

# Immobilized Rh, Ru, Pd and Ni complexes as catalysts in the hydrogenation of cyclohexene

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## Abstract

Complexes of Rh, Ru, Pd and Ni with tridecylamine and chloride as ligands were prepared and tested as heterogeneous catalysts for the hydrogenation of cyclohexene. The Wilkinson's complex was used as a reference catalyst. Supported complexes turned out to be more active and more resistant to a sulphur poison than the homogeneous systems also evaluated for comparison. The rhodium-tridecylamine complex was the most active, slightly less than the Wilkinson's complex but more sulphur resistant than the latter. XPS and FTIR studies revealed that the complexes kept their chemical identity and remained attached to the support even after the reaction. This suggests that the coordination compounds studied are the catalytically active species or that they are converted to the actual active species during the catalytic process. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Transition metal complexes; Catalytic hydrogenation; Heterogeneous catalysts

## 1. Introduction

In the last decades, transition metal complexes have been extensively used as catalysts for hydrogenation reactions, not only in homogeneous but also in heterogeneous phase [1,2]. Several supported complexes have exhibited good activity and selectivity at mild conditions of temperature and pressure [3,4]. In many cases, they show better performances than some supported metal catalysts [5,6] traditionally predominant in these fields. Complexes of transition metals like Pd, Rh, Ru and Pt have been successfully suited to this type of reactions, mostly in homogeneous systems [7–11]. Although, Ni systems, to our knowledge, have been paid less attention and are less active and selective catalysts, Ni precursor salts are considerably less costly.

The d<sup>8</sup> species, e.g. Rh(I), Ir(I), Pd(II), Ni(II) and Pt(II), form complexes for which the square planar geometry is

specially favoured. These square planar complexes, particularly those from the second row, have proved to be active species for the catalytic hydrogenation of multiple bonds and other reactions [12]. They are important in catalysis since the metal atom can increase its coordination number by accepting ligands in the apical sites [13] or interacting with the support. These complexes have also the ability to dissociate molecular dihydrogen, and stabilize a variety of reaction intermediates through coordination as ligands in relatively stable but reactive complexes. This is made possible by promoting rearrangements within their coordination spheres [14].

Ruthenium is another active metal and Ru(II) d<sup>6</sup> complexes such as the five-coordinate [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] and [RuHCl(PPh<sub>3</sub>)<sub>3</sub>] among others, have turned out to be very active for the hydrogenation of terminal olefins [15,16] and for asymmetric hydrogenation [17].

The aim of this work is to obtain complexes of some of the metals mentioned above, i.e. Rh(I), Ru(II), Pd(II) and Ni(II), with chloride and tridecylamine as ligands, and to

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evaluate their catalytic behaviour mainly as heterogeneous catalysts without any pre-reaction treatment.

As a basic, sigma donor ligand, tridecylamine was expected to make the metal centre electron-rich, thus allowing the overlap of the appropriate filled metal d orbital with the empty H<sub>2</sub> sigma antibonding molecular orbital [18]. This contributes to the H–H bond cleavage, a crucial step in the hydrogenation catalytic process.

Supported complexes have an important advantage over homogeneous systems, namely the easy way to separate them from the remaining solution. In this work, two different supports,  $\gamma$ -alumina and a carbonaceous material were used. Anyhow, comparison of their behaviour with that at homogeneous conditions was also addressed. On the other hand, the Wilkinson's complex [RhCl(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub>] was used as a reference, because it is a very effective system, traditionally run homogeneously for the catalytic hydrogenation of a variety of alkenes at mild conditions [19,20]. The hydrogenation of cyclohexene to cyclohexane was performed as a test reaction.

In addition, because of the scientific and industrial interest in catalyst deactivation by poisoning, and the frequent occurrence of sulphur compounds in some hydrogenation feedstocks, tests were also run to evaluate the performance of the catalysts in the presence of a sulphur poison such as tetrahydrothiophene.

## 2. Experimental

### 2.1. Complex preparation and purification

#### 2.1.1. Rh-TDA complex

This complex, where TDA stands for tridecylamine, NH<sub>2</sub>(CH<sub>2</sub>)<sub>12</sub>CH<sub>3</sub>, was prepared from RhCl<sub>3</sub> and TDA, in carbon tetrachloride as solvent. A glass equipment with agitation and reflux was used, in a purified argon atmosphere at 348 K, for 4.5 h with a molar ratio TDA/RhCl<sub>3</sub> = 6. A yellow–orange solution resulted. The purification was made by column chromatography with silica gel as the stationary phase and a 5/1 v/v chloroform/methanol solution as the solvent. All the aliquots were tested to determine the presence of free TDA by thin layer chromatography. After drying the TDA-free solution in a rotary evaporator a yellow–orange solid was obtained.

