

1-Heptyne semihydrogenation catalized by palladium or rhodium complexes

Influence of: metal atom, ligands and the homo/heterogeneous condition

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Abstract

[RhCl(TDA)₃], [RhCl(HA)₃], [PdCl₂(TDA)₂] and [PdCl₂(HA)₂] (TDA = tridecylamine, HA = hexylamine) were synthesized and tested as catalysts in homogeneous and heterogeneous condition for the 1-heptyne semihydrogenation, using γ -alumina as support. The Lindlar catalyst was used as a reference. XPS, FTIR and Atomic Absorption results showed that the active catalytic species in each case is the complex itself. All of the catalytic systems exhibited a better performance than the Lindlar catalyst, with the exception of [PdCl₂(HA)₂]. The analysis of activity and selectivity values allowed to say that the best system is [RhCl(TDA)₃]/Al₂O₃, an heterogeneous catalyst with an electron-rich transition metal and an electron-donating ligand (TDA) containing a long-chain hydrocarbon substituent. The complex system catalytic behaviour could be explained by means of electronic and geometric effects.

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Keywords: 1-Heptyne semihydrogenation; Rh/Pd complexes; Coordination sphere; Homo/heterogeneous condition

1. Introduction

It is well known that many products derived from several non-saturated hydrocarbons are used as the starting point for obtaining high added value substances related to fine and commercial chemistry [1,2], by means of reactions such as hydrogenation, using metallic and bimetallic catalysts [3–9]. Also, since many years ago, coordination compounds have gained increasing importance as catalysts for such reactions [10–19]. This is so because they allow higher values of activity and selectivity at mild conditions of pressure and temperature. Complexes have a two-folded action: on one hand the possibility of forming an intermediate organometallic compound with the non-saturated substrate; on the other hand, the ability of weakening the H–H bond, both factors that favour the expected semihydrogenation process.

Our previous work has dealt with hydrocarbon hydrogenation catalized by Pd(II), Rh(I), Ru(II) and Ni(II) complexes

with different types of ligands, such as Cl[−], (CH₃)₂SO, NH₂C₁₃H₂₇, NH₂C₆H₁₃ and P(Ph)₃ [20–25].

The present work has the following purposes: (a) to perform the partial hydrogenation of a non-saturated hydrocarbon, as 1-heptyne, at mild conditions of temperature and pressure, using d⁸ transition metal complexes, as Pd(II) and Rh(I) with chloride and a primary amine (tridecylamine or hexylamine) as ligands; (b) to evaluate the influence of some coordination sphere parameters (metal atom and ligands), and the homo/heterogeneous condition, on 1-heptyne conversion and selectivity.

The semihydrogenation of ethyne has been the most extensively studied reaction, lacking information on semihydrogenation of higher chain alkynes [9,26]. Due to this, 1-heptyne – a relatively long chain alkyne – is used as the test substrate in the present research.

d⁸ transition metals in a low oxidation number form electron-rich complexes with a square planar geometry, that are suitable species to act as catalysts for the hydrogenation of multiple C–C bonds and other reactions [27]. These coordination compounds are important in catalysis since the metal atom can increase its coordination number by accepting ligands in the apical sites [28], interact with the support or transfer

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electron density towards the dihydrogen molecule. The last point, that favours the H–H bond cleavage [29], can be enhanced by basic sigma donor ligands. For these reasons Rh(I) and Pd(II) and a primary amine (tridecyl- or hexylamine) are chosen as metal atoms and at least part of the ligands respectively to obtain the complex species.

Previously reported data on the same test reaction performed using the widely known Lindlar catalyst operated at the same conditions, are taken as a reference [30].

2. Experimental

2.1. Complexes synthesis and purification

The $[\text{PdCl}_2\text{L}_2]$ and $[\text{RhClL}_3]$ complexes ($\text{L} = \text{NH}_2(\text{CH}_2)_{12}\text{CH}_3$ or $\text{NH}_2(\text{CH}_2)_5\text{CH}_3$, from now on TDA and HA, respectively) were obtained by reaction of PdCl_2 (Fluka, cat. 76050) and RhCl_3 (Aldrich, cat. 30,786-6) with the corresponding amine in toluene, using a molar ratio amine/ $\text{PdCl}_2 = 2$ and a molar ratio amine/ $\text{RhCl}_3 = 6$, respectively, in a glass equipment with agitation and reflux, under a purified Ar atmosphere at 353 K, during 4.5 h. After 1 h it was observed the disappearance of the brown solid phase (PdCl_2 and RhCl_3 , insoluble in toluene). Upon ending the reaction, the solvent was evaporated and the new obtained solids were purified by column chromatography. All of the aliquots obtained were analysed for excess L by thin layer chromatography. Then the L-free aliquots were collected and subjected to an evaporation process.

