High active, selective and sulfur resistant supported palladium tetra-coordinated complex as catalyst in the selective hydrogenation of styrene

P.C. L'Argentière [a,b,*], D. Liprandi [a], D.V. Marconetti [a], N.S. Fígoli [b]

[a] Química Inorgánica, Departamento de Química General e Inorgánica (FIQ, UNL), Santiago del Estero 2829, Santa Fe, Argentina
[b] Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ, UNL), Santiago del Estero 2654, Santa Fe, Argentina

Abstract

The [PdCl$_2$(CH$_3$SOCH$_3$)$_2$] complex supported on γ-Al$_2$O$_3$ was studied as catalyst in the selective hydrogenation of styrene to ethylbenzene. This catalyst is considerably more active, selective and sulfur-resistant than a conventional catalyst obtained from an acid solution of PdCl$_2$. As determined by XPS and IR, 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 less sulfur resistant catalyst. The highest sulfur resistance can be attributed to electronic and geometrical effects.

1. Introduction

Supported and unsupported transition metals, e.g. Pd, Ni, and Rh, are widely used as catalysts in the selective hydrogenation of organic compounds [1]. An important limitation in the useful life of these catalysts is that they are easily poisoned by sulfur compounds normally present in hydrocarbon streams.

The use of metal complexes as catalysts for homogeneous and heterogeneous hydrogenation reactions is mentioned in the literature as a useful way to obtain high activity and/or sulfur resistance [2–7]. Olivier et al. [8] studied the catalytic behavior of different nickel complex ions in homogeneous and heterogeneous hydrogenation reactions. Sakai et al. [9] found that the σ-allylnickel complex [NiH(PPh$_3$)(AlCl$_4$)] is an active catalyst for homogeneous selective hydrogenation of diolefins. Other authors [10,11] reported about the use of rhodium complexes in homogeneous and in heterogeneous hydrogenation reactions carried out in mild conditions of temperature and pressure. They found that the hydrogenation proceeds with the participation of the Rh complexes rather than rhodium metal centers.

* Corresponding author. Fax: +54-42-553727.

Palladium complexes showed high catalytic activity and selectivity in homogeneous selective hydrogenation of dienes. The influence of different ligands was investigated, e.g. nitrogen compounds [12,13], allene and its derivatives [14], and η^2-phosphinate [15]. Other authors [16,12] reported that palladium complexes with sulfur ligands are good catalysts for the homogeneous hydrogenation of unsaturated compounds. They found that these complexes became catalytically active only after treatment with a reducing reagent such as $LiAlH_4$ or KBH_4.

Despite its scientific and industrial importance, there are only a few publications about the use of palladium complexes in heterogeneous catalysis [3,17–20]. There are also few reports about the sulfur resistance of Pd complexes [12]

The objective of this paper is to present our studies on activity and sulfur-resistance of the palladium complex [PdCl$_2$(CH$_3$SOCH$_3$)$_2$] supported on alumina, taking the selective hydrogenation of styrene to ethylbenzene, carried out at a low temperature (353 K), as a test reaction. Styrene is a useful model compound to investigate the catalytic performance of selective hydrogenation catalysts at a laboratory scale due to the presence of two types of unsaturated groups [21].

2. Experimental

2.1. Complex synthesis

The [PdCl$_2$(CH$_3$SOCH$_3$)$_2$] complex was obtained by reaction of PdCl$_2$ with CH$_3$SOCH$_3$ (DMSO), in a glass equipment with agitation and refluxing, under a purified argon atmosphere at 338 K, during 4 h. DMSO was added in excess because it is simultaneously ligand and solvent. The disappearance of the solid phase (PdCl$_2$ insoluble in DMSO) and the simultaneous appearance of a yellow–orange color in the liquid phase was observed after 1 h. At the end of the reaction, the solvent was evaporated in a rotavap equipment and a yellow solid was obtained; this color was quite different from the brown of PdCl$_2$

The complex was purified by column chromatography, using silicagel as stationary phase and methanol:ethyl acetate (1:5 v/v) as solvent. All the aliquots obtained were analyzed by thin layer chromatography using silicagel as support, methanol:ethyl acetate (1:5 v/v) as mobile phase and potassium permanganate as revealing agent.

