

# Supported Wilkinson's complex used as a high active hydrogenation catalyst

M.E. Quiroga<sup>a</sup>, E.A. Cagnola<sup>a</sup>, D.A. Liprandi<sup>a</sup>, P.C. L'Argentière<sup>a,b,\*</sup>

<sup>a</sup> *Química Inorgánica, Facultad de Ingeniería Química, Santiago del Estero 2829, 3000 Santa Fe, Argentina*

<sup>b</sup> *Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FiQ, UNLCONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina*

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## Abstract

Supporting Wilkinson's complex on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> rendered a high active catalyst for cyclohexene to cyclohexane hydrogenation. The activity was higher than that of the same complex unsupported, in the presence or absence of a S-containing poison (tetrahydrothiophene). XPS results suggested that, after poisoning, there was an insertion of a sulfur atom into the rhodium coordination sphere. Comparison of Wilkinson's complex with other palladium and nickel complexes was also made. The Wilkinson's complex proved to be more active and sulfur resistant than the Pd and Ni complexes in both homogeneous and heterogeneous conditions. For the Pd and Ni complexes there was a change in the coordination sphere after poisoning, as shown by the XPS results. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Wilkinson's catalyst; Heterogeneous hydrogenation; Homogeneous hydrogenation; Rh, Pd and Ni complexes

## 1. Introduction

Hydrogenation of organic compounds carried out by transition metal complexes has been of great interest during the past decades [1–3]. One of the most studied catalytic systems is the Rh(I) complex [RhCl(PPh<sub>3</sub>)<sub>3</sub>], often called Wilkinson's catalyst [4]. This complex is very useful in the catalytic hydrogenation of a variety of alkenes in mild conditions, at hydrogen pressures close to 1 atm. Most of the work has been

done in homogeneous systems, mainly in organic synthesis and in the production of fine chemicals [5–9]. However, the use of the unsupported complex as catalyst has an obvious disadvantage: the reactant solution must be purified after reaction by a costly procedure in order to recover the expensive rhodium catalyst.

An important limitation in the useful life of transition metal catalysts is that sulfur compounds, normally present in hydrocarbon streams, may poison them [10]. Despite the importance of the problem, the literature, according to our knowledge lacks reports referred to the sulfur resistance of Rh complexes. Because of this, the main purposes of this work

\* Corresponding author. Fax: +54-42-553727; E-mail: plargent@fiqus.unl.edu.ar

are: (a) to evaluate the Wilkinson's catalyst activity and resistance to sulfur poisoning, under homogeneous and heterogeneous conditions, and (b) to compare the Wilkinson's catalyst activity and sulfur resistance with that of the supported and unsupported  $[\text{PdCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$  and  $[\text{NiCl}_2(\text{NH}_2(\text{CH}_2)_{12}\text{CH}_3)_2]$  complexes which proved to be very efficient for these purposes [11,12]. The hydrogenation of cyclohexene to cyclohexane, carried out in mild conditions (353 K and 500 kPa) was used as a test reaction and tetrahydrothiophene as a poisoning reagent.

## 2. Experimental

The  $[\text{RhCl}(\text{PPh}_3)_3]$  complex was purchased at Aldrich, catalogue number 20,503-6; the  $[\text{PdCl}_2(\text{TDA})_2]$  and  $[\text{NiCl}_2(\text{TDA})_2]$  complexes, where  $\text{TDA} = \text{NH}_2(\text{CH}_2)_{12}\text{CH}_3$ , were prepared in a glass equipment with stirring and reflux under a purified argon atmosphere at 338 K, with a molar ratio  $\text{TDA}/\text{M} = 2$  ( $\text{M} = \text{Pd}$  or  $\text{Ni}$ ) during 4.5 h, as previously described [11,12]. Palladium and nickel chlorides were mixed with TDA, respectively, in toluene as solvent. The palladium complex was purified by column chromatography using silica gel as stationary phase and chloroform as solvent [11]. All the aliquots were tested to determine the presence of free TDA using the thin layer chromatography technique. All the fractions showing no impurities were gathered up and dried in a rotavap equipment to get the corresponding complex species in the solid state. On the other hand, the nickel complex was purified by successive toluene washes at room temperature [12].

Heterogeneization of the metal complexes were carried out by means of the incipient wetness technique [13]. A solution of the corresponding metal complex in toluene was used for impregnation in a suitable concentration to obtain catalysts containing 0.3% Rh, 0.3% Pd and 2% Ni, respectively. The supporting material

was  $\gamma\text{-Al}_2\text{O}_3$  Ketjen CK 300, pellets (3 mm), having  $180 \text{ m}^2 \text{ g}^{-1}$  BET surface area after calcination in air at 773 K for 3 h.