2.2. Complexes centesimal composition

The presence and weight percent of the metal (Pd or Rh), chlorine and nitrogen elements were evaluated for each pure complex on a C- & H-free base, according to standard methods [31–34].

2.3. Complexes heterogenization

All of the complexes were supported to obtain 0.3 wt.% M catalysts ($\text{M} = \text{Pd}$ or Rh) by the incipient wetness technique [35], on a Ketjen CK 300 γ -alumina, previously calcined in air at 773 K for 3 h (cylinders of 1.5 mm diameter, BET surface area: $180 \text{ m}^2 \text{ g}^{-1}$, pore volume: 0.52 mL g^{-1}). All of the complexes were dissolved in a mixture of chloroform/methanol (5/1 vol/vol) to impregnate the support.

2.4. 1-heptyne semihydrogenation

The catalytic evaluations were made using 100 mL of a 2 vol/vol% 1-heptyne in toluene solution, in a PTFE-coated batch stainless steel stirred tank reactor, operated at 600 rpm. The weight of the supported complex catalysts was 0.075 g in all cases. In the catalytic evaluation of the unsupported complexes, a suitable mass of these ones was used to provide the same amount of metal (Pd or Rh) as in the corresponding supported catalysts. The same criterion was used for the Lindlar catalyst. Every catalytic test was carried out in triplicate at

$P = 150 \text{ kPa}$ and $T = 303 \text{ K}$, with a relative experimental error of about 3%; relatively low values of P and T are chosen as a compromise between avoiding overhydrogenation and keeping a high reaction rate [36–39].

Detection of possible diffusional limitations during the catalytic runs was taken into account according to the procedures described in the literature [40–41]. External diffusional limitations were examined by varying the stirring velocity in the range of 180–1400 rpm. Conversion and selectivity constancy above 500 rpm allows to say that this type of limitation is absent at the selected rotary speed. On the other hand, intraparticle mass transfer limitations were considered by crushing the heterogenised complex catalyst up to 1/4 the original size and using the obtained samples to carry out the hydrogenation reaction. Conversion and selectivity values, equal to those obtained with the uncrushed heterogenised catalyst, permit to state that this type of limitation is also absent in the physical operational conditions of this work. Last but not least, the catalyst cylinders were properly treated and weighted after end of reaction. The difference in the mass of catalyst cylinders (before and after the test reaction) was within the experimental error of the analytical balance method, meaning that there was no mass loss from the cylinders. Thus, it can be considered that the attrition effect is absent or is negligible enough to play a role in determining an additional mass transfer limitation. The analysis of reactants and products was made by gas chromatography, using a FID and a CP Sill 88 capillary column.

2.5. Fourier transform infra-red spectroscopy (FTIR)

The spectra, for the pure complexes and the pure TDA and HA, were taken to determine the presence of these ligands in the corresponding coordination compounds. The analysis was carried out using the TDA and HA characteristic normal wave numbers [42–44]. A $4100\text{--}900 \text{ cm}^{-1}$ range was covered with a Shimadzu FTIR 8101/8101 M single beam spectrometer. Solid samples were dried at 353 K, and they were examined in potassium bromide disks in a concentration ranging from 0.5 to 1 wt.% to ensure non-saturated spectra, while the liquid sample (HA) was examined in the chamber for liquids provided with KBr windows.

2.6. X-ray photoelectron spectroscopy (XPS)

The studies were carried out to evaluate: (a) the electronic state of atoms, (b) the atomic ratios, for the pure complexes and for the supported complexes before and after the reaction, and (c) the atomic ratios M/Al (where $\text{M} = \text{Rh}$ or Pd) for the supported complexes before and after reaction. This information was used to determine a minimum stoichiometric formula and to evaluate the possibility of complex leaching during the hydrogenation reaction. A Shimadzu ESCA 750 Electron Spectrometer coupled to a Shimadzu ESCAPAC 760 Data System was used. As previously described [45], 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.