2.2. Catalyst preparation

Heterogeneization of the palladium complex was carried out by means of the incipient wetness technique. γ-alumina Ketjen CK 300, cylinders of 1.5 mm diameter, having 180 m^2 g^{-1} BET surface area and a pore volume of 0.52 ml g^{-1}, was used as support, after calcination in air at 773 K for 3 h. A solution of the palladium complex in DMSO was used for impregnation in a suitable concentration such as to obtain a catalyst containing 2% Pd. The catalyst was then dried at room temperature under vacuum during 24 h. 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)$^{-1}$.

For comparative purposes, a Pd/Al$_2$O$_3$ 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 (480 ml h^{-1} (g cat)$^{-1}$) for 3 h, as previously described [22]. It has been reported that the optimum reduction temperature for this catalyst is 393 K [23].

2.3. Complex and catalysts characterization

2.3.1. Hydrogen chemisorption capacity

Determinations were made using the method of the double isotherm proposed by Benson et al. [24], following a procedure previously described [25].

2.3.2. X-ray photoelectron spectroscopy (XPS)

Analyses were carried out on a Shimadzu ESCA 750 electron spectrometer coupled to a Shimadzu ESCAPAC 760 Data System. The C 1s line was taken as an internal standard at 285.0 eV and it was used to correct possible deviations caused by electric charge on the samples, as previously described [22]. The position of the maximum of the Pd $3d_{5/2}$, S 2p and Cl 2p peaks was used to follow the superficial electronic state of palladium, sulfur and chlorine. After pretreatment with hydrogen the samples were introduced into the sample holder following the operation procedure described by Mallat et al. [26]. This operating procedure ensures that there is no modification on the electronic state of the species analyzed [27]. 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 = S, Cl) 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 [28].

2.3.3. Infrared spectroscopy

The pure and the supported complex were analyzed in the 4600–350 cm^{-1} range in a Shimadzu FTIR 8101/8101 M single beam spectrometer with Fourier transform (equipment I), operated as previously reported [29]. 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 DMSO molecule [30] were used to determine whether [PdCl$_2$(CH$_3$SOCH$_3$)$_2$] kept its properties after heterogeneization and during all the steps of the catalytic procedures. 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 and selectivity were measured in a stirred tank reactor operated at 353 K, w/v 0.002 g cm^{-3}, and stirring velocity 700 rpm, as previously described [31]. No diffusional limitations were observed under these conditions [32,23]. The selective hydrogenation of styrene to ethylbenzene was used as test reaction. As previously reported [33], ethylbenzene can be further hydrogenated to ethylcyclohexane, and polymerization of styrene can also occur as a side reaction. A 5% styrene in toluene solution (I) or the same solution with the addition of 1000 ppm thiophene (II) was used as feed. Thiophene is usually taken as a model compound for sulfur resistance studies [34]. Reactants and products were chromatographically analyzed by means of a flame ionization detector and a DC 200 column. The catalytic activity (N_T) was calculated from the conversion versus time plots as the number of styrene molecules reacted per second and per exposed active species. The selectivity to ethylbenzene (S_E) was calculated from the chromatographic data; to follow the polymerization consecutive reaction, benzene was added to the reaction mixture as an internal standard.

3. Results

Table 1 presents the activity per exposed active site, N_T (as estimated from H$_2$ chemisorption), and the selectivity to ethylbenzene (S_E) values obtained with feeds I and II for catalyst A (run at 5, 10 and 20 kg cm^{-2} hydrogen pressure, after pretreatment at 353 K) and for catalyst B (run at 20 kg cm^{-2} hydrogen pressure). It has been previously found that the optimum pressure for catalyst B was 20 kg cm^{-2} [23].

Table 1

Activity per exposed active species (N_T) and selectivity to ethylbenzene (S_E) obtained with the poison free feed (I) and the feed containing 1000 ppm thiophene (II) for catalyst A (evaluated at different H_2 pressures) and B (evaluated at 20 kg cm^{-2} H_2 pressure). The temperatures of the pretreatment with hydrogen procedures (T_P) are also shown. Reaction temperature: 353 K

Catalyst	Feed	T_P (K)	H_2 pressure (kg cm^{-2})	N_T (s^{-1})	S_E (%)
A	I	353	5	0.57	85
		353	10	0.98	100
		353	20	0.98	100
	II	353	5	0.23	71
		353	10	0.56	79
		353	20	0.55	78
B	I	393	20	0.57	87
	II	393	20	0.05	65

The influence of the pretreatment temperature ($T_P = 353$, 393 and 573 K) on the activity, selectivity and sulfur resistance of catalyst A was also investigated, as shown in Table 2. Runs were performed at 10 kg cm^{-2} H_2 pressure.