The electronic state of Rh, Pd, Cl, N, P and S, as well as the atomic ratios X/M (where  $\text{X} = \text{Cl}, \text{P}, \text{S}$  for  $\text{M} = \text{Rh}$  and  $\text{X} = \text{N}, \text{Cl}, \text{S}$  for  $\text{M} = \text{Pd}, \text{Ni}$ ) in the supported, unsupported and poisoned samples were analyzed 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 electronic charge of the samples, the C 1s line was taken as an internal standard at 285.0 eV, as previously reported [13]. The samples were introduced into the XPS equipment sample holder following the operational procedure described by other authors [14] in order to ensure that there were no modifications on the electronic states of the species analyzed [15]. Anyhow, exposing the samples to the atmosphere for different periods confirmed that there were no electronic modifications. Determinations of the superficial atomic ratios X/M were made by comparing the areas under the peaks after background subtraction and corrections due to differences in escape depths [16] and in photoionization cross sections using Scofield's results [17].

Pure and supported rhodium complex samples were also analyzed in the  $4000\text{--}625 \text{ cm}^{-1}$  range in a Shimadzu FTIR 8101/8101 M single-beam spectrometer. The equipment has a Michelson type optical interferometer. Two chambers are available to improve the quality of the spectra. The first one has a pyroelectric detector made of a high sensitivity LiTaO element, and the other has an MCT detector and the possibility to create a control  $\text{N}_2$  (or dry air) atmosphere [18]. The characteristic group frequencies corresponding to  $\text{PPh}_3$  molecule [19] were used to determine whether complex species kept their properties after heterogeneization and during all the steps of the catalytic tests. All the samples were dried at 353 K and they were examined in potassium bromide disks in a con-

Table 1

Activity ( $k$ ) and sulfur resistance obtained with poison-free feed (PF) and with the feed containing 300 ppm tetrahydrothiophene (THT)

Complex	Support	Reactant solution	$k (\times 10^5) (s^{-1})$	$R_{THT} (\%)$
[RhCl(PPh <sub>3</sub> ) <sub>3</sub> ]	Unsupported	PF	5.30	–
		THT	1.38	74
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	6.79	–
		THT	1.90	72
[PdCl <sub>2</sub> (TDA) <sub>2</sub> ]	Unsupported	PF	4.20	–
		THT	1.45	65
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	5.42	–
		THT	1.87	65
[NiCl <sub>2</sub> (TDA) <sub>2</sub> ]	Unsupported	PF	2.80	–
		THT	0.45	84
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	3.75	–
		THT	0.91	76

Reaction temperature, 353 K; hydrogen pressure, 500 kPa;  $R_{THT}$ : relative decrease in activity values after poisoning.

centration ranging from 0.5 to 1% to assure nonsaturated spectra.

Catalytic activities and sulfur resistances were determined in the hydrogenation of cyclohexene to cyclohexane, using a 5% solution of cyclohexene in toluene (named PF, meaning poison free, in the following considerations). For the poisoning experiments, the same solution with the addition of 300 ppm tetrahydrothiophene (named THT) was used. The reaction was carried out at 353 K and 500 kPa hydrogen pressure in a batch stainless-steel stirred tank reactor,  $V = 100$  ml and stirring velocity 600 rpm.

No diffusional limitations were observed under these conditions [20]. The weight of the supported catalyst was 0.2 g in the case of the catalytic tests carried out in heterogeneous conditions. For the catalytic evaluation of the unsupported complex, the Wilkinson's catalyst was dissolved in the solvent in a suitable concentration to obtain the same amount of Rh complex species as in the supported catalyst. Reactants and products were analyzed in a Konik 3000 gas chromatograph, using an FID and a CP Sill 88 capillary column. The catalytic activity (expressed as the kinetic constant,  $k$ ) was deter-

Table 2

XPS results for the unsupported and supported Wilkinson's complex (fresh and after evaluation with tetrahydrothiophene)

