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$[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ supported on γ-Al_2O_3 as catalyst for selective hydrogenation

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The $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ complex supported on γ-Al_2O_3 has proved to be a considerably more active, selective and sulfur-resistant catalyst in the selective hydrogenation of styrene to ethylbenzene than a traditional catalyst obtained from acid solutions of $PdCl_2$, and even than the same complex unsupported. The active species is the complex itself and it is stable under the reaction conditions. Hydrogen treatments above 353 K destroy the complex, at least partially, leading to a less active and sulfur resistant catalyst. The higher sulfur resistance, when compared to a conventional Pd/Al_2O_3 catalyst, can be attributed to electronic and geometrical effects.

Keywords: metal complexes, heterogeneous catalysis, selective hydrogenation, palladium catalysts

1. Introduction

The use of some supported and unsupported transition metals as catalysts in the selective hydrogenation of organic compounds is extensively reported in the literature [1,2]. A major limitation in the useful lifetime of such catalysts is the fact that those metals are easily poisoned by sulfur compounds normally present in hydrocarbon streams [3,4].

Transition metals complexes proved to be excellent catalysts for both homogeneous and heterogeneous hydrogenation reactions [5–7]. Considerable higher activity, selectivity and sulfur resistance levels may be obtained using these catalysts than traditional ones. In addition, complex catalysts may be operated under milder conditions [8].

Several authors studied the catalytic behavior of different nickel [9,10] and rhodium [11,12] complexes in homogeneous and heterogeneous hydrogenation reactions. Khar'kova et al. [13] reported about the synthesis of a catalytically active homogeneous Pd–Ni complex containing oligoallene ligands which was treated with tri-isobutyl-aluminium hydride. Frolov studied the catalytic behavior of Pt and Rh complexes [8], as well as the promoting effect of Pd on the catalytic properties of a ruthenium-based complex used for the hydrogenation of aromatic rings [14].

Several papers have been published about the catalytic properties of Pd complexes used in the homogeneous selective hydrogenation of dienes. The influence of different ligands was reported, e.g. allyl alcohol derivatives [15], sulfur compounds (such as reduced chlorodimethyl sulfoxide) [16,17], nitrogen compounds [16,18], allene and its derivatives [19,20], η^2-phosphinate [21]. Some of these complexes have been reported to become catalytically active only after treatment with a strong reducing reagent, generally an organoaluminium compound.

Some papers in the literature deal with the use of palladium complexes supported on oxides (such as Al_2O_3 and SiO_2) [6,22–25] or polymers (e.g. polyacrylamides, polyvinyl pyridine, polystyrene) [26,27]. There are few reports about the sulfur resistance of Pd complexes [8,16].

The objective of this paper is to present our studies on the influence of the pretreatment temperature and hydrogen pressure on the activity, selectivity and sulfur-resistance of the $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ complex supported on γ-Al_2O_3. The selective hydrogenation of styrene to ethylbenzene, carried out at a low temperature (353 K), was used as a test reaction and thiophene as poisoning reagent. Due to the presence of two types of unsaturated groups on the styrene molecule, this compound is very useful to investigate the catalytic behavior of selective hydrogenation catalysts [28]. Thiophene is usually taken as a model compound for sulfur resistance studies [29].

2. Experimental

2.1. Complex synthesis

The $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ complex was obtained by reaction of $PdCl_2$ with $CH_3(CH_2)_{12}NH_2$ in toluene, in a glass equipment with agitation and reflux, under a purified Ar atmosphere at 338 K, during 4 h and with a molar ratio amine/Pd = 2. After 1 h the disappearance of the solid phase ($PdCl_2$ insoluble in toluene) and the simultaneous appearance of a yellow-orange color in the liquid phase were observed. Upon ending the reaction the solvent was evaporated and a yellow solid was obtained, which was quite different from the brown color of $PdCl_2$. In parallel, and as a test experiment, the same procedure was followed using only $PdCl_2$ in toluene. In this case, no color changes were detected and the initial separation of phases was maintained; this indicates that the amine effectively reacted with the palladium salt to give a complex species.