Table 3 shows the Pd $3d_{5/2}$, Cl 2p and S 2p peaks B.E. and the atomic ratios S/Pd and Cl/Pd for the unsupported complex and for catalyst A, fresh (before and after pretreatment with hydrogen at 353, 393 and 573 K) and after evaluation with feeds I and II. Table 3 also presents the hydrogen chemisorption capacity of catalysts A and B as well as the dispersion and XPS results for catalyst B.

Table 2

Activity per exposed active species (N_T) and selectivity to ethylbenzene (S_E) for catalyst A pretreated with hydrogen at different temperatures (T_P), with the poison free feed (I) and with the feed containing 1000 ppm thiophene (II). Hydrogen pressure: 10 kg cm^{-2}; reaction temperature: 353 K

Feed	T_P (K)	N_T (s^{-1})	S_E (%)
I	353	0.98	100
	393	0.80	94
	573	0.51	81
II	353	0.55	79
	393	0.37	67
	573	0.12	62

The following samples were analyzed by FTIR spectroscopy (equipment I): (a) pure $[PdCl_2(CH_3SOCH_3)_2]$, (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. 1. Samples a and b were also analyzed below 500 cm^{-1} using equipment II (Fig. 2).

In order to determine the stability of catalyst A, it was evaluated with feed I in runs of 100 h length (operating the stirred tank reactor in a continuous way). The activity and selectivity
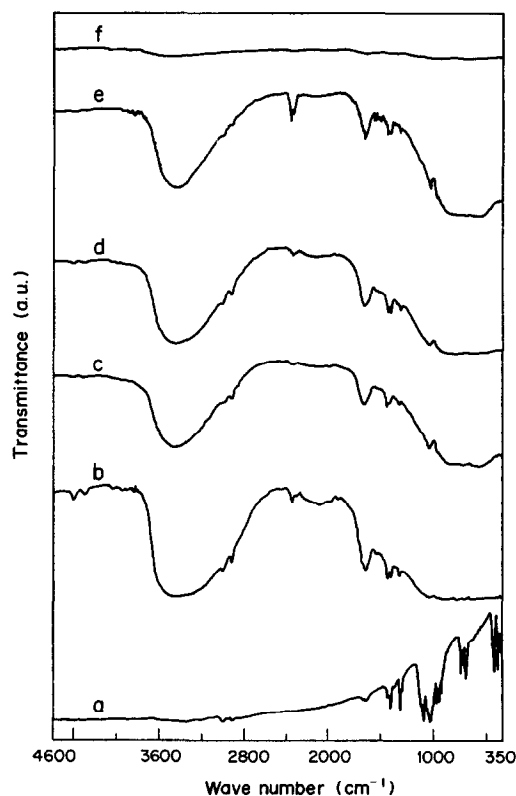

Fig. 1. FTIR spectra obtained using Shimadzu FTIR 8101/8101 equipment: (a) pure $[PdCl_2(CH_3SOCH_3)_2]$, (b) catalyst A without pretreatment with hydrogen, (c) catalyst A pretreated at 353 K, (d) catalyst A pretreated at 353 K after evaluation with feed I, (e) catalyst A pretreated at 353 K after evaluation with feed II and (f) catalyst A pretreated at 573 K.
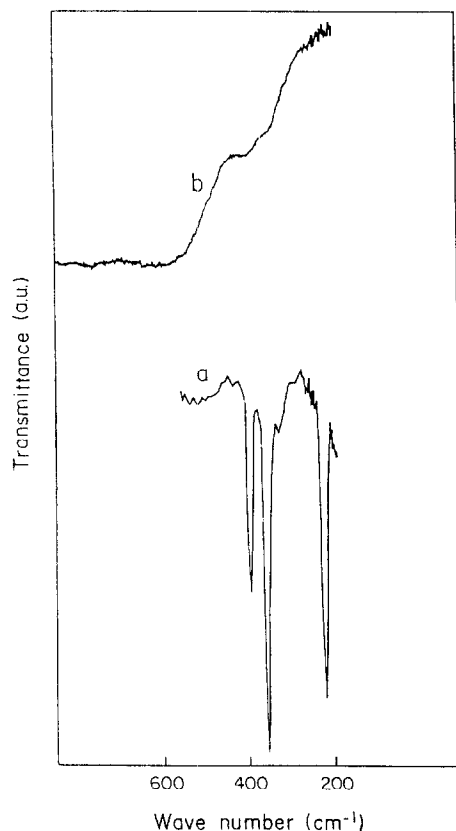
Fig. 2. IR spectra of samples a and b below 500 cm^{-1} using Perkin-Elmer 520 B equipment.

