalyst highly active for the cyclohexene hydrogenation has been obtained by heterogenisation of $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ on zeolite $NH_4ZSM\text{-}5$. TOF is more than twenty times higher than for the homogeneous catalyst or the activated carbon heterogenised complex. Changes in the electronic state of palladium have been observed by XPS analysis. Palladium reduction is produced upon heterogenisation on the $NH_4ZSM\text{-}5$ zeolite.

KEY WORDS: palladium–amine complex; heterogenisation; zeolite; hydrogenation

1. Introduction

Catalysts separation from products is a key challenge in homogeneous catalysis for commercial processes [1]. A feasible solution is the heterogenisation of the catalysts (usually metal complexes) on solid supports. A good example has been shown in previous work, in which the catalytic activity of the $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ complex (named Pd(TDA)) was tested for the cyclohexene hydrogenation in homogeneous form and heterogenised on alumina and on activated carbon [2–6]. The heterogenised complex was effectively anchored on the supports, showing catalytic properties similar or even better than those of the homogeneous catalyst [4,5] with the advantage of an easy recovery from the reaction media. Pd(TDA)/γ-Al_2O_3 was also found to be more active than the classical Pd heterogeneous catalysts (Pd on γ-Al_2O_3) for the styrene hydrogenation [2]. Comparing γ-Al_2O_3 and activated carbon as supports, a better catalytic performance was found with the carbon heterogenised complex [4,5].

In relation with the heterogenisation process, it has been recently reported [7] that transition metal complexes encapsulated in the cavities of zeolites and mesoporous materials usually show enhanced catalytic activity, compared to the "neat" complexes.

In the present publication, preliminary results on the heterogenisation of the Pd(TDA) complex on zeolite $NH_4ZSM\text{-}5$ are presented. The objective is to study the behaviour of this system as a hydrogenation catalyst and to compare it with a previously reported catalyst based on activated carbon (a commercial one named GF-45) [4,6]. Also, the Wilkinson's catalyst has been used as a reference in homogeneous conditions.

2. Experimental

The $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ complex was prepared by reaction of $PdCl_2$ with $CH_3(CH_2)_{12}NH_2$ in toluene, as previously reported [4]. The Wilkinson's complex used was a commercial product (Sigma-Aldrich). The zeolite $NH_4ZSM\text{-}5$ was synthesised by the conventional hydrothermal procedure and calcined at 550 °C for 6 h [8]. Ammonium exchange was carried out three times using a NH_4NO_3 1 M solution overnight. The zeolite was characterised by XRD and DRIFTS which confirmed that the desired highly crystalline material was selectively prepared [8].

The complex was anchored on the zeolite by incipient wetness impregnation using a toluene solution of the appropriate concentration to obtain a Pd loading of 0.3 wt%. The sample was dried overnight at 80 °C [4]. The resulting catalyst was named Pd(TDA)/NZ.

The textural properties of the support and the heterogenised sample were characterised by gas adsorption (N_2 at 77 K). To study the effect of the solvent on the pore structure, the support was also characterised after impregnation with toluene. The samples were previously degassed overnight at 80 °C in a high vacuum system.

The pure and the heterogenised complex were analysed by DRIFTS. The spectra (between 600 and 4000 cm^{-1}) were collected in a ATI Mattson Infinity Series equipment using the diffuse reflectance method. KBr was used as background and diluting agent, and N_2 as purge gas.

The electronic state of Pd, N, Cl, O and their atomic ratios in the supported (fresh and used) and unsupported metal complex were studied by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained with a VG-Microtech Multilab electron spectrometer, using the Mg K_α (1253.6 eV) radiation of twin anode in the constant analyser energy mode with pass energy of 50 eV.

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The cyclohexene hydrogenation was selected as test reaction. Catalytic activity determinations were carried out in a 300 ml stainless-steel stirred tank reactor (Autoclave Engineers) operated at 353 K and with a stirring velocity of 600 rpm. A hydrogen pressure of 1 MPa, 100 ml of a solution of 5 vol% cyclohexene in toluene and 0.1 g of catalyst were employed. In the homogeneous experiment, a similar amount of the metal complex present in the heterogeneous test was dissolved in the cyclohexene–toluene solution. The hydrogenation reaction was carried out for 1 h. Reactants and products were chromatographically analysed using a HP-6890 equipment with a FID detector and a HP-1 capillary column.

3. Results and discussion

Table 1 presents the cyclohexene conversion (expressed as turnover frequency (TOF), mol olefin converted per mol Pd per hour) after 1 h reaction time, for the Pd(TDA)/NZ catalyst and the other samples analysed for comparative purposes. The Pd(TDA)/NZ sample shows a catalytic activity highly enhanced compared to the homogeneous catalyst and the activated carbon supported sample. It is even more active than the Wilkinson's complex (a well-known active homogeneous catalyst for the reduction of olefins).