The final purification of the complex was made by column chromatography, using silicagel as stationary phase and chloroform as solvent. All the aliquots obtained were analyzed by thin layer chromatography using silicagel as support, chloroform–methanol (in a molar ratio 6 : 1) as mobile phase and potassium dichromate in concentrated sulfuric acid as revealing agent.

2.2. Catalyst preparation

The incipient wetness technique [30] was used to carry out the heterogenization of the Pd complex on γ-alumina Ketjen CK 300 (cylinders of 1.5 mm diameter, BET surface area: 180 $m^2\ g^{-1}$, pore volume: 0.52 ml g^{-1}). The support was previously calcined in air at 773 K for 3 h. A solution of the palladium complex in toluene was used for impregnation in a suitable concentration to obtain a catalyst containing 2% Pd. This catalyst, which will be named A in the following considerations, was divided in three fractions and each one was pretreated with hydrogen at a different temperature: 353, 393 and 573 K, for 5 h under a hydrogen flow rate of 480 ml $h^{-1}\ g_{cat}^{-1}$. Pretreatments with hydrogen were also used by other authors [12].

For comparative purposes, a Pd/Al_2O_3 catalyst (B) was prepared by means of the incipient wetness technique using an acid aqueous solution of $PdCl_2$ (pH = 1) as precursor, in adequate concentration to obtain 2% Pd on the solid. After washing with distilled water and drying at 393 K, the sample was calcined at 623 K in a dry air stream (480 ml $h^{-1}\ g_{cat}^{-1}$) for 3 h. Finally, the catalyst was pretreated at 393 K in flowing hydrogen for 3 h, as previously described [31]. In previous studies we have found that the optimum pretreatment temperature for this catalyst is 393 K [32].

The catalytic behavior of the unsupported [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] complex was also evaluated in order to make a comparison with the supported complex and the supported palladium metal catalyst.

2.3. Complex and catalysts characterization

2.3.1. Hydrogen chemisorption capacity of the supported catalysts

Determinations were made using the method of the double isotherm, following a procedure previously described [3].

2.3.2. X-ray photoelectron spectroscopy (XPS)

The electronic state of Pd, N and Cl and their atomic ratios in the supported and unsupported complex as well as the presence of S in the poisoned samples were studied by XPS. Determinations were carried out on a Shimadzu ESCA 750 electron spectrometer coupled to a Shimadzu ESCAPAC 760 data system. In order to correct possible deviations caused by electric charge on the samples, the C 1s line was taken as an internal standard at 285.0 eV, as previously described [30]. The superficial electronic states of palladium, nitrogen, chlorine and sulfur were studied following the position of the maximum of the Pd $3d_{5/2}$, N $1s_{1/2}$, Cl 2p and S 2p peaks. The samples were introduced into the XPS equipment sample holder following the operational procedure described by Mallat et al. [34] in order to ensure that there was no modification on the electronic states of the species analyzed [35]. Anyhow, exposing the samples after pretreatment with hydrogen to the atmosphere for different periods of time confirmed that there were no electronic modifications. Determinations of the atomic x/Pd (x = N, Cl and S) ratios were made by comparing the areas under the peaks after background subtraction and corrections due to differences in escape depths and in photoionization cross sections [36].

2.3.3. Infrared spectroscopy

The pure and the supported complex were analyzed in the 4600–200 cm^{-1} range in a Shimadzu FTIR 8101/8101 M single beam spectrometer with Fourier transform (equipment I), operated as previously reported [37]. Due to the low detector sensitivity below 500 cm^{-1}, a Perkin-Elmer 580 B double beam spectrometer (equipment II) was also used. The characteristic group frequencies corresponding to the $CH_3(CH_2)_{12}NH_2$ molecule [38] were used to determine whether the [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] complex kept its properties after heterogenization and during all the steps of the catalytic procedures. The cis–trans isomerism was determined in the 500–200 cm^{-1} range. All the samples were dried at 353 K and they were examined either in potassium bromide or cesium iodide disks.