Table 1

Pure complexes elemental composition for M (Pd or Rh), N and Cl (on a C- & H-free base) and the Cl/M and N/M molar ratios

Complex	Centesimal Composition (wt.%)			Molar ratios	
	M	Cl	N	Cl/M	N/M
[RhCl(HA) ₃]	57.28	20.28	22.44	1.03	2.88
[RhCl(TDA) ₃]	56.86	19.61	23.53	1.00	3.04
[PdCl ₂ (HA) ₂]	51.6	34.8	13.6	2.02	2.00
[PdCl ₂ (TDA) ₂]	52.0	34.3	13.7	1.99	2.00

The superficial electronic state of the atoms were studied according to the position of the following peak maxima: Rh 3d_{5/2} and Pd 3d_{5/2}, N 1s_{1/2} for the TDA and HA ligands and Cl 2p_{3/2} for all the complexes. 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 [46]. Exposing the samples to the atmosphere for different periods of time confirmed that there were no electronic modifications. Determination of the atomic ratios x/M ($x = N, Cl$) and M/Al were made by comparing the areas under the peaks after background subtraction and corrections due to differences in escape depths [47] and in photoionization cross sections [48].

2.7. Atomic Absorption spectroscopy

The possible presence of M (Rh or Pd), provoked by a solvent leaching effect, in each solution after catalytic evaluation of the heterogeneous systems, was analysed by means of the Atomic Absorption technique.

3. Results

Table 1 shows the elemental composition for M (Pd or Rh), N and Cl obtained for the pure complexes on a C- & H-free base, as well as the Cl/M and N/M molar ratios.

On the other hand XPS values, corresponding to the M systems (M = Pd or Rh) for the pure Rh or Pd complexes

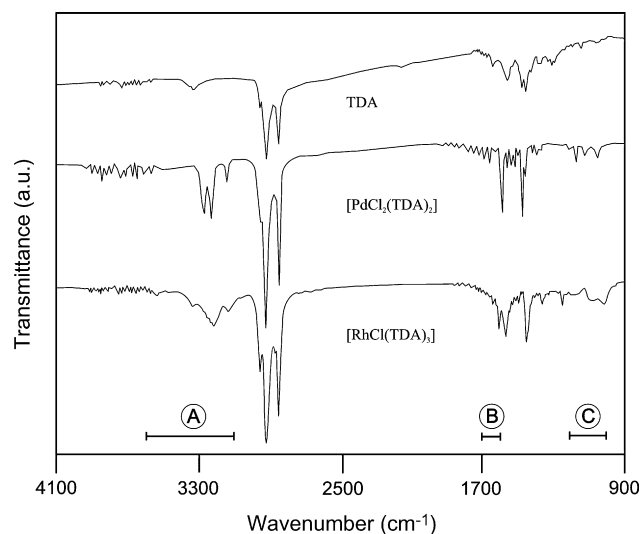


Fig. 1. FTIR spectra corresponding to TDA, and [RhCl(TDA)₃] and [PdCl₂(TDA)₂].

and before and after reaction in heterogeneous conditions: (a) M 3d_{5/2}, N 1s_{1/2} and Cl 2p_{3/2} binding energies (BE), and (b) N/M, Cl/M and M/Al atomic ratios, can be seen in Table 2.

Besides, maximum conversion and selectivity to 1-heptene values for the catalytic systems are presented in Table 3.

The plots in Figs. 1 and 2 are the FTIR spectra corresponding to the pure species: Rh or Pd complexes and ligands.

Figs. 3 and 4 show conversion to 1-heptene (%) versus 1-heptyne total conversion (%) for the following systems: Rh or Pd complexes in homogeneous and heterogeneous conditions and the Lindlar catalyst. In addition, graphs in Figs. 5 and 6, corresponding to the selectivity to 1-heptene (%) versus 1-heptyne total conversion (%), are displayed for Rh or Pd complexes in homogeneous and heterogeneous conditions and for the Lindlar catalyst.

