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Journal of Molecular Catalysis A: Chemical 122 (1997) 141–146



Deactivation and regeneration of sulfur-poisoned supported palladium complexes

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Received 12 September 1996; accepted 20 January 1997

Abstract

The deactivation by thiophene of the $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ and the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ complexes supported on $\gamma\text{-Al}_2\text{O}_3$, during the selective hydrogenation of styrene has been studied at 353 K and 10 kg cm^{-2} . Although both complexes are deactivated when the feed contains more than 300 ppm thiophene, the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ supported complex is more sulfur resistant. Thiophene is partially eliminated by hydrogen treatments at 353 K and 10 kg cm^{-2} , thereby indicating that thiophene has not substituted, at least totally, the complex ligands.

Keywords: Sulfur resistance; Palladium; Supported complexes; Regeneration

1. Introduction

Transition metals complexes have proved to be excellent catalysts for both homogeneous and heterogeneous hydrogenation reactions [1]. Several papers have been published about the catalytic properties of Pd complexes used in the homogeneous selective hydrogenation of dienes [2–7]. Some papers in the literature deal with the use of palladium complexes supported on polymers [8,9] or oxides [10]. There are few reports about the sulfur resistance of Pd complexes [3]. Despite the importance of the prob-

lem, no attempts have been reported about their regeneration.

The objective of this paper is to study the poisoning effect of thiophene on the activity and selectivity of the $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ and the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ complexes supported on $\gamma\text{-Al}_2\text{O}_3$, during the selective hydrogenation of styrene to ethylbenzene and to look at the regenerability of the catalysts.

2. Experimental

2.1. Complexes synthesis

The $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ complex was obtained by reaction of PdCl_2 with

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$\text{CH}_3(\text{CH}_2)_{12}\text{NH}_2$ (TDA) in toluene, in a glass equipment with agitation and reflux, under a purified argon atmosphere at 338 K, during 4 h and with a molar ratio $\text{TDA}/\text{Pd} = 2$. After one h it was observed the disappearance of the solid phase (PdCl_2 insoluble in toluene) and the simultaneous appearance of a yellow–orange color in the liquid phase. 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 thus indicating that the TDA has effectively reacted with the PdCl_2 to give a complex species.

The $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ complex was obtained by reaction of PdCl_2 with CH_3SOCH_3 (DMSO), with agitation and refluxing, under a purified argon atmosphere at 338 K, during 4 h, as previously described [11].

The final purification of the two complexes was made by column chromatography, using silicagel as stationary phase and chloroform for $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ and methanol–ethyl acetate for $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$, respectively, as solvents. All the aliquots obtained were analyzed by thin layer chromatography using silicagel as support.

2.2. Catalysts preparation

The incipient wetness technique was used to carry out the heterogenization of the Pd complexes on γ -alumina Ketjen CK 300 (cylinders of 1.5 mm diameter, BET surface area: $180 \text{ m}^2 \text{ g}^{-1}$, 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 for $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ and in DMSO for $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$, respectively, was used for impregnations, in a suitable concentration to obtain a catalyst containing 2% Pd.

2.3. Catalysts characterization

2.3.1. X-ray photoelectron spectroscopy (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 C1s line was taken as an internal standard at 285.0 eV. The superficial electronic state of palladium, nitrogen, chlorine and sulfur and their atomic ratios were studied following the position of the maximum of the $\text{Pd}3d_{5/2}$, $\text{N}1s_{1/2}$, $\text{Cl}2p$ and $\text{S}2p$ peaks. The samples were introduced into the XPS equipment sample holder following the operational procedure described by Mallat et al. [12] in order to ensure that there was no modification on the electronic state of the species analyzed [13]. 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 ($x = \text{N}, \text{Cl}, \text{Al}$ 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 [14].