#### 2.1.2. Pd-TDA complex

PdCl<sub>2</sub> with TDA were mixed in toluene, in a glass equipment with agitation and reflux, under a purified Ar atmosphere at 338 K, for 4 h and with a molar ratio TDA/PdCl<sub>2</sub> = 2. After 1 h the appearance of a yellow–orange colour in the liquid phase was observed, giving a yellow solid after solvent evaporation. The purification was made in a similar fashion to that of Rh-TDA but using chloroform as the eluting solvent; a yellow solid was obtained after solvent evaporation.

#### 2.1.3. Ru-TDA complex

A deep blue Ru-TDA complex was obtained by reaction of RuCl<sub>3</sub> and TDA (molar ratio TDA/RuCl<sub>3</sub> = 6) in toluene at 373 K, for 7 h, in a glass equipment with agitation and reflux, under purified Ar. The purification and drying of the substance were made in a similar way to those corresponding to Rh-TDA.

#### 2.1.4. Ni-TDA complex

Anhydrous NiCl<sub>2</sub> and TDA (molar ratio TDA/NiCl<sub>2</sub> = 2) were mixed in toluene, in glass equipment with agitation and reflux, under an Ar atmosphere, at 353 K for 10 h. At the end of the reaction a solid phase of excess solid NiCl<sub>2</sub> and a pale-green liquid phase were observed. After separating both phases by filtration, the solution was cooled to room temperature, and a solid phase appeared. The solvent was evaporated to dryness and a pale-green solid was obtained. The presence of free excess tridecylamine was detected by thin layer chromatography, using silica gel as the support and chloroform–methanol solution (v/v ratio 5:1) as the mobile phase. The solid was subjected to several toluene washes at room temperature. After each wash an aliquot of the complex (toluene solution at 333 K) was analysed by means of the chromatographic method outlined above, until verifying the complete removal of the amine.

#### 2.1.5. Blank test

In each preceding complex preparation, a blank experiment was run to verify the complex formation, following the corresponding procedure but using only the salt and solvent.

#### 2.1.6. Wilkinson's complex

The [RhCl(PPh<sub>3</sub>)<sub>3</sub>] complex was purchased at Aldrich, catalogue number 20,503-6.

### 2.2. Complex immobilization

All of the complexes were supported on  $\gamma$ -alumina, and additionally the Rh complexes were also anchored on a carbon support. In order to check for a possible leaching of the immobilized complexes, each fresh-supported system was subjected to a 100 h run in the corresponding reaction solvent at 353 K. After the test, none metal was detected in the remaining solution by a spectrophotometric method, thus revealing a strong adherence to the support. In this respect, atomic ratios obtained by XPS before and after the mentioned test, were also taken into account.

#### 2.2.1. Alumina-supported complexes

The impregnation of the complexes was performed by means of the incipient wetness technique, on  $\gamma$ -alumina Ketjen CK 300, cylinders of 1.5 mm diameter, 3 mm length, previously calcined in air at 773 K for 3 h, Brunauer–Emmet–Teller (BET) surface area: 180 m<sup>2</sup> g<sup>-1</sup>, pore volume 0.10 mL g<sup>-1</sup> (N<sub>2</sub>) [11]. The solvents used for impregnation and the metal weight percent were as follows: Rh-TDA: 5/

1 v/v chloroform–methanol, 0.3% Rh; Rh-PPh<sub>3</sub>: chloroform, 0.3% Rh; Pd-TDA: chloroform, 0.3% Pd; Ru-TDA: chloroform, 1% Ru; Ni-TDA: toluene, 2% Ni.

### 2.2.2. Carbon-supported complexes

The carbonaceous support used for the rhodium complexes was a char of phenolformaldehyde polymer resins, prepared by carbonisation of the raw material at 1273 K (heating rate of 5 K/min) for 2 h in N<sub>2</sub> (80 mL/min STP). Then, the carbon was exhaustively washed to the complete removal of soluble substances and dried, resulting a coarse powder with a 610 m<sup>2</sup> g<sup>-1</sup> BET surface area, pore volume 0.34 mL g<sup>-1</sup> (N<sub>2</sub>) [11]. The anchoring step was made in a similar way to that used for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, to give 0.3 wt.% Rh catalysts.