Finally, the results from the Atomic Absorption analysis reveal no presence of M (Rh or Pd) at all in the remaining solutions from the catalytic tests.

Table 2

Pure, fresh and run heterogenized M complexes (M = Rh or Pd): XPS binding energies and XPS atomic ratios

Complex	Condition	Binding energies (eV)			Atomic ratios (at/at)		
		M 3d _{5/2}	N 1s _{1/2}	Cl 2p _{3/2}	N/M	Cl/M	M/Al
[RhCl(TDA) ₃]	Pure	307.1	402.1	198.1	3.00	1.01	–
	γ-Al ₂ O ₃ fresh	307.2	402.2	198.3	2.99	1.02	0.05
	γ-Al ₂ O ₃ run	307.1	402.2	198.2	2.99	0.99	0.05
[RhCl(HA) ₃]	Pure	307.1	402.0	198.1	3.00	1.02	–
	γ-Al ₂ O ₃ fresh	307.1	402.0	198.0	3.00	1.00	0.05
	γ-Al ₂ O ₃ run	307.1	402.1	198.1	2.99	1.02	0.05
[PdCl ₂ (TDA) ₂]	Pure	338.2	401.9	198.3	2.00	1.99	–
	γ-Al ₂ O ₃ fresh	338.3	401.7	198.2	2.01	2.00	0.09
	γ-Al ₂ O ₃ run	338.2	402.0	198.1	1.99	1.99	0.09
[PdCl ₂ (HA) ₂]	Pure	338.1	401.4	198.2	1.98	2.00	–
	γ-Al ₂ O ₃ fresh	338.2	401.5	198.1	2.00	2.00	0.10
	γ-Al ₂ O ₃ run	338.3	401.7	198.2	2.00	2.00	0.10

Table 3
Maximum conversion and selectivity to 1-heptene values for the catalytic systems

Complex compound	Condition	Maximum conversion to 1-heptene (%)	Maximum selectivity to 1-heptene (%)
[RhCl(TDA) ₃]	Heterogeneous	80.0	92–93 (plateau-shaped up to ca. 80% 1-heptyne conv.)
	Homogeneous	60.4	~93 (plateau-shaped up to ca. 65% 1-heptyne conv.)
[RhCl(HA) ₃]	Heterogeneous	59.0	~93 (plateau-shaped up to ca. 55% 1-heptyne conv.)
	Homogeneous	52.0	~97 (monotonously decreasing)
[PdCl ₂ (TDA) ₂]	Heterogeneous	68.5	>95 (plateau-shaped up to ca. 70% 1-heptyne conv.)
	Homogeneous	55.0	97–98 (plateau-shaped up to ca. 45% 1-heptyne conv.)
[PdCl ₂ (HA) ₂]	Heterogeneous	48.0	91.4 (monotonously decreasing)
	Homogeneous	32.0	62.6 (monotonously decreasing)
Lindlar catalyst [from ref. [30]]	Heterogeneous	43.0	~98 (plateau-shaped up to ca. 45% 1-heptyne conv.)

4. Discussion

4.1. Rhodium and palladium complexes minimum formulae

The Rh:Cl:N and Pd:Cl:N molar ratios for the pure complexes calculated from the weight percent values (detailed

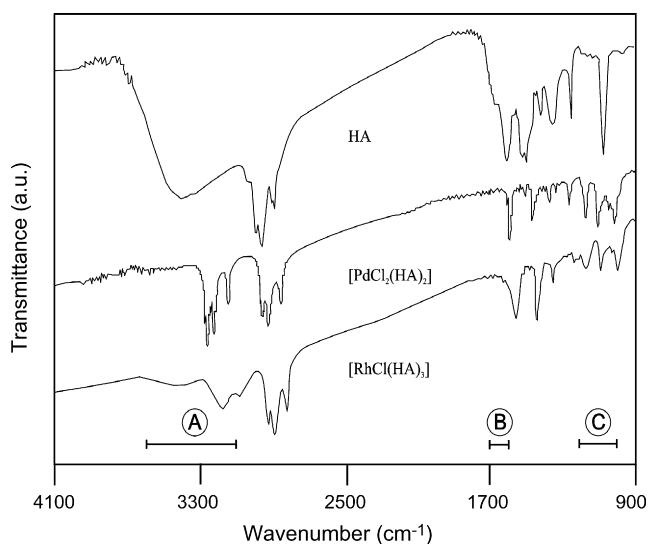


Fig. 2. FTIR spectra corresponding to HA, and [RhCl(HA)₃] and [PdCl₂(HA)₂].