remained constant, revealing that the complex is not destroyed under the reaction conditions and that it is strongly attached to the support.

4. Discussion

The catalyst prepared from the Pd complex evaluated at 10 kg cm^{-2} with feed I is very active and selective for the hydrogenation of styrene to ethylbenzene, as shown in Table 1. There were no modifications in the activity and selectivity when the pressure was raised up to 20 kg cm^{-2}, but there was a noticeable decrease when the pressure was lowered to 5 kg cm^{-2}. When the catalyst was evaluated with the poison containing feed II, the activity decreased 44% 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 60%. 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 adsorption of thiophene may cause a partial electronic deficiency [35], thus causing the decrease in selectivity observed, which is possible considering the electron acceptor properties of sulfur on thiophene. Other authors [36] stated that these electron transfers can modify the relative rates of superficial competitive reactions, thus modifying the selectivity. Table 1 also shows that catalyst A pretreated with hydrogen at 353 K and evaluated at 10 kg cm^{-2} is much more active, selective and sulfur-resistant than catalyst B.

Table 3

Hydrogen chemisorption capacity ($H_{2\,chem}$) and XPS results for the pure [$PdCl_2(CH_3SOCH_3)_2$] complex, for catalyst A (fresh and after evaluation with feeds I and II) and for catalyst B (fresh)

Sample	T_P (K)	$H_{2\,chem}$ (μmol (g cat)$^{-1}$)	Pd 3d$_{5/2}$ (eV)	S 2p (eV)		Cl 2p (eV)	S_T/Pd (at/at)	S_D/Pd (at/at)	Cl/Pd (at/at)
Unsupported complex	—	—	337.6		165.4	198.1	—	2.00	2.00
Catalyst A, fresh	—	—	337.8		165.5	198.0	—	2.10	2.05
	353	321	337.6		165.4	198.2	—	1.95	2.08
	393	358	336.8		165.2	198.2	—	1.27	1.11
	573	339	335.9		165.1	198.0	—	0.42	0.30
Catalyst A, evaluated with feed I	353	—	337.8		165.5	198.0	—	1.97	2.10
	393	—	336.9		165.5	197.9	—	1.10	1.20
	573	—	336.1		165.4	198.1	—	0.41	0.46
Catalyst A, evaluated with feed II	353	—	338.2	164.1,	165.4	198.1	0.01	1.80	1.98
	393	—	337.7	164.1,	165.3	198.1	0.03	1.10	1.45
	573	—	337.0	164.2,	165.4	198.1	0.35	0.60	0.61
Catalyst B, fresh	393	310	336.6	—	—	198.0	—	—	2.00

S_T/Pd = thiophenic sulfur/Pd atomic ratio; S_D/Pd = DMSO sulfur/Pd atomic ratio.

The activity and selectivity of catalyst A decreased when T_P was raised up to 393 or 573 K (Table 2). After poisoning with feed II there was an activity decrease which was greater 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. The results displayed in Table 3 show that the hydrogen chemisorption capacity of catalyst A was not significantly modified by the pretreatment temperature.