### 2.3. Catalytic tests

The catalytic performance in the hydrogenation of cyclohexene to cyclohexane was firstly evaluated for complexes of the metals Pd, Rh, Ru and Ni with chloride and tridecylamine as ligands, in alumina-supported systems. With the purpose of comparison, runs in homogeneous systems were executed at the same conditions as those for the heterogeneous systems, in solutions containing the same complex weight as in the corresponding supported catalyst. The purified complexes, supported or unsupported, were used as obtained without any previous treatment before the catalytic tests. The Wilkinson's catalyst was used as a reference, in homogeneous and heterogeneous conditions.

As the most active systems were those of alumina-supported Rh complexes, further evaluations were made for this complexes on a carbonaceous support, with a much higher BET surface and porosity than those of alumina.

In all cases, hydrogenation was performed in 180 min runs, using 100 mL of a 0.49 M cyclohexene solution in toluene for Pd and Ni complexes and CCl<sub>4</sub> for Rh and Ru complexes (to prevent the aromatic solvent hydrogenation), in a batch PTFE-coated stainless steel reactor, at 353 K, 500 kPa hydrogen pressure and 600 rpm stirring velocity. The weight of the supported catalysts was 0.2 g.

The possibility of diffusional limitations was investigated following procedures described in the literature [21,22]. Experiments carried out in the range 180–1400 rpm stirring velocity, showed an invariable catalytic performance above 500 rpm. On account of this, external diffusional limitations were considered to be absent at the rotary speed selected. On the other hand, in order to check for the possibility of intraparticle mass transfer limitations, the heterogenised complex catalyst was crushed up to 1/4 the original size of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pellets used as support. In every case, the conversion values obtained with the crushed material were the same than those corresponding to the catalyst that was not crushed. Hence, it may be concluded that internal diffusional limitations were absent at the operational conditions of this work.

In order to evaluate also, the sulphur resistance of the catalysts runs were carried out in hetero and homogeneous systems, adding 300 ppm tetrahydrothiophene (THT), at the same conditions as those of the poison-free experiments.

All the catalytic tests were executed in triplicate with an error within 3%. The reactants and products were analysed by gas chromatography, using a flame ionisation detector and a CP Sill 88 capillary column. On analysing the remaining solution for metal by a spectrophotometric method, no leaching of the complexes to the liquid phase was verified in any case. As in all cases, cyclohexane was the only product detected, the selectivity was 100%.

### 2.4. Spectroscopic characterization

#### 2.4.1. X-Ray photoelectron spectroscopy (XPS)

The studies were carried out to evaluate: (a) the electronic state of atoms and (b) the atomic ratios, for the pure complexes and for the supported complexes before and after the reaction. A Shimadzu ESCA 750 Electron Spectrometer coupled to a Shimadzu ESCAPAC 760 Data System was used. As previously described [23], the C 1s line was taken as an internal standard at 285.0 eV so as to correct possible deviations caused by electric charge on the samples. The superficial electronic state of the atoms were studied according to the position of the following peak maxima: Rh 3d<sub>5/2</sub>, Ru 3p<sub>3/2</sub> and Pd 3d<sub>5/2</sub> for the metal atoms, N 1s<sub>1/2</sub> for the TDA ligand, P 2p for the Wilkinson complex, Cl 2p for all the complexes, and S 2p in the case of poisoning with THT. In order to ensure that there was no modification on the electronic state of the species, the sample introduction was made according to the operational procedure reported earlier [24]. Exposing the samples to the atmosphere for different periods of time confirmed that there were no electronic modifications. Determination of the atomic ratios  $x/\text{Metal}$  ( $x = \text{N, Cl, P or S}$ ) and  $\text{Metal}/Z$  ( $Z = \text{Al or C, depending on the support}$ ) were made by comparing the areas under the peaks after background subtraction and corrections due to differences in escape depths [25] and in photoionization cross sections [26].

#### 2.4.2. Fourier transform infrared spectroscopy (FTIR)

The characteristic frequencies corresponding to tridecylamine and triphenylphosphine [27–29] were used to trace the presence of these ligands in the corresponding pure complexes, as well as in the alumina supported systems before and after the catalytic tests. The analyses were executed in the 4400–400 cm<sup>-1</sup> range in a Shimadzu FTIR 8101/8101M 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 controlled N<sub>2</sub> (or dry air) atmosphere. All of the samples were dried at 353 K and they were examined in potassium bromide disks in a concentration ranging from 0.5 to 1% to ensure spectra non-saturation.