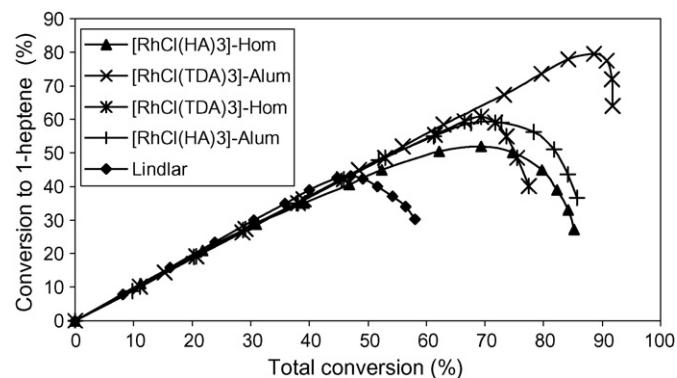


Fig. 3. Conversion to 1-heptene (%) vs. total 1-heptyne conversion (%) for the Rh complexes in homogeneous and heterogeneous conditions and the Lindlar catalyst.

in Table 1) and the molar masses of these elements, can be expressed as ca. 1:1:3 and 1:2:2, respectively, for all the ligands.

According to the literature [49,50], XPS binding energies for the pure substances (Table 2) show that the elements Rh or Pd, N and Cl are present in the corresponding products obtained after the synthesis and purification stages. Besides, the electronic states of these atoms may be considered as follows: (a) $n+$ for Rh or Pd, with n close to 1 and $n = 2$, respectively; this is based on data in Table 2 and the literature values ranging

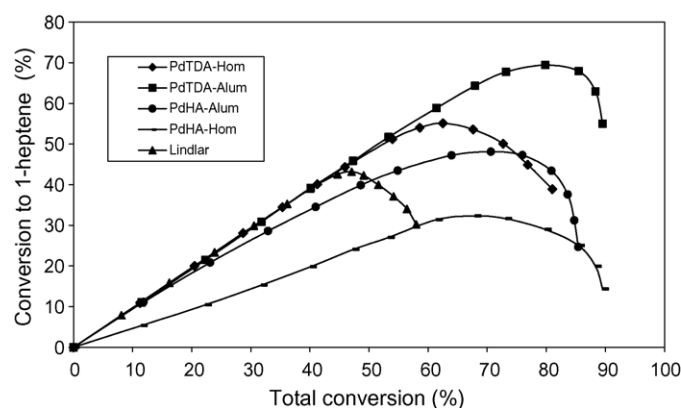


Fig. 4. Conversion to 1-heptene (%) vs. total 1-heptyne conversion (%) for the Pd complexes in homogeneous and heterogeneous conditions and the Lindlar catalyst.

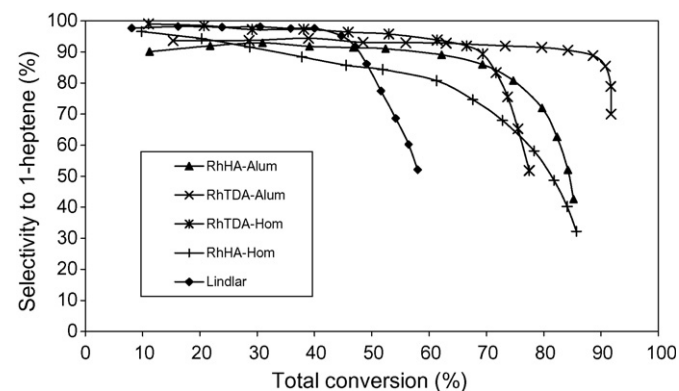


Fig. 5. Selectivity to 1-heptene (%) vs. total 1-heptyne conversion (%) for the Rh complexes in homogeneous and heterogeneous conditions and the Lindlar catalyst.