2.3.4. Activity and selectivity determinations

Catalytic activity, selectivity and sulfur resistance were determined in a batch stainless-steel stirred tank reactor operated at 353 K, $V = 200$ cm^3 and stirring velocity 700 rpm, as previously described [39]. These operational conditions ensured that no diffusional limitations were present [31,40]. The weight of catalyst was 1 g in the case of the supported catalysts (A or B). For the catalytic evaluation of the unsupported complex, [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] was dissolved in the reactant solution in a suitable concentration to obtain the same amount of active species as in catalyst A. The selective hydrogenation of styrene to ethylbenzene was used as test reaction; as previously reported [41], ethylbenzene can be further hydrogenated to ethylcyclohexane, and polymerization of styrene can also occur as a side reaction. A 5% styrene in toluene solution (named feed I in the following considerations) was used. For the poisoning experiments, the same solution with the addition of 1000 ppm thiophene (feed II) was used. Reactants and products were analyzed by gas chromatography using a FID and a DC 200 column. The catalytic activity (expressed as turnover number, N_T) was calculated from the conversion versus time plots as the number of styrene molecules reacted per second and per exposed active species. Selectivity to ethylbenzene (S_E) was determined from the chromatographic data; benzene was added to the reaction mixture as an internal standard in order to follow the polymerization consecutive reaction.

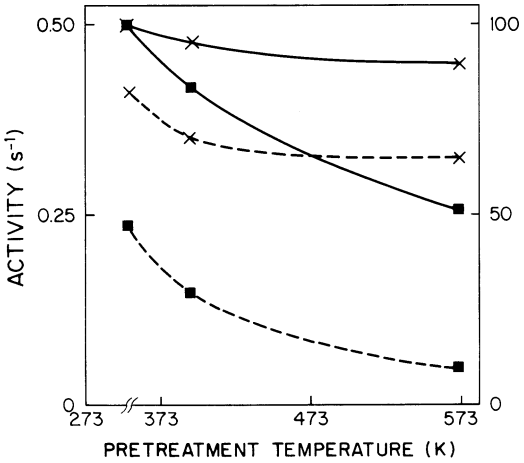

Fig. 2. Activity (×) and selectivity to ethylbenzene (■) as a function of the pretreatment temperature using the poison-free feed (—) and the feed containing 1000 ppm thiophene (- - -). Catalyst A. Hydrogen pressure: 10 kg cm^{-2}. Reaction temperature: 353 K.

3. Results

The surface area covered by the adsorbed complex in fresh catalyst A, as estimated from H_2 chemisorption, was 21%; the number of active complex molecules in the catalyst sample (1 g) was 6.5×10^{17}. The values of the activity (N_T) and the selectivity to ethylbenzene (S_E) obtained with feeds I and II for catalyst A (run at 5, 10 and 20 kg cm^{-2} hydrogen pressure, after being pretreated with hydrogen at 353 K) are presented in fig. 1. The influence of the pretreatment temperature ($T_P = 353, 393$ and 573 K) on the activity, selectivity and sulfur resistance of catalyst A at 10 kg cm^{-2} hydrogen pressure is shown in fig. 2.

Table 1 shows the activity and selectivity values for catalyst B with feeds I and II at 20 kg cm^{-2} hydrogen pressure, which is the optimum operational pressure for this catalyst, as has been previously reported [31]. In table 1 are also presented the activity and selectivity values for the soluble unsupported $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ complex pretreated with H_2 at 373 K (evaluated at 10 kg cm^{-2} H_2 pressure). The number of active species of the soluble complex present in the reactant solution was the same as in 1 g of catalyst A, as previously mentioned.

The stability of catalyst A was determined with feed I in runs of 80 h length (operating the stirred tank reactor in a continuous way). The activity and selectivity remained constant, revealing that the complex is not destroyed under the reaction conditions and that it is strongly attached to the support.

In every case, selectivity values below 100% are indicative of the loss of styrene through polymerization; ethylcyclohexene was never detected in any of the tests performed. This is logical since it is unlikely that palladium catalysts would hydrogenate the benzene ring under the operational conditions used.