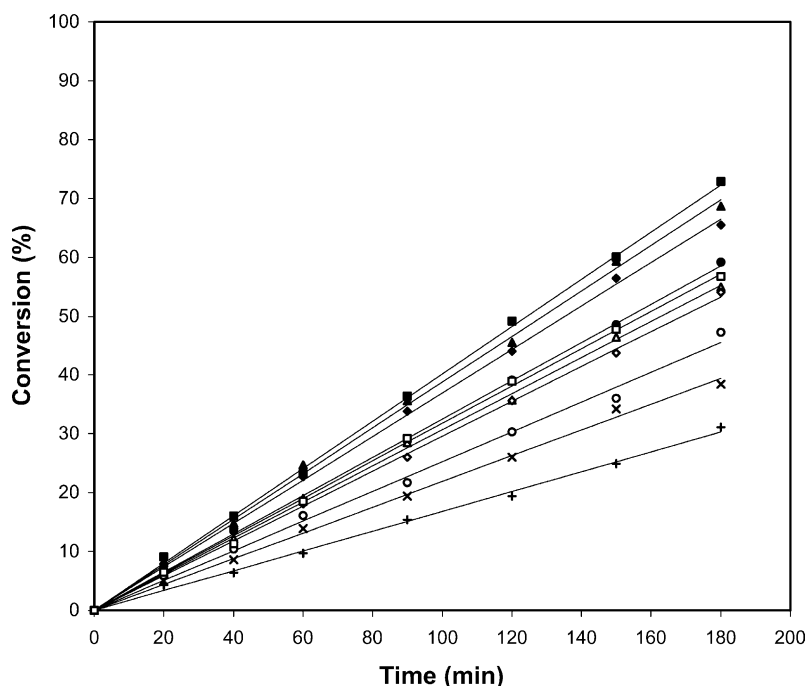


Fig. 1. Cyclohexene conversion (poison-free cases) vs. time of operation for M-TDA complexes and Wilkinson's complex, unsupported and alumina-supported; (■) Rh-PPh<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>; (▲) Rh-TDA/Al<sub>2</sub>O<sub>3</sub>; (◆) Ru-TDA/Al<sub>2</sub>O<sub>3</sub>; (●) Pd-TDA/Al<sub>2</sub>O<sub>3</sub>; (□) Rh-PPh<sub>3</sub>; (Δ) Rh-TDA; (◇) Ru-TDA; (○) Pd-TDA; (×) Ni-TDA/Al<sub>2</sub>O<sub>3</sub> and (+) Ni-TDA.

### 3. Results

#### 3.1. Catalytic tests

The catalytic performance was evaluated by plotting the results of the cyclohexene–cyclohexane conversion versus time. The plots for the 180 min reaction time fitted the best to straight lines, obtained with a fitting factor  $R$  not lower than 0.99. Thus, zero-order reaction was assumed within this time interval. Attempts to fit the plots to other kinetic orders were not successful. Examples of zero-order in hydrogenation reactions of unsaturated hydrocarbons can be found in the literature [30].

Table 1

Percent relative decrease in cyclohexene conversion in the presence of poison for Rh, Ru, Pd and Ni complexes, alumina-supported and unsupported

Metal	Ligand	Support	$D_p$
Rh	TDA	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	35
Ru	TDA	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	56
Pd	TDA	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	65
Ni	TDA	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	76
Pd	TDA	–	65
Ru	TDA	–	66
Rh	TDA	–	72
Ni	TDA	–	84

$D_p = (x_f - x_p) \cdot x_f^{-1} \cdot 100$ ;  $D_p$ : percent relative decrease in cyclohexene conversion in the presence of poison with respect to the cyclohexene conversion in the poison-free evaluation;  $x_f$ : final cyclohexene conversion for poison-free evaluation;  $x_p$ : final cyclohexene conversion in the presence of 300 ppm tetrahydrothiophene.

Fig. 1 depicts the plots of percent cyclohexene conversion versus time for the catalysts of metals Pd, Rh, Ru and Ni with ligands chloride and TDA, supported on  $\gamma$ -alumina and unsupported.

Fig. 2 displays the plots of percent cyclohexene conversion versus time for Rh-TDA catalyst and Wilkinson's catalyst, homogeneous and alumina- or carbon-supported.

The sulphur resistance of the catalysts was evaluated by means of the relative decrease in cyclohexene conversion, as shown in Tables 1 and 2. This percent relative decrease was calculated as follows:  $D_p = (x_f - x_p) \cdot x_f^{-1} \cdot 100$ , where  $x_f$  is the final cyclohexene conversion in the poison-free case, and  $x_p$  is the final cyclohexene conversion in the presence of the THT poison. Thus, the lowest the  $D_p$  value, the highest the sulphur resistance.