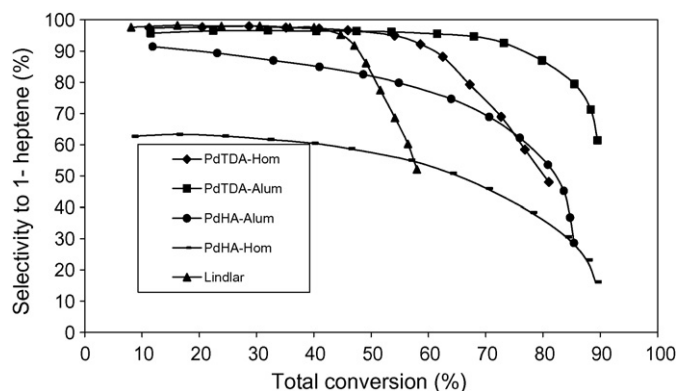


Fig. 6. Selectivity to 1-heptene (%) vs. total 1-heptyne conversion (%) for the Pd complexes in homogeneous and heterogeneous conditions and the Lindlar catalyst.

from 307.3 to 308.5 eV for Rh(I) and 338.3 eV for $[\text{PdCl}_2(\text{NH}_3)_2]$ [49,50], (b) for Nitrogen, the $1s_{1/2}$ binding energies in Table 2 fall within the values found in the literature (ranging from 400.9 to 402 eV [49,50]), corresponding to an ammonium-like Nitrogen; this information suggests a bonding character for the N lone pair towards an electrophilic centre, in this case the Rh or Pd atom; and (c) for chlorine: -1 , as in chloride compounds (literature values: from 197.9 to 198.5 eV [49,50]) for all the cases. At the same time, from the mentioned table, the atomic ratios indicate that these elements appear in the proportion Rh:Cl:N equal to 1:1:3 and Pd:Cl:N equal to 1:2:2 for both complexes of each metal.

On the other hand, Figs. 1 and 2 show the FTIR spectra of TDA and HA, respectively. At high wave numbers, the following characteristic peaks of a primary aliphatic amine [43], are present: NH_2 “stretching” ($3600\text{--}3100\text{ cm}^{-1}$) (A), CH “stretching” ($3000\text{--}2800\text{ cm}^{-1}$), NH_2 “bending” ($1700\text{--}1600\text{ cm}^{-1}$) (B), CH “bending” ($1500\text{--}1300\text{ cm}^{-1}$) and CN “stretching” ($1200\text{--}1000\text{ cm}^{-1}$) (C). In particular, labels A, B and C, related to the nitrogen atom, are taken as a reference because they are sensitive to its environment. Figs. 1 and 2 show that the FTIR peaks in the pure Rh or Pd complexes globally agree with those corresponding to pure ligands (TDA or HA). Anyhow, differences are found in the labeled wave numbers indicated above: A, B and C as they show a slight shift to lower frequencies with respect to the pure ligands, meaning an interaction between the nitrogen lone pair and the Rh or Pd atom. This argument is reinforced by the fact that when a primary amine is bonded, the NH_2 stretching peak is considerably different in shape and intensity from the original NH_2 band [51], as seen in the shown spectra. This information confirms that the TDA or HA molecule is one of the constituents of the complex coordination sphere.

At this point, on the basis of the preceding elemental composition, XPS and FTIR arguments, it can be concluded that the Rh and Pd substances are complexes with chloride and TDA or HA as ligands, with a minimum formula expressed by $[\text{RhCl}(\text{TDA})_3]$ and $[\text{RhCl}(\text{HA})_3]$ or $[\text{PdCl}_2(\text{TDA})_2]$ and $[\text{PdCl}_2(\text{HA})_2]$, respectively.