2.3.2. Activity and selectivity determinations

Catalytic activity, selectivity and sulfur resistance were determined in a batch stainless steel stirred tank reactor operated at 353 K, $W/V = 0.002 \text{ g cm}^{-3}$, 10 kg cm^{-2} pressure and stirring velocity 700 rpm. Under these operational conditions, no diffusional limitations were present [15]. The selective hydrogenation of styrene to ethylbenzene was used as test reaction; ethylbenzene can be further hydrogenated to ethylcyclohexane, and polymerization of styrene can also occur as a side reaction. A 5% styrene in toluene solution was used as feed. For the poisoning experiments, the same solution with the addition of different amounts of thiophene, were used. Regeneration experiments were carried

out over both complexes poisoned with the highest thiophene concentration. After running with the poison containing feed, temperature was decreased to 293 K and the liquid was drained; then hydrogen was introduced at 10 kg cm⁻² pressure, temperature was raised to 353 K and the system was left for 10 h. The temperature was selected because we have previously found that the [PdCl₂(CH₃SOCH₃)₂] complex is destroyed at higher temperatures [11]. Thermal effects on complexes stability were also observed by Frolov [1]. After that, a new run was carried out using the unpoisoned feed. In order to assure that the regeneration is not produced by the change for the unpoisoned feed, a similar procedure was followed without the intermediate hydrogen treatment. Reactants and products were analyzed by gas chromatography using a FID 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 palladium atom. 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.

3. Results

It was previously demonstrated from XPS and FTIR studies that the complex obtained from PdCl₂ and TDA correspond to the structure [PdCl₂(NH₂(CH₂)₁₂CH₃)₂] and that obtained from PdCl₂ and DMSO to the [PdCl₂(CH₃SOCH₃)₂] structure. Both complexes do not undergo modifications of their structures after heterogeneization [11,16]. Both supported complexes are also more active and selective for the hydrogenation of styrene to ethylbenzene than a catalyst prepared from a PdCl₂ acid solution containing the same palladium concentration. [11,16]. A test reaction using only alumina as catalyst, under the same operational conditions, showed no activity.

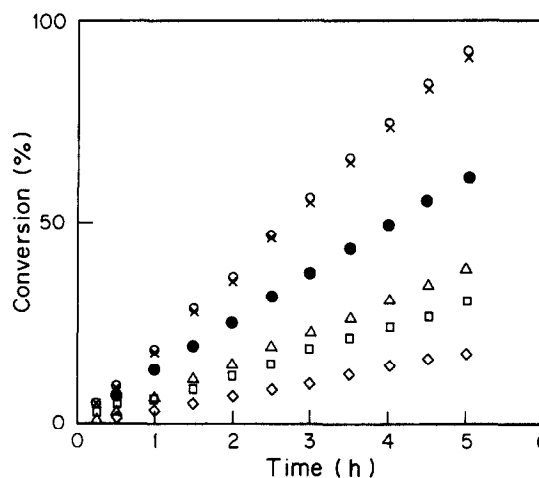


Fig. 1. Conversion versus time plots of the [PdCl₂(NH₂(CH₂)₁₂CH₃)₂] supported complex run with poison free feed: (O); with different thiophene concentrations, (x):300 ppm, (Δ): 2000 ppm, (□): 4000 ppm, (◇): 6000 ppm and after regeneration (●).

Figs. 1 and 2 present the conversion versus time plots for the [PdCl₂(NH₂(CH₂)₁₂CH₃)₂] and the [PdCl₂(CH₃SOCH₃)₂] supported complexes, respectively, run using the unpoisoned feed as well as feeds containing different thiophene concentrations. Results of the regenerating treatments with hydrogen as well as using the fresh feed after running with 6000 ppm

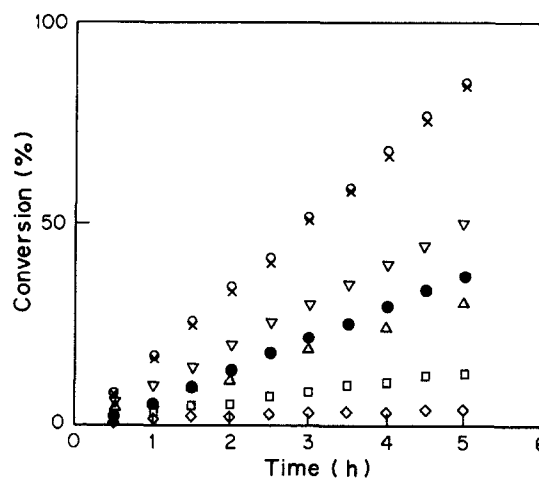


Fig. 2. Conversion versus time plots of the [PdCl₂(CH₃SOCH₃)₂] supported complex run with poison free feed: (O); with different thiophene concentrations, (x):300 ppm, (▽): 1000 ppm, (Δ): 2000 ppm, (□): 4000 ppm, (◇): 6000 ppm and after regeneration (●).

Table 1

Activity and selectivity during selective styrene hydrogenation for the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ and the $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ complexes using unpoisoned feed, feeds containing different thiophene concentrations, and the unpoisoned feed after regeneration

Feed	$[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$		$[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$	
	N_T (s^{-1})	S_E (%)	N_T (s^{-1})	S_E (%)
Without poison	0.51	100	0.49	100
300 ppm thiophene	0.50	96	0.49	95
1000 ppm thiophene	n.m.	n.m.	0.28	78
2000 ppm thiophene	0.22	80	0.15	73
4000 ppm thiophene	0.17	76	0.08	72
6000 ppm thiophene *	0.10	70	0.03	70
* And then without poison	0.10	70	n.m.	n.m.
* Regenerated with H_2 and then run without poison	0.34	98	0.21	96

n.m.: not measured.

thiophene, are also shown. Table 1 shows the corresponding activity and selectivity values. The activity of a palladium catalyst obtained from PdCl_2 , using the unpoisoned feed, was 0.27 s^{-1} [11].

Table 2 shows the XPS results for both complexes run with different thiophene-containing feeds, as well as for the regenerated samples. Two peaks appear in the S2p region of the $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ supported complex run with the poisoned feeds. One, at about 165.4

eV, corresponds to DMSO species [17], and it is called S_D . The other, at about 164.1 eV corresponds to adsorbed thiophene (S_T), as previously reported [11]. Only one peak was detected at about 164.1 eV in the S_{2p} region of the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ supported complex after being run with thiophene-containing feeds. Hence, it was possible to calculate de S_T/Pd superficial atomic ratios corresponding to thiophene poisoning for both catalysts.

Fig. 3 shows the relation between the relative

Table 2

XPS results for the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ and $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ supported complexes using feeds containing different thiophene (Th) concentrations and after regeneration

Feed	Pd3d _{5/2} (eV)	N1s _{1/2} (eV)	Cl2p (eV)	S2p S _D (eV)	S2p S _T (eV)	N/Pd (at/at)	Cl/Pd (at/at)	S _D /Pd (at/at)	S _T /Pd (at/at)	Al/Pd (at/at)
$[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$										
0 ppm T	337.9	402.2	198.2	–	–	2.0	2.0	–	–	11
4000 ppm T	338.2	402.1	198.1	–	164.1	1.9	1.9	–	0.015	11
6000 ppm T	338.3	401.9	198.1	–	164.2	1.9	1.9	–	0.030	11
0 ppm T ^a	337.7	402.0	198.1	–	164.1	1.9	1.9	–	0.007	11
$[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$										
0 ppm T	337.6	–	198.2	165.4	–	–	2.1	2.0	–	11
1000 ppm T	338.2	–	198.1	165.4	164.1	–	2.0	1.8	0.010	11
4000 ppm T	338.2	–	198.2	165.5	164.0	–	1.9	1.8	0.037	11
6000 ppm T	338.3	–	198.0	165.5	164.1	–	1.8	1.7	0.092	11
0 ppm T ^a	338.0	–	198.1	165.4	164.2	–	1.8	1.7	0.013	11

^a After regeneration with hydrogen.

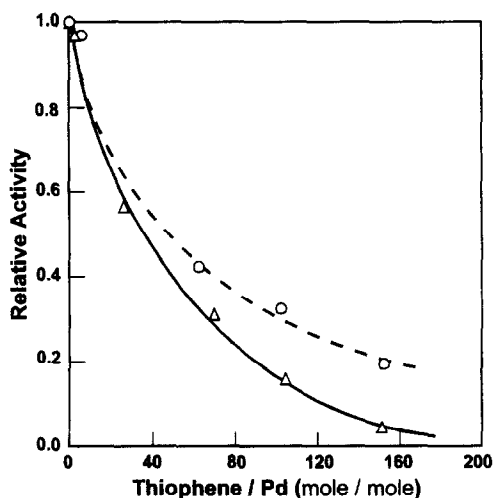


Fig. 3. Relative activity as a function of thiophene/palladium molar ratio for the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ (O) and the $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ (Δ) supported complexes.

activity and the number of thiophene molecules in the feed per palladium molecule in the catalyst, for both complexes.

4. Discussion

Both, the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ and the $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ supported complexes are very active and selective for styrene selective hydrogenation. A decrease in activity is observed in the presence of thiophene, being the decrease noticeable when the molar ratio thiophene/palladium is higher than 10. The increase in the S_T/Pd ratio when increasing poison concentration is indicative of thiophene adsorption on the catalysts. It is also noticeable that the $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ complex is more severely poisoned than the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ one and that higher S_T/Pd ratios correspond to the former. The different sulfur-resistance can be attributed to steric effects related with the different size and spatial distribution of both complexes, which may affect thiophene adsorption. Electronic effects can be neglected because the palladium

electronic state is almost the same for both complexes run either with poison-free or poison-containing feeds.

A decrease in the S_D/Pd ratio, as well as an increase of the S_T/Pd ratio was observed for the $[\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2]$ supported complex when increasing thiophene concentration in the feed. It has been postulated that the poisoning mechanism of palladium complexes by sulfur compounds is by the insertion of the poisoning molecule into the coordination sphere of palladium to form a Pd–S bond [3]. According to our results, some DMSO ligands might be substituted by thiophene ligands, generating less catalytic active species. In the case of the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ supported complex, such substitution does not occur, because the N/Pd ratio remains constant when increasing the thiophene concentration in the feed.

After treating with hydrogen at 353 K, an important recovery in activity was observed, which was higher (67%) for the $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$ supported complex than for the other one (43%). The selectivity recovery was also important. The hydrogen treatment also produced an important decrease in the S_T/Pd ratio, thus indicating the elimination of thiophene from the catalyst surface, possibly due to the hydrogenolysis of thiophene favored by the high hydrogen pressure. The activity recoveries were not produced by the contact with the poison free feed, because when the treatment with hydrogen was omitted and the catalysts were run with the poison free feed (after being run with the feed containing 6000 ppm thiophene), no activity recuperation was observed.

The decrease in selectivity after poisoning may be due to a partial electronic deficiency of palladium caused by the adsorption of thiophene [18] which can be observed from the XPS results; this is possible considering the electron-acceptor properties of sulfur on thiophene. These electron transferences can modify the relative rates of superficial competitive reactions, thus modifying the selectivity [19].

XPS results show that there are no important modifications in the Pd, N, Cl and S_D B.E. after the catalysts have been run with the poison-containing feeds, thereby indicating that the complexes had not been destroyed after being used with thiophene concentrations as high as 6000 ppm. The constant Al/Pd ratios are indicative that palladium has not been lost. The S_T/Pd ratios are higher when higher thiophene concentrations were used, thus indicating that more poison molecules have remained attached to the catalyst surface. After treatment with hydrogen, a decrease in the S_T/Pd ratio is observed for both catalysts, indicating that the treatment allowed the elimination of poisoning molecules.

5. Conclusion

Both [PdCl₂(NH₂(CH₂)₁₂CH₃)₂] and [PdCl₂(CH₃SOCH₃)₂] complexes supported on γ-Al₂O₃ are poisoned when feeds containing more than 10 moles of thiophene per mole of palladium are used, being the first complex more sulfur-resistant. Both complexes are still active when a feed containing 150 moles of thiophene per mole of palladium is used. A partial regeneration can be obtained by hydrogen treatments at 353 K and 10 kg cm⁻². For the [PdCl₂(NH₂(CH₂)₁₂CH₃)₂] complex, a substitution of ligands by the poisoning molecule can be neglected.

Acknowledgements

The authors are indebted to JICA for the donation of a XPS equipment and to UNL (CAI + D Program, Project 94-0858-007-057)

for partial financial support. The experimental assistance of C.A. Mázzaro, D.A. Liprandi, E.A. Cagnola and D.V. Marconetti is also acknowledged.

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