Table 1 exhibits the percent relative decrease of cyclohexene conversion in the presence of THT poison with respect to cyclohexene conversion in the poison-free

Table 2

Percent relative decrease in cyclohexene conversion in the presence of poison for the supported and unsupported Rh complexes

Metal	Ligand	Support	$D_p$
Rh	TDA	Carbon	31
Rh	PPh <sub>3</sub>	Carbon	67
Rh	TDA	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	35
Rh	PPh <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	72
Rh	TDA	–	72
Rh	PPh <sub>3</sub>	–	74

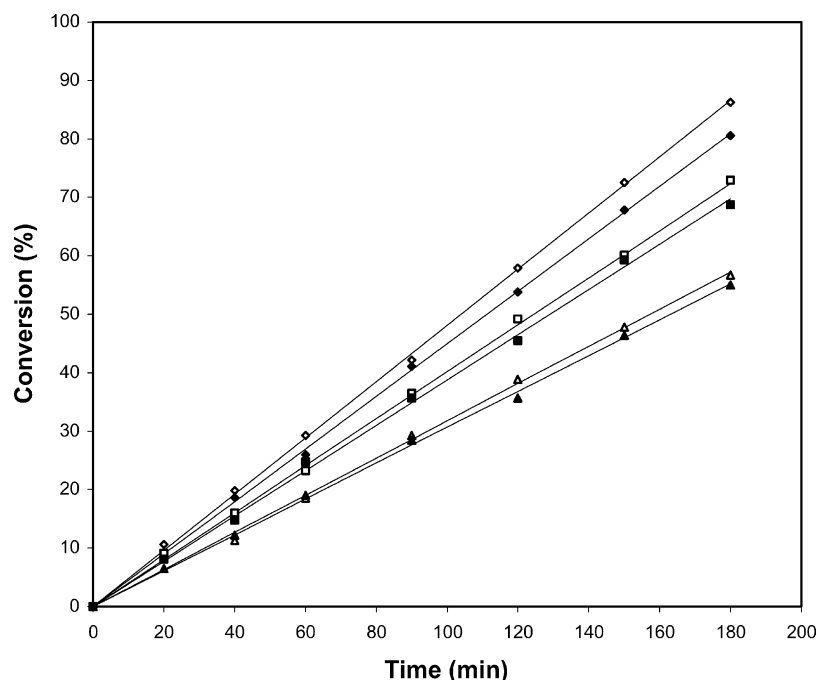


Fig. 2. Cyclohexene conversion (poison-free cases) vs. time of operation for the complexes Rh-TDA and Wilkinson, unsupported, Al<sub>2</sub>O<sub>3</sub>-supported and carbon-supported (◇) Rh-PPh<sub>3</sub>/Carbon; (◆) Rh-TDA/Carbon; (□) Rh-PPh<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>; (■) Rh-TDA/Al<sub>2</sub>O<sub>3</sub>; (Δ) Rh-PPh<sub>3</sub> and (▲) Rh-TDA.

evaluation, for the homogeneous and alumina-supported systems involved in Fig. 1.

Similarly, Table 2 displays the percent relative decrease of the cyclohexene conversion in the presence of THT poison with respect to the cyclohexene conversion in the case of poison-free catalytic evaluation for the Rh systems involved in Fig. 2, calculated in the same fashion as that of Table 1.

### 3.2. XPS and FTIR results

XPS binding energies and atomic ratios for the pure and fresh heterogenized complexes are shown in Table 3 and

those corresponding to the heterogeneous systems after reaction with or without poison are displayed in Table 4. In the latter, binding energies for metal, N, Cl and P are omitted, as they are almost the same as those in Table 3.

The FTIR spectra of the tridecylamine complexes, presented the characteristic peaks of the tridecylamine ligand molecule [27,28], for the pure and alumina-supported systems. As an example, in Fig. 3 are depicted the spectra for the Rh-TDA complex pure, fresh-supported, and supported after reaction in poison-free and poisoned solution. The Wilkinson's complex spectrum showed all the characteristic peaks of the ligand triphenylphosphine, in accordance with the reported data [29]. In the spectrum of the supported

Table 3

Pure and fresh heterogenized complexes: XPS binding energies (M = Rh 3d<sub>5/2</sub>, Ru 3p<sub>3/2</sub>, Pd 3d<sub>5/2</sub>, Ni 2p<sub>3/2</sub>) and XPS atomic ratios (Z = Al or C depending on the support)