Table 2 presents the Pd $3d_{5/2}$, N $1s_{1/2}$, Cl 2p and S 2p peaks binding energies (BE) and the atomic ratios N/Pd, Cl/Pd and S/Pd for the unsupported complex and for catalysts A and B (fresh and after evaluation with feeds I and II). In table 2 is also shown the full width at half

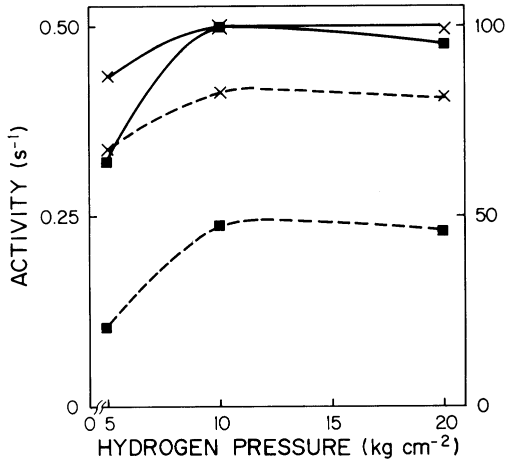

Fig. 1. Activity (×) and selectivity to ethylbenzene (■) using the poison-free feed (—) and the feed containing 1000 ppm thiophene (- - -) as a function of the H_2 pressure. Catalyst A (pretreated with H_2 at 353 K). Reaction temperature: 353 K.

Table 1

Activity (N_T) and selectivity to ethylbenzene (S_E) obtained with the poison-free feed (I) and with the feed containing 1000 ppm thiophene (II), for catalyst B (evaluated at 20 kg cm^{-2} H_2 pressure) and the unsupported complex pretreated with H_2 at 373 K (evaluated at 10 kg cm^{-2} H_2 pressure). Reaction temperature 353 K

Sample	Feed	N_T (s^{-1})	S_E (%)
catalyst B	I	0.270	87
	II	0.025	45
unsupported complex	I	0.40	100
	II	0.16	50

Table 2
Hydrogen chemisorption capacity ($H_{2\,chem}$) and XPS results for the pure unsupported [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] complex and for catalysts A and B (fresh and after evaluation with feeds I and II)

Sample	$H_{2\,chem}$ (μmol g_{cat}^{-1})	T_P (K)	Pd $3d_{5/2}$		N $1s_{1/2}$ (eV)	Cl 2p (eV)	N/Pd (at./at.)	Cl/Pd (at./at.)	S 2p (eV)	S/Pd (at./at.)
			BE (eV)	FWHM (eV)						
unsupported complex	–	–	338.2	2.8	401.9	198.3	2.00	1.99	–	–
catalyst A, fresh	–	–	338.3	2.9	401.7	198.2	2.01	2.00	–	–
	316	353	337.9	2.9	402.0	198.0	1.99	2.00	–	–
	349	393	336.8	3.4	401.9	198.0	1.20	1.16	–	–
	328	573	335.6	3.9	402.1	197.9	0.42	0.40	–	–
catalyst A, evaluated with feed I	–	353	338.2	3.0	402.2	198.0	1.98	1.98	–	–
	–	393	337.0	3.5	401.8	197.9	1.21	1.18	–	–
	–	573	336.1	3.9	402.0	198.2	0.38	0.39	–	–
catalyst A, evaluated with feed II	–	353	338.0	3.1	401.8	197.8	1.98	1.99	163.9	0.01
	–	393	337.4	3.6	401.7	197.9	1.19	1.21	164.0	0.02
	–	573	336.3	4.0	402.0	198.0	0.36	0.37	164.1	0.04
catalyst B fresh	310	393	336.6	3.9	–	198.0	–	2.00	–	–
catalyst B, evaluated with feed I	–	393	336.9	4.0	–	198.1	–	1.98	–	–
catalyst B, evaluated with feed II	–	393	337.0	4.1	–	198.1	–	1.99	164.2	0.07

maximum intensity (FWHM) of the Pd $3d_{5/2}$ peak. The Pd/Al superficial atomic ratio was 0.088 for all the supported samples listed in table 2.