The Pd $3d_{5/2}$, Cl 2p and S 2p peaks B.E. of the pure complex and of catalyst A (pretreated or not with hydrogen at 353 K) were almost the same, as presented in Table 3. The position of the S 2p and Cl 2p peaks corresponds, in all cases, to sulfur in DMSO (S_D) and to chloride species, respectively [37], in agreement with the theoretical electronic state that could be expected for the complex under study. The atomic ratios S_D/Pd and Cl/Pd were also the same for the samples previously mentioned. The superficial atomic ratios S_D/Pd and Cl/Pd of the pure complex and catalyst A (with or without pretreatment with hydrogen at 353 K) correspond to the theoretical stoichiometric ratios of the $[PdCl_2(CH_3SOCH_3)_2]$ complex. There was a great decrease in the S_D/Pd and Cl/Pd ratios when the catalyst was pretreated at 393 K and even more at 573 K, suggesting that the complex is, at least, partially destroyed by thermal treatments above 353 K. Comparing the XPS results of the fresh catalyst A pretreated at 353 K with those after evaluation with feed I, it can be observed that the supported complex is not destroyed under reaction conditions.

The B.E. of the Pd 3d5/2 peak at 337.6 eV for catalyst A pretreated at 353 K indicates the existence of electrodeficient palladium species, which differ from those of catalyst B pretreated at 393 K (336.6 eV), thereby indicating the presence of different palladium species. The electrodeficient palladium species are more active, selective and sulfur-resistant for styrene selective hydrogenation. The existence of a geometric effect cannot be neglected, because the ligands bound to palladium in the complex may inhibit the coplanar adsorption of the poison molecule, thus increasing the sulfur-resistance.

As shown in the left part of the column corresponding to the S 2p peak position of Table 3, a second sulfur peak is detected by XPS at 164.1 eV (in addition to the one corresponding to the DMSO species at 165.4 eV) when catalyst A is evaluated with feed II; this peak corresponds to adsorbed thiophene (S_T), as previously reported [29]. Hence, it was possible to determine the S_T/Pd superficial atomic ratios corresponding to thiophene poisoning. The superficial atomic ratio S_D/Pd decreased, while the superficial atomic ratio S_T/Pd increased when T_P was raised from 353 K to 573 K, indicating that the complex is destroyed, at least partially, when the pretreatment temperature is increased. On the other hand, these XPS results suggest that the poisoning species is adsorbed thiophene. Moreover, n-C_4H_{10} and H_2S were never detected at the reactor outlet.

The FTIR spectrum of the unsupported complex (Fig. 1a) is quite in accordance with that reported by Cotton et al. [38], meaning that the DMSO molecule is coordinated to palladium through the sulfur atom. The most remarkable frequencies are ca. 1100 cm^{-1} (SO stretching), 3050–2900 cm^{-1} (CH$_3$ asymmetric and symmetric stretching) and ca. 700 cm^{-1} (CS stretching). The peaks appearing at low frequencies (Fig. 2a) are assigned to the complex structure following Tranquille and Forel [39]; the main frequency is ca. 350 cm^{-1} (PdCl asymmetric stretching). The complex can be considered the trans isomer because of the presence of single peaks, which obey to the principle of mutual exclusion, typical of center-symmetric species (in this case, local D_{2h} symmetry). The IR spectra of samples b–e (Figs. 1 and 2) show similar peaks: a group corresponding to alumina

and CO_2 (which will be not considered further) and a second group due to the adsorbed complex. It must be noticed that after adsorption the transitions below 1000 cm^{-1} disappear completely, suggesting that the supported complex has lost some degree of freedom, being unable to vibrate in the low frequencies. Results of catalyst A poisoned with feed II (Fig. 1e) do not show the thiophene characteristic group frequencies, thereby indicating that thiophene (the presence of which was demonstrated by XPS) is adsorbed coplanarly to the catalyst surface, as previously reported [29]. The FTIR spectrum of catalyst A pretreated al 573 K (Fig. 1f) does not show the characteristic peaks of the adsorbed complex, suggesting that the complex has been destroyed, at least substantially, by temperature. This result agrees with the decrease in the Pd $3d_{5/2}$ B.E. when increasing pretreatment temperature.

The $[PdCl_2(CH_3SOCH_3)_2]$ complex is catalytically active although it was not treated with any 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 catalytical behavior differs from those reported by other authors [16,12].

5. Conclusion

Starting from the $[PdCl_2(CH_3SOCH_3)_2]$ complex, it is possible to obtain a complex supported catalyst which is considerably more active, selective and sulfur-resistant for the styrene selective hydrogenation than a conventional catalyst obtained from an acid solution of $PdCl_2$. 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.

Acknowledgements

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