Complex	Condition	Binding energies (eV)				Atomic ratios (at/at)			
		M	N 1s <sub>1/2</sub>	Cl 2p	P 2p	N/M	Cl/M	P/M	M/Z
Rh-TDA	Pure	307.1	402.1	198.1	–	3.00	1.01	–	–
	γ-Al <sub>2</sub> O <sub>3</sub>	307.1	402.2	198.2	–	2.99	0.99	–	0.052
	Carbon	307.2	402.1	198.2	–	2.99	1.00	–	0.043
Rh-PPh <sub>3</sub>	Pure	307.2	–	198.3	130.1	–	1.02	3.01	–
	γ-Al <sub>2</sub> O <sub>3</sub>	307.2	–	198.1	130.2	–	1.01	3.00	0.093
	Carbon	307.3	–	198.3	130.2	–	0.99	3.00	0.10
Ru-TDA	Pure	463.0	401.7	198.3	–	1.90	1.90	–	–
	γ-Al <sub>2</sub> O <sub>3</sub>	463.3	402.0	198.2	–	1.90	2.00	–	0.032
Pd-TDA	Pure	338.2	401.9	198.3	–	2.00	1.99	–	–
	γ-Al <sub>2</sub> O <sub>3</sub>	338.1	401.9	198.1	–	1.99	2.01	–	0.088
Ni-TDA	Pure	856.2	401.8	198.2	–	2.00	2.02	–	–
	γ-Al <sub>2</sub> O <sub>3</sub>	856.3	402.0	198.3	–	1.99	2.00	–	1.04

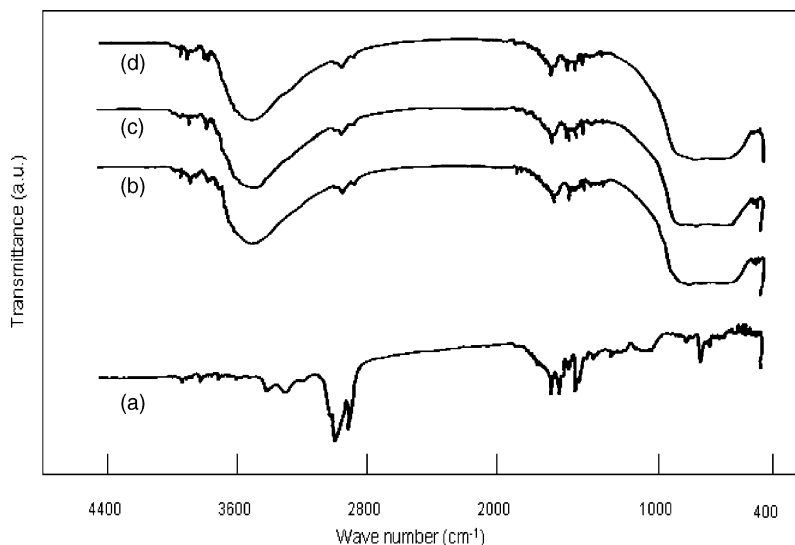


Fig. 3. FTIR spectra obtained for: (a) pure Rh-TDA complex, (b) fresh Rh-TDA/Al<sub>2</sub>O<sub>3</sub>, (c) Rh-TDA/Al<sub>2</sub>O<sub>3</sub> after reaction in the poison-free solution, and (d) Rh-TDA/Al<sub>2</sub>O<sub>3</sub> after reaction in the THT-poisoned solution.

Table 4

XPS S 2p binding energy (BE) and atomic ratios for the supported complexes after reaction: poison-free (PF) and with poison (THT), M and Z: see Table 3

Complex	Support	Condition	S 2p BE (eV)	S/M (at./at.)	N/M (at./at.)	Cl/M (at./at.)	P/M (at./at.)	M/Z (at./at.)
Rh-PPh <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	–	–	–	1.01	2.99	0.093
		THT	162.8	1.09	–	1.01	3.00	0.093
Rh-PPh <sub>3</sub>	Carbon	PF	–	–	–	0.99	2.99	0.10
		THT	162.9	0.65	–	1.00	3.01	0.10
Rh-TDA	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	–	–	2.99	0.99	–	0.051
		THT	162.9	0.99	2.99	1.00	–	0.051
Rh-TDA	Carbon	PF	–	–	2.99	1.00	–	0.040
		THT	162.9	0.52	3.01	0.99	–	0.041
Pd-TDA	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	–	–	1.99	2.01	–	0.087
		THT	162.8	1.09	1.00	2.01	–	0.088
Ni-TDA	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	–	–	1.99	2.00	–	1.04
		THT	162.8	1.08	1.10	1.98	–	1.04
Ru-TDA	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PF	–	–	1.90	2.00	–	0.032
		THT	162.7	1.10	1.00	1.90	–	0.032

complex the main peaks corresponded to the alumina dominant structure.