The following samples were analyzed by FTIR spectroscopy (equipment I): (a) pure [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] ,(b) catalyst A without pretreatment with hydrogen, (c) catalyst A pretreated at 353 K, (d) catalyst A pretreated at 353 K after evaluation with feed I, (e) catalyst A pretreated at 353 K after evaluation with feed II and (f) catalyst A pretreated at 573 K. The spectra are shown in fig. 3. Samples a and b were also analyzed below 500 cm^{-1} using equipment II (fig. 4).

4. Discussion

The catalyst prepared from the [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] complex evaluated at 10 kg cm^{-2} is very active and selective for the hydrogenation of styrene to ethylbenzene, as shown in fig. 1. There was a little decrease in the activity when the pressure was raised up to 20 kg cm^{-2}, while the selectivity to ethylbenzene remained constant. Both activity and selectivity decreased noticeably when the pressure was lowered to 5 kg cm^{-2}. When the catalyst was evaluated with the poison-containing feed II, the activity decreased 53% at 10 kg cm^{-2}, a similar decrease was obtained at 20 kg cm^{-2}. When the pressure used was 5 kg cm^{-2}, the activity decreased 68%. S_E decreased in the presence of thiophene; the lowest value was obtained at 5 kg cm^{-2}. Hence, the optimum working pressure is 10 kg cm^{-2}. The results displayed in table 1 show that catalyst B was severely poisoned when it was evaluated with feed II: the activity decreased 91% and the selectivity 51%. Table 1 also shows that the activity of the unsupported complex decreased 40% after evaluation with feed II and the selectivity 50%. Hence, comparing the results shown in fig. 1 and table 1 it can be seen that catalyst A pretreated with H_2 at 353 K and evaluated at 10 kg cm^{-2} is much more active, selective and sulfur-resistant than catalyst B. Catalyst A is also more active, selective and sulfur-resistant than the unsupported complex. In addition, catalyst A may be easily recovered from the reactant solution after reaction; in the case of the unsupported complex catalyst, the solution must be purified after reaction by a generally expensive procedure. Other authors have also found a higher activity and resistance to inhibitors after heterogeneization of several palladium complexes used in the hydrogenation of organic compounds [8,22,25].

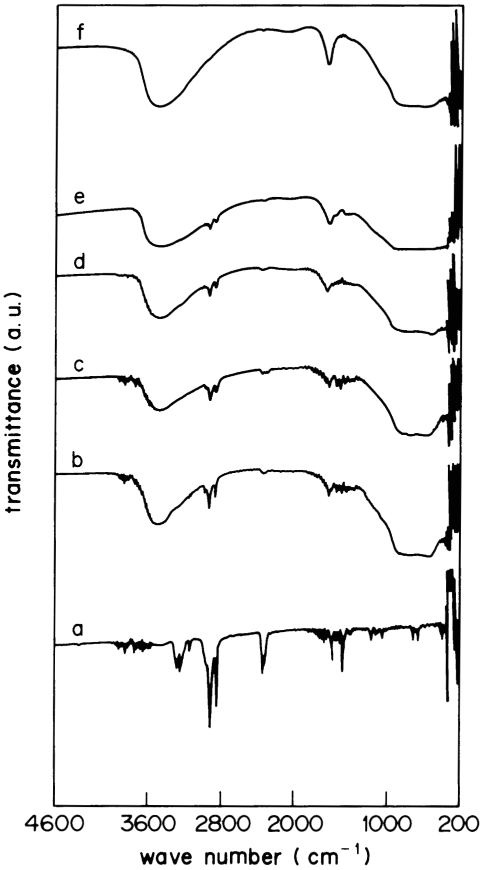

Fig. 3. FTIR of: (a) pure $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$, (b) catalyst A without pretreatment with hydrogen, (c) catalyst A pretreated with hydrogen at 353 K, (d) catalyst A pretreated with hydrogen at 353 K, after evaluation with feed I, (e) catalyst A pretreated with hydrogen at 353 K, after evaluation with feed II and (f) catalyst A pretreated with hydrogen at 573 K.