Complex	Support	Reactant solution	M 3d <sub>5/2</sub> (eV)	P 2p (eV)	Cl 2p (eV)	N 1s <sub>1/2</sub> (eV)	S 2p (eV)
[RhCl(PPh <sub>3</sub> ) <sub>3</sub> ]	Unsupported	Fresh	307.2	130.1	198.3	–	–
		Fresh	307.3	130.2	198.2	–	–
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	307.2	130.2	198.1	–	–
		THT	307.2	130.1	198.3	–	162.8
[PdCl <sub>2</sub> (TDA) <sub>2</sub> ]	Unsupported	Fresh	338.2	–	198.3	401.0	–
		Fresh	338.3	–	198.2	401.7	–
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	338.1	–	198.1	401.9	–
		THT	338.4	–	198.3	402.0	162.8
[NiCl <sub>2</sub> (TDA) <sub>2</sub> ]	Unsupported	Fresh	–	–	198.2	401.8	–
		Fresh	–	–	198.1	401.9	–
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	–	–	198.3	402.0	–
		THT	–	–	198.0	402.1	162.8

M = Rh, Pd or Ni.

Table 3

Atomic ratios for the unsupported and supported Wilkinson's complex (fresh and after evaluation with tetrahydrothiophene) obtained by XPS

Complex	Support	Reactant solution	P/M (at./at.)	N/M (at./at.)	Cl/M (at./at.)	S/M (at./at.)
[RhCl(PPh <sub>3</sub> ) <sub>3</sub> ]	Unsupported	Fresh	3.01	–	1.02	–
		Fresh	3.00	–	1.00	–
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	2.99	–	1.01	–
		THT	3.00	–	1.01	1.09
[PdCl <sub>2</sub> (TDA) <sub>2</sub> ]	Unsupported	Fresh	–	2.00	1.99	–
		Fresh	–	2.01	2.00	–
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	–	1.99	2.01	–
		THT	–	1.00	2.01	1.09
[NiCl <sub>2</sub> (TDA) <sub>2</sub> ]	Unsupported	Fresh	–	2.00	2.02	–
		Fresh	–	1.98	1.99	–
	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	–	1.99	2.00	–
		THT	–	1.10	1.98	1.08

M = Rh, Pd or Ni; L = P, Cl, N or S.

mined from the conversion vs. time plots assuming a zero order reaction [21].

### 3. Results

The activity values obtained for the supported and unsupported Wilkinson's complex, evaluated with the poison-free solution and with solution containing 300 ppm tetrahydrothiophene, are shown in Table 1. For comparative purposes, the activity and sulfur resistance values for the Pd and Ni complexes [11,12] are also presented in Table 1. The relative decrease in activity values after poisoning ( $R_{\text{THT}}$ ), determined from the activity data obtained with the poison free solution ( $k_{\text{PF}}$ ) and with the solution containing tetrahydrothiophene ( $k_{\text{THT}}$ ) [calculated as:  $R_{\text{THT}} = (k_{\text{PF}} - k_{\text{THT}})/k_{\text{PF}} \cdot 100$ ], has been also included. In all the cases, the selectivity to cyclohexane was 100%.

Tables 2 and 3 present the Rh 3d<sub>5/2</sub>, P 2p, Cl 2p and S 2p peaks binding energies (BE) and the atomic ratios P/Rh, Cl/Rh and S/Rh for the supported and unsupported Wilkinson's complex, fresh and after evaluation with solutions PF and THT. In both tables are also reported the corresponding values for the Ni and Pd complexes [11,12]. The Rh/Al superficial

atomic ratio was 0.047 for the Wilkinson's complex/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, while the corresponding value for S/Al superficial atomic ratio was 0.046.

The following samples were analyzed by FTIR spectroscopy: (a) pure [RhCl(PPh<sub>3</sub>)<sub>3</sub>], (b) fresh supported Wilkinson's complex, (c) supported Wilkinson's complex after evaluation with solution PF and (d) supported [RhCl(PPh<sub>3</sub>)<sub>3</sub>] complex after evaluation with solution THT. Spectra are shown in Fig. 1.

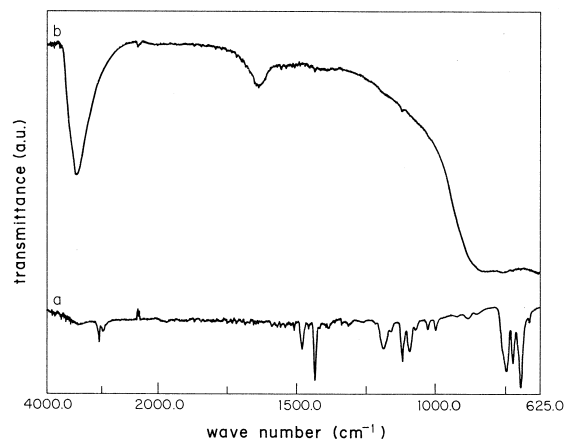


Fig. 1. FTIR spectra using Shimadzu FTIR 8101/8101 equipment: (a) pure [RhCl(PPh<sub>3</sub>)<sub>3</sub>], (b) fresh supported Wilkinson's complex.