#### 4. Discussion

According to Fig. 1, all of the complexes showed higher conversions when supported than in homogeneous conditions. Of all the coordination compounds supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or unsupported, the immobilized Wilkinson's complex showed the higher final cyclohexene conversion, with Rh-TDA/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system having a comparable though slightly lower value.

With reference to Fig. 2, the order of conversion at 180 min for the alumina-supported TDA complexes was: Rh > Ru > Pd > Ni, and the same held for the unsupported species.

The evaluation of the two most active complexes of this series, those of Rh, namely Rh-TDA and Rh-PPh<sub>3</sub>, shows the order: C-supported > Al<sub>2</sub>O<sub>3</sub>-supported > unsupported, for each one of the two coordination compounds. This means an important influence of the supports that made the heterogenised systems far better than the homogeneous ones. The enhanced cyclohexane yield obtained with the carbon support with respect to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, may have a relationship to the former's BET surface three times higher and a higher pore volume than that of the latter [11]. However, further research is needed regarding these aspects, including besides the evaluation of the surface chemistry and its effect on the catalyst's performance.

For each support condition, the Rh-PPh<sub>3</sub> complex exhibited a slightly higher cyclohexane yield than that of the Rh-TDA complex.

As known, the success of the Wilkinson's complex and other Rh complexes may be attributed, on the one hand, to the fact that the most important oxidation states for Rhodium are I and III, i.e. separated by two units [12,13,18]; this allows the oxidative addition of dihydrogen to give dihydride intermediates species which are considered essential in the catalytic cycle; the required dihydrogen molecule cleavage is proposed to occur because of the interaction of a filled metal d orbital with the empty sigma antibonding  $H_2$  molecular orbital, thus weakening the H–H bond; this bond breaking may be facilitated when the metal atom is electron-rich [15,18]. This might be the case for basic ligands as tridecylamine used in this work and amines in general. Thus, these ligands pose an alternative to other more toxic electron-donating ligands as phosphines [1], typically found in  $d^8$  complexes (e.g. Wilkinson's). On the other hand, the intermediates in catalytic cycles such as that proposed for the homogeneous Wilkinson's systems, are not so stable as to form bottlenecks in the cycle or too unstable to break it; in this way, the intermediates are in delicate balance and present in low concentrations, reacting predominantly within the cycle rather than giving dead-end species [12]. These features may be also important in the performance of the heterogenised Wilkinson complex, as well as in the Rh-TDA systems.

Hydride complexes, as intermediates species or starting materials, are considered to play a key role in most, if not all, catalytic hydrogenations [1,11,13]. Dihydride intermediates of Pd(IV) have been reported for hydrogenation reactions with Pd(II) complexes as catalysts [31], indicating the occurrence of an oxidative addition. This might be the case also for the Pd-TDA complex and the less effective Ni-TDA complex, and appear to be a remarkable feature of square planar  $d^8$  complexes. In general, on undergoing oxidative addition these complexes give six-coordinate dihydride species.

Hydride intermediates may be produced not only by oxidative addition, but also by other mechanisms, e.g. dihydrogen heterolytic splitting, as is the case for some Ru complexes [32].

For the catalytic evaluation with THT as a sulphur poison, Tables 1 and 2 show, in all cases, positive  $D_p$  values that exhibit a remarkable decrease in catalytic activity in such a condition. In general, the alumina-supported complexes were more sulphur-resistant than the unsupported complexes (Table 1). This may be attributed to the fact that, because of an interaction of the complex with the support, the central metal atom decreases its coordinative unsaturation, thus making the attachment of the poison as a ligand more difficult; in addition, some part of the poison molecules may be blocked by adsorption on the support in positions not occupied by the active species; obviously, this protective feature provided by the support is not possible for the complex in solution, where the active species are then more exposed to poison attack.

The complex Rh-TDA supported on alumina is much more sulphur resistant than the other M-TDA/ $Al_2O_3$  systems (Table 1). When comparing the two Rh complexes (Table 2), it is seen that the Rh-TDA complex, supported on alumina or on carbon is also more sulphur-resistant than the Wilkinson's complex. The latter is expected to pose a more effective steric hindrance to the poison molecule attack on the complex metal atom, because of  $PPh_3$  ligand bulkiness; but as the TDA system is more resistant to poison, the effect appears to be not steric but mainly electronic, as a result of the metal atom environment. By far, then, the most significant enhancing of sulphur resistance on anchoring occurred for Rh-TDA.