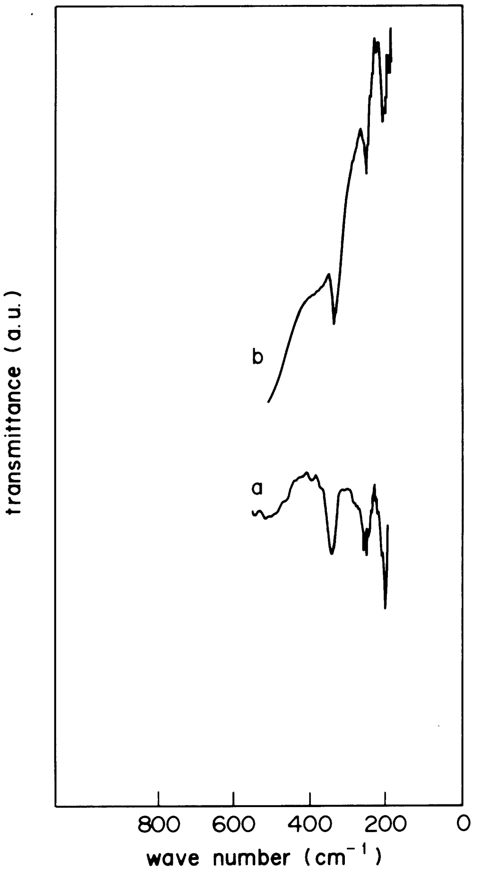

Fig. 4. IR spectra of samples a and b (see fig. 1) below 500 cm^{-1}.

As shown in fig. 2, the activity and selectivity of catalyst A decreased when T_P was raised up to 393 or 573 K. Activity decreases after poisoning with feed II and this was more noticeable at high T_P values. There were little modifications in selectivity when varying catalyst hydrogen pretreatment temperature with feed I, but there was a significant decrease in the presence of thiophene. As in the case of activity, the maximum selectivity was obtained pretreating the catalyst with hydrogen at 353 K, both in the presence or absence of thiophene.

As presented in table 2, the Pd $3d_{5/2}$, Cl 2p and N $1s_{1/2}$ peaks BE and the atomic ratios N/Pd and Cl/Pd of the pure complex and of catalyst A (either without pretreatment or pretreated with hydrogen at 353 K) were almost the same. The mentioned ratios correspond to the theoretical stoichiometric ratios of the $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$ complex. In agreement with the theoretical electronic state that could be expected for the complex under study, the position of the N $1s_{1/2}$ and Cl 2p peaks correspond, in all cases, to nitrogen in an amine and to chloride species, respectively [42]. Evidently, some complex entities are destroyed by thermal treatments above 353 K as there was a great decrease in the N/Pd and Cl/Pd ratios when catalyst A was reduced at 393 K and even more at 573 K although the Cl/N atomic ratio remained constant. The FWHM corresponding to the Pd $3d_{5/2}$ peak increased with the pretreatment temperature, thereby indicating that new species are generated; these species may be palladium-free ones generated after the ligands elimination. Comparing the XPS results of catalyst A fresh pretreated with H_2 at 353 K with those after evaluation with feed I, it can be observed that the supported complex is not destroyed under the reaction conditions.

The Pd $3d_{5/2}$ and Cl 2p peaks BE and the atomic ratio Cl/Pd of catalyst B are also shown in table 2. The presence of superficial Pd electrodeficient species can be suggested; this is in agreement with the position of the Cl 2p peak, which corresponds mainly to chloride species [42]. The Cl/Pd superficial atomic ratio corresponds to the theoretical stoichiometric ratio of the precursor salt used for preparing catalyst B.

After evaluation of catalysts A and B with feed II, a sulfur peak is detected by XPS at 164.1 eV (table 2). As previously reported [28], this peak corresponds to adsorbed thiophene, which is the actual poisoning species. This is in agreement with the fact that n-C_4H_{10} and

H_2S were never detected in the gas phase. For catalyst A, the superficial atomic ratio S/Pd increased when T_P was raised from 353 to 573 K, thus explaining the greater poisoning effect of feed II observed at high T_P. Table 2 shows that the superficial atomic ratio S/Pd in catalyst B is considerably higher than the one corresponding to catalyst A, even pretreated at 573 K, thus explaining the higher sulfur resistance of catalyst A.