Using active carbon as support, no modification of the Pd(TDA) complex was observed after heterogenisation [4,6]. In the present case, however, the noticeable increase in catalytic activity found for the zeolite based catalyst suggests that some structural changes could have taken place. Trying to elucidate such possible modifications, the characterisation by several techniques (N_2 adsorption, DRIFTS and XPS) has been conducted.

Data on the micropore volume (applying the DR method) of the NZ zeolite, the Pd(TDA)/NZ catalyst and the zeolite impregnated with toluene are shown in table 2. Analogous data corresponding to the activated carbon sample are also included [4]. It can be observed that the effect of the complex heterogenisation on the porosity is quite different for the two supports. Although the pore volume decrease is larger for the activated carbon, the relative variation is similar in both supports. Data show that an important reduction in the pore volume is due to the adsorption of toluene. However, the complex adsorption has also a noticeable effect on the micropore volume, which suggests that the complex adsorbs not only on the external surface of the support, but it is, in both cases, strongly adsorbed in the micropores.

Table 1
Catalytic activity: expressed as turnover frequency (mol C_6H_{10} converted (mol Pd(TDA))$^{-1}$ h^{-1}).

	Pd(TDA)/NZ	Pd(TDA)	Pd(TDA)/GF-45	Wilkinson's catalyst
TOF	12494	550	576	7375

Table 2
Specific surface area and pore volume.

	V_m[a] (cm^3/g)	ΔV[a] (cm^3/g)
NZ	0.137	–
Tol/NZ	0.051	−0.086
Pd(TDA)/NZ	0.024	−0.113
GF-45	0.843	–
Tol/GF-45	0.439	−0.404
Pd(TDA)/GF-45	0.325	−0.518

[a] Applying DR method.

The size estimated for the Pd(TDA) complex is 4 nm long (by the long aliphatic chains of the amine ligand), 0.6 nm broad and 0.3 nm high (the maximum breadth and height on the Pd coordination sphere) [4], the maximum diameter of the aliphatic chains being about 0.3 nm. The pore diameter of the NH_4ZSM-5 zeolite cavities is about 0.55 nm. This means that the adsorption of the Pd(TDA) complex on this zeolite can only occur by partial adsorption of the aliphatic chains of the amine ligand into the pores and the Pd coordination sphere must remain on the external surface.

The comparison of the DRIFTS spectra of the pure complex, the zeolite and the heterogenised complex allows the following observations: (i) heterogenisation produces no variations in the IR spectrum of the zeolite, and (ii) weak bands appear at 2850–3000 cm^{-1} corresponding to the metal complex, specifically to the C–H aliphatic tensions of the TDA ligands, that are the strongest bands on the Pd(TDA) IR spectrum. Consequently, it can be concluded that the aliphatic chains of the ligands do not change upon heterogenisation. A similar observation was found for the carbon-heterogenised complex [6].

Table 3 presents the Pd $3d_{5/2}$, N $1s_{1/2}$ and Cl 2p binding energies (BE) and the atomic ratios N/Pd, Cl/Pd and Pd/O. Important differences can be observed in the state of Pd after the heterogenisation and the utilization of the Pd(TDA)/NZ catalyst in the cyclohexene hydrogenation. As expected, the position of the N $1s_{1/2}$ and Cl 2p peaks for the pure metal complex corresponds to nitrogen in an amine and to chloride species, respectively [9]. As previously reported [4], the N/Pd and Cl/Pd molar ratios found for the homogeneous catalyst are those corresponding to the theoretical stoichiometry of the $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ molecule. However, in the fresh heterogenised complex, palladium is partially reduced. About half of the total amount is in the zero valence state, but corresponding to complexed Pd^0 [9]. Palladium could have been reduced by the NH_4^+ ions of the zeolite surface. The Pd^{II} state shows, compared to the unsupported complex, a slight decrease in the BE, while the Cl^- species increases its BE (decrease in the electronic density) by 1.1 eV. This variation can be the average result of Cl bonded to Pd^{II} and free Cl^- (related with the Pd reduction) on the support surface, not distinguishable in the XPS spectra. This result and the slight decrease in the BE of Pd^{II} can also suggest an increase in the covalent character of the Pd–Cl bond. Nitrogen is found as NH_4^+ ion, from the NH_4ZSM-5 support and as $–NH_2$, from the complex. Whereas in the pure complex the Cl/Pd and the N/Pd molar ratios are those

Table 3
XPS data for Pd(TDA) and Pd/NZ samples.