The XPS  $N\ s_{1/2}$  signals in Table 3 correspond in all cases to N in an amine, as expected, and the same applies to Cl 2p as chloride, P 2p in a phosphine and S 2p in THT [33]. XPS binding energies for the metals also remained unaltered in the different samples, namely: Pd  $3d_{5/2}$  for Pd as Pd(II) in  $[Pd(NH_3)_4Cl_2]$ , Rh  $3d_{5/2}$  for Rh as Rh(I) in the Wilkinson's complex, Ru  $3p_{3/2}$  for Ru as Ru(II) in  $RuCl_2$ , and Ni  $2p_{3/2}$  for Ni as Ni(II) in  $NiCl_2$ .

Thus, the XPS binding energies kept almost constant for each element in every pure and immobilized complex before reaction (Table 3) as well as after reaction, with or without poison. This leads to the supposition that each complex remained attached to its support without losing its chemical identity. The constancy of the atomic ratios N/M, Cl/M and P/M in Table 3 supports this statement for the pure and fresh heterogenised complexes. Besides, it suggests the complex minimum formulas:  $[PdCl_2(TDA)_2]$ ,  $[RuCl_2(TDA)_2]$ ,  $[RhCl(TDA)_3]$  and  $[NiCl_2(TDA)_2]$ , respectively. The preceding arguments concerning a strong adherence to the support are also corroborated by the absence of complex leaching and by the constancy of the metal/aluminium and metal/carbon atomic ratios for the supported complexes before and after reaction.

In the cases corresponding to the presence of the THT poison, Table 4 shows the constancy of Cl/M ratios. However, the N/M ratio for Pd, Ru and Ni complexes underwent a remarkable decreasing from two to approximately one; this, in addition to the appearance of a S/M ratio approximately equal to 1, indicates the occurrence of a sulphur atom insertion in the metal atom's coordination sphere, replacing at least in part the nitrogen atoms. For the Rh complexes, the N/M (or P/M) ratio remained constant. So, in these cases THT appears to insert in the metal's coordination sphere but without displacing the other ligands. The THT molecule, as a competing ligand, may tightly bind to the metal centre via the sulphur atom, thus disturbing the catalytic cycle or even shutting it down [12]; in this context the metal–sulphur bond strength may play a key role; as a result, cyclohexane production decreases outstandingly in the presence of the poison. However, additional work is needed to evaluate whether there is

also a poison adsorption on the support, and if any, to what extent.

In Fig. 3a, the FTIR spectrum of the Rh-TDA complex displays the wavenumbers corresponding to the characteristic peaks of a primary aliphatic amine, i.e.  $\text{NH}_2$  stretching:  $3100\text{--}3250\text{ cm}^{-1}$ , CH stretching:  $2800\text{--}3000\text{ cm}^{-1}$ ,  $\text{NH}_2$  bending around  $1600\text{--}1700\text{ cm}^{-1}$ , CH bending:  $1300\text{--}1500\text{ cm}^{-1}$ , and CN stretching:  $1000\text{--}1200\text{ cm}^{-1}$ , according to the literature [27,28]. The other spectra in Fig. 3 show mainly the  $\gamma\text{-Al}_2\text{O}_3$  peaks together with some of the strongest ones mentioned above:  $\text{NH}_2$  and CH stretching modes (weak) and  $\text{NH}_2$  and CH bending modes (strong).

All this suggests that a complex species was produced in the reaction of the precursor salt with TDA as a ligand, and that the complex remained chemically unchanged after heterogenisation and after the reaction. Similar considerations apply for the other complexes.

## 5. Conclusions

XPS and FTIR results permit the assumption that the metal complexes studied are the catalytic active species in the cyclohexene hydrogenation, or they are converted to the actual active species during the catalytic cycle or process. Previous reports from other authors also ascribe catalytic activity to complex species rather than to the metal, metal oxides or others [2]. When supported, all the complexes showed higher conversions than all the unsupported systems, including the Wilkinson's complex itself. Besides, supported complexes present the advantage, over homogeneous catalysts, of an easy separation from the remaining solution. Heterogeneous Rh catalysts showed the best performance of all the catalysts tested. Rh-TDA was the most successful prepared complex, exhibiting a greatly enhanced performance and sulphur resistance specially when supported. In comparison with the Wilkinson's catalyst used as a reference, it showed just a slightly final lower conversion, but a higher sulphur resistance. Thus, the Rh-TDA complex may be considered as a very good alternative to the Wilkinson's complex.

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