4.2. Complexes state after supporting

Table 2 shows the binding energies corresponding to Rh or Pd complexes after being supported. The electronic states of the main atoms may be considered as follows: (a) according to literature values ranging from 307.3 to 308.5 eV for Rh(I) and 338.3 eV for $[\text{PdCl}_2(\text{NH}_3)_2]$ [49,50], an $n+$ state may be assigned to Rh or Pd, with n close to 1 and $n = 2$, respectively, (b) for nitrogen, the $1s_{1/2}$ binding energies fall within the values found in the literature (ranging from 400.9 to 402 eV [49,50]), corresponding to an ammonium-like N; this information suggests a bonding character for the N lone pair towards an electrophilic centre, in this case the Rh or Pd atom; and (c) for chlorine: -1 , as in chloride compounds (literature values: from 197.9 to 198.5 eV [49,50]) for all the cases. At the same time, from the mentioned table, the atomic ratios for the anchored complexes indicate that these elements appear in the proportion Rh:Cl:N equal to 1:1:3, and Pd:Cl:N equal to 1:2:2. These results, equal to those previously obtained for the determination of each complex minimum formula, suggest that the coordination compounds maintain their identities after anchoring and, that they are adsorbed as a whole on the support surface. Last but not least, the constancy of the M (Rh or Pd), Cl and N electronic states in the supported Rh or Pd complexes with respect to those of the pure ones, allow the assumption that none of them interacts with the support. In view of this, the anchoring of the complexes occurs via a portion of the amine hydrocarbon chain. As the inductive influence of the hydrocarbon chain on the nitrogen atom is exerted up to the second/third carbon atom, it can be proposed that the rest of the chain is the one involved in the anchoring process.

4.3. Conversion and selectivity analysis for the catalytic systems

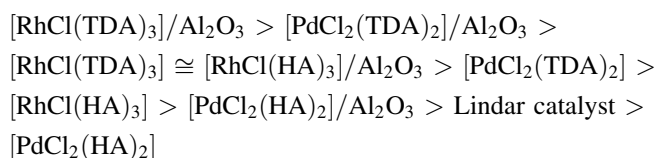
It can be seen, from Figs. 3 and 4, that the catalytic systems show an initial part with an almost 45° linear slope, with the exception of homogeneous $[\text{PdCl}_2(\text{HA})_2]$. From that part onwards, all the systems show a similar profile shape, with increasing conversion to 1-heptene up to a maximum value, after which the conversion falls. However, it can be noted that the Pd systems appeared in a more spaced way (Fig. 4).

The selectivity plots displayed in Fig. 5 show a plateau-shaped behaviour in a very important range of 1-heptyne total conversion followed then by a decreasing tendency for the Rh catalytic systems, with the exception of $[\text{RhCl}(\text{HA})_3]$ in homogeneous condition, which decreases monotonously. As for Pd systems (Fig. 6), those with the TDA ligand exhibit a plateau-shaped profile, while those with the HA ligand show a monotonously decreasing profile shape.

Trends and selection of the best catalytic systems are drawn taking two factors into account: (a) maximum conversion values to 1-heptene versus 1-heptyne total conversion and (b) maximum selectivity values to 1-heptene, and the range of 1-heptyne total conversion in which they are self-maintained. Table 3, which summarizes the ideas previously stated, was constructed using the values of the variables from Figs. 3–6.

4.3.1. 1-Heptyne to 1-heptene maximum conversion

4.3.1.1. *General trend.* According to the values in the third column, Table 3, the following order of maximum conversion can be established:



4.3.1.2. *Trends depending on metal, ligand or condition.* - Having in mind that only one of these three variables is changed at a time (keeping the other two constant) the following sequences can be written:

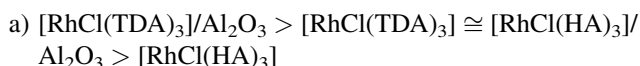
Metal: Rh systems > Pd systems;

Ligand: TDA systems > HA systems;

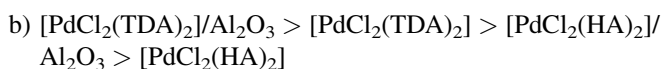
Condition: heterogeneous systems > homogeneous systems.

From the last three tendencies, it can be stated that the best combination is Rh-TDA-heterogeneous system, which is in the first place in the general trend. The worst option is the combination Pd-HA-homogeneous, being this the only system that does not show a better maximum conversion than the Lindlar catalyst.

Focusing the attention on the metal atom two new trends may be established in the respective groups of Rh or Pd complexes, as follows:



Analyzing the in-between portion of this sequence, it can be said that the change of ligand or condition produces a similar catalytic effect while the last position corresponds to the worst catalytic system when both parameters are simultaneously changed.