	BE (eV)					Atomic ratios (at/at)		
	Pd[a]		Cl	N		N/Pd[b]	Cl/Pd	Pd/O
	Pd^0	Pd^{II}	Cl^-	$-NH_2$	NH_4^+			
Pd(TDA)	–	337.7	198.0	399.6	–	1.94	2.00	–
Pd(TDA)/NZ fresh	335.6 (52%)	337.4 (48%)	199.1	400.0	402.4	2.41	2.57	5.3×10^{-4}
Pd(TDA)/NZ used	335.2 (67%)	337.7 (33%)	–	–	402.4	–	–	5.2×10^{-4}

[a] In parentheses: percentage of Pd atoms in the indicated oxidation state.
[b] N from amine ($-NH_2$).

corresponding to the molecular stoichiometry, after heterogenisation, the mentioned ratios slightly increase (table 3). However, due to the low complex loading on the catalyst, the observed variation in the ratios might be related to the experimental error.

The results obtained for the catalyst Pd(TDA)/NZ are very different from those previously reported for Pd(TDA)/GF-45 [4,6]. XPS data showed that after impregnation on the carbon support no changes appear in the state of the Pd(TDA) complex. These results indicate that on activated carbons the complex remains unaltered after impregnation, while on the zeolite a strong interaction between the complex and the support exists. If the Pd(TDA) molecule remains unchanged after impregnation on the carbon support, it is likely that the catalytic activity be similar in the homogeneous and Pd(TDA)/GF-45 samples. It could be slightly higher in the heterogenised form due to the increase of the reactants concentration in the proximity of the active species as consequence of adsorption on the surface [10]; or slightly lower due to the diffusional problems inside the pores [11]. But, if the electronic state and the coordination sphere of Pd are modified, as occurs in Pd(TDA)/NZ, the catalytic activity of the complex and even the reaction mechanism can be different.

The XPS results of the Pd(TDA)/NZ sample after having been used in a catalytic cycle (table 3), are also quite different from those of the fresh catalyst. The main changes are: (i) the complex seems to be totally destroyed: Cl^- and N ($-NH_2$) disappear from the coordination sphere, and (ii) the percentage of Pd^0 increases and the BE value found in this case is slightly lower, but still not corresponding to bulk metallic Pd. If the complex is destroyed, the remaining Pd^{II} is probably exchanged on the zeolite surface.

Table 3 also includes the estimated Pd/O ratio (oxygen from the zeolite) in the fresh and used Pd(TDA)/NZ catalyst (as a qualitative or semi-quantitative result). The constant value indicates that Pd is not leached from the support under reaction conditions and it does not migrate to the internal pores, remaining on the surface.

It can be concluded that the Pd(TDA) complex is strongly modified when it is supported on NH_4ZSM-5. The resulting Pd(TDA)/NZ catalyst is highly active, more active than the homogeneous Pd(TDA) complex, the carbon supported catalyst and even more than the expensive Wilkinson's rhodium based catalyst, with the added advantage of reutilisation. The large increase in the catalytic activity is probably due to changes in the reaction mechanism. The effect of the zeolite structure and surface chemistry is the object of future work.

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References

[1] B.E. Hanson and J.R. Zoeller, Catal. Today 42 (1998) 371.
[2] P.C. L'Argentière and N.S. Fígoli, React. Kinet. Catal. Lett. 64 (1998) 221.
[3] P.C. L'Argentière, D.A. Liprandi, E.A. Cagnola and N.S. Fígoli, Catal. Lett. 44 (1997) 101.
[4] J.A. Díaz-Auñón, M.C. Román-Martínez, C. Salinas-Martínez de Lecea, P.C. L'Argentière, E.A. Cagnola, D.A. Liprandi and M.E. Quiroga, J. Mol. Catal. A 153 (2000) 243.
[5] P.C. L'Argentière, D.A. Liprandi, E.A. Cagnola, M.C. Román-Martínez and C. Salinas-Martínez de Lecea, Appl. Catal. A 172 (1998) 41.
[6] J.A. Díaz-Auñón, M.C. Román-Martínez, C. Salinas-Martínez de Lecea and P.C. L'Argentière, in: *Studies on Surface Science and Catalysis*, Vol. 130 D, eds. A. Corma, F.V. Melo, S. Mendioroz and J.L.G. Fierro (Elsevier, Amsterdam, 2000) p. 2075.
[7] S. Chavan, D. Srinivas and P. Ratnasamy, J. Catal. 192 (2000) 286.
[8] J. García-Martínez, Ph.D. thesis, Universidad de Alicante, Alicante, Spain (2000) (Spanish).
[9] D. Briggs and M.P. Seah, in: *Practical Surface Analysis*, Vol. 1, 2nd Ed. (Wiley, London, 1993).
[10] M.J. Alcón, A. Corma, M. Iglesias and F. Sánchez, J. Mol. Catal. A 144 (1999) 337.
[11] E.G. Derouane, C.J. Dillon, D. Bethell and S.B. Derouane-Abd Hamid, J. Catal. 187 (1999) 209.