The selectivity to ethylbenzene of catalyst A and of the unsupported complex is 100% under the optimum conditions ($T_P = 353$ K, H_2 pressures $= 10$ kg cm^{-2}), but it decreases when the pretreatment or operational conditions are not optimal for the stability of the complex. Since some complex entities are destroyed (as shown by the XPS results presented in table 2), the decrease in selectivity observed may be due to chlorine species that belonged to the coordination sphere. The decrease in selectivity observed in catalyst B may be due to the presence of chloride ions remaining in the surface after the thermal pretreatment in air at 623 K, as shown by the XPS results presented in table 2 (the binding energy of the Cl $2p_{3/2}$ peak corresponds to Cl^- species). There is an important decrease in selectivity for all of the catalysts after evaluation with feed II. This may be due to a partial electronic deficiency caused by the presence of thiophene [43], this is possible considering the electron-acceptor properties of sulfur on thiophene. These electron transfers can modify the relative rates of competitive reaction, thus modifying the selectivity [44].

The FTIR spectrum of the unsupported complex (fig. 3a) shows, at high frequencies, all the characteristic peaks of a primary aliphatic amine, in total accordance with that reported by Silverstein et al. [45] (an additional peak appears due to the presence of CO_2, which will not be considered any longer). The spectrum of catalyst A without pretreatment with hydrogen (fig. 3b) shows some of the most remarkable peaks mentioned above, suggesting that the complex is present after its heterogenization. At this point it is remarked the presence of the γ-Al_2O_3 dominant structure which masks part of the spectra of all supported species. The spectra of samples c–e (fig. 3) are quite alike to that obtained for sample b, thus indicating that the same species is present during all the catalytic procedures, even under poisoning conditions. Results of sample e (fig. 3) do not show the thiophene characteristic group frequencies, thereby meaning that thiophene (whose presence was demonstrated by XPS) is absorbed coplanar to the catalyst surface, as previously reported [37]. The spectrum of sample f (fig. 3) is quite different from all the others (peaks in the 3100–2800 cm^{-1} range disappear while those in the 1800–1200 cm^{-1} range get fused in only one, with a maximum at about 1650 cm^{-1}), suggesting that the Pd complex is destroyed, at least substantially, due to a temperature effect. This result agrees with the decrease in the Pd $3d_{5/2}$ BE when increasing the pretreatment temperature.

The spectra presented in fig. 4 (a and b) show the peaks belonging to the Pd–ligand vibrations [46] for the pure and adsorbed species. In both cases the complex can be considered the trans isomer because of the presence of single peaks, which obey the principle of mutual exclusion, typical of center-symmetric species, in this situation local D_{2h} symmetry.

All these results suggest that the selective hydrogenation of styrene is catalyzed by the [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] complex, which presents high activity, selectivity and sulfur resistance. Similar results were obtained by Trzeciak et al. [12] for Rh-supported complexes used for the hydrogenation of hex-1-ene and benzene in mild conditions. The ligands bond to palladium in the [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] complex may decrease the coplanar adsorption of the thiophene molecule, thus increasing the sulfur-resistance; hence, the existence of a geometric effect cannot be neglected. As in the case of the Rh complexes reported in ref. [12], it was not necessary to treat the Pd complex with a reducing reagent (such as $LiAlH_4$ or KBH_4) during the preparation steps. Hence, for the reaction and operational conditions of this work, the complex stability and catalytic behavior differs from those reported by other authors [8,19].

5. Conclusion

Supporting the [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] complex on γ-Al_2O_3 it is possible to obtain a catalyst which is considerably more active, selective and sulfur-resistant for the styrene selective hydrogenation to ethylbenzene than a conventional catalyst obtained from acid solutions of $PdCl_2$ and even than the same complex unsupported. The active species is the complex itself, which is stable under the reaction conditions. The complex is destroyed, at least partially, by hydrogen treatments above 353 K, leading to a less active and sulfur-resistant catalyst. The highest sulfur resistance can be attributed to electronic and geometrical effects.

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