Reasoning in a similar way as in the previous paragraph, in this ordering it can be seen that the change of ligand produces a greater lowering of the maximum conversion than the change of condition, and again, the change of both factors produces a catalytic system that occupies the last position.

4.3.2. Selectivity to 1-heptene

In this item, two points regarding the selectivity behaviour were taken into account. On one hand, the maximum selectivity value, and on the other hand the way in which the selectivity behaves with increasing 1-heptyne total conversion. In this respect the best catalytic systems are those having high selectivity and a plateau-shaped profile up to a high 1-heptyne total conversion value.

4.3.2.1. *Trends depending on metal, ligand or condition.* - Comparing the M systems (M = Rh or Pd), at equal ligand or condition, it can be seen that the complex species with Rh as the central metal keep high selectivity values over a wider range of 1-heptyne total conversion. Besides, Rh systems exhibit plateau-shaped selectivity profiles, with the exception of $[\text{RhCl}(\text{HA})_3]$.

As far as the ligand is concerned, TDA catalytic systems show higher selectivity values than those of HA systems, keeping a plateau-shaped selectivity profile over an important part of the 1-heptyne total conversion range.

On the other hand, analysing the homo-heterogeneous condition, it can be said that supported complexes show better selectivities than their counterparts over a wide range of 1-heptyne total conversion range.

Finally, the Lindlar catalyst exhibits a very high selectivity (close to 100 %), but maintains this performance only up to ca. 45 % 1-heptyne total conversion. After this point the selectivity diminishes abruptly. So, of all the systems under study, the Lindlar catalyst presents the shortest plateau-shaped selectivity profile.

4.4. The optimum catalytic system

Based on the information obtained from Sections 4.3.1 and 4.3.2, it can be concluded that the $[\text{RhCl}(\text{TDA})_3]$ complex supported on $\gamma\text{-Al}_2\text{O}_3$ is the best option to carry out the 1-heptyne semihydrogenation.

As this complex has a d^8 metal and a combination of ligands $L'/L = 3$ ($L' = \text{TDA}$, $L = \text{Cl}$), a square planar geometry with C_{2v} local site symmetry can be assumed. This type of coordination compound usually participates in chemical changes via a dissociative mechanism. In this respect, the trans effect series indicates that the labile ligand is TDA opposite to the Cl ligand. Some features related to the central atom, the TDA ligand, the complex coordination number, the site symmetry and the supported condition, could explain this optimum performance.

4.4.1. Central atom

Molecular orbitals with symmetries corresponding to the irreducible representations of the molecular point group automatically satisfy the Fock equation. For complex species the terminal atom symmetry orbital (TASO)/molecular orbitals (MO) and the metal atomic orbitals are taken into account to explain metal–ligand bonding according to their symmetry properties. In this respect, the $(n - 1)d$ and ns metal atomic orbitals are those that match best the energy of the TASO/MO. Based on this, the anti-bonding molecular orbitals have considerably more metal character than ligand character. Anti-bonding molecular orbitals lie high in energy, a fact that will be a little bit more pronounced in the case of Rh(I) (versus Pd(II)), because of its low oxidation state. The relative energy distribution of these anti-bonding molecular orbitals for Rh(I) (d^8), predicted by means of the Angular Overlap Model (AOM) [52], is as follows in an increasing order of energy: non-bonding (d_{xy}), double-degenerate e_{π} ($(dxz, dyz)^*$), $7/4e_{\sigma}$ ($(dz^2)^*$) and $9/4e_{\sigma}$ ($(dx^2 - y^2)^*$). Assigning the eight electrons to this scheme,

it turns out that dz^2 and $dx^2 - y^2$ are the HOMO and LUMO frontier orbitals, respectively. The former is useful to produce the cleavage of the H–H bonding and the latter is available to receive electron density from the substrate molecule; both of them are key factors in the catalytic cycle leading to hydrogenation of the substrate.

4.4.2. Ligands

Based on the last paragraph, the complex bonding molecular orbitals have a predominant character from the TASO/MOs of the coordination sphere constituted by tridecylamine and chloride ligands. Tridecylamine is a σ ligand with an electron-donating effect and chloride is a σ/π ligand with an electron-withdrawing effect. Thus, due to the 3/1 (TDA/chloride) ligand ratio, there is a net