## 4. Discussion

### 4.1. Comparison of the Wilkinson's catalyst in homogeneous vs. heterogeneous conditions in the presence or absence of poison

As shown in Table 1, the supported Wilkinson's complex is more active than the unsupported one. Table 1 also shows that both catalysts are poisoned to some extent after being evaluated in the presence of tetrahydrothiophene, but the alumina-supported catalyst is still more active than the Wilkinson's catalyst run in homogeneous condition.

Data in Tables 2 and 3 show that the Rh  $3d_{5/2}$ , P 2p and Cl 2p peaks BE and the atomic ratios P/Rh and Cl/Rh measured for the supported fresh complex sample and the unsupported one are almost the same. The ratios found are those corresponding to the theoretical stoichiometry in the molecule  $[\text{RhCl}(\text{PPh}_3)_3]$ . In all the cases, the BE of P 2p and Cl 2p peaks correspond to phosphorous in a phosphine and chlorine in a chloride species, respectively. This is in agreement with the theoretical electronic states that could be expected for the complex under study [22]. These results suggest that the rhodium complex maintains its coordination number even after heterogeneization.

No changes in the catalyst properties were detected by XPS after reaction in the PF solution, as shown in Tables 2 and 3. However, after treatment of the supported catalyst with the THT solution, a sulfur peak is detected at 162.8 eV (Table 2) with an atomic ratio S/Rh equal to 1.09. This peak may be attributed to sulfur in tetrahydrothiophene [22], which is the actual poisoning species. At the same time, Table 3 also shows that the P/Rh and Cl/Rh atomic ratios remain constant after the catalytic reaction in the presence of the tetrahydrothiophene. These results seem to suggest that after poisoning there is an insertion of the poisoning molecule into the coordination sphere of rhodium to form a Rh–S bond, giving a higher coordination number.

The FTIR spectrum of the unsupported complex (Fig. 1a) shows all the characteristic peaks of the triphenylphosphine. This is in total accordance with data reported in the literature [23]. An additional peak appears due to the presence of  $\text{CO}_2$ , which will not be considered any longer. The spectrum of the supported complex (Fig. 1b) shows mainly the presence of  $\gamma\text{-Al}_2\text{O}_3$  dominant structure. The spectra of samples c and d (not shown in Fig. 1) are quite alike to that obtained for sample b. These results may be interpreted in two different ways. On one hand, the concentration of the adsorbed species is not sufficiently high to give observable peaks in comparison with those given by the alumina. On the other hand, the absence of the characteristic peaks of  $\text{PPh}_3$  molecule (present in the complex species) may be explained due to the loss of freedom of the phenyl group, assuming a coplanar adsorption on the alumina surface.

### 4.2. Wilkinson's complex vs. palladium and nickel complexes

As shown in Table 1, Wilkinson's catalyst is more active and sulfur resistant than the Pd and Ni complexes. This holds not only for the homogeneous condition but also for the heterogeneous one. The same conclusion can also be obtained when considering the catalytic test carried out for the solutions named PF and THT.

The atomic ratios shown in Tables 2 and 3, suggest that in the presence of THT rhodium changes its coordination sphere incorporating sulfur atoms, and giving a higher coordination number; while the palladium and nickel complexes preserve the original coordination number with a change in the coordination sphere, replacing a N-ligand by a S-ligand.

## 5. Conclusions

Wilkinson's catalyst supported on alumina proved to be more active and sulfur resistant than the homogeneous one for cyclohexene hydrogenation. The pure and supported rhodium

complex are both tetra-coordinated, as shown by the XPS results.

[RhCl(PPh<sub>3</sub>)<sub>3</sub>] complex supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is more active and sulfur resistant than the Pd and Ni complexes.

XPS results for Wilkinson's catalyst suggest that after poisoning with tetrahydrothiophene, there is an insertion of the poisoning molecule into the coordination sphere of rhodium to form a Rh–S bond giving a higher coordination number. While for palladium and nickel complexes, the original coordination number is preserved, but there is a change in the coordination sphere: N-ligands are partially replaced by S-ligands.

Last but not least, it is a fact that even though the rhodium complex is more active than palladium and nickel ones, its precursor salt is much more costly, making the final selection of the catalyst a matter of balance between chemical behavior and the catalyst's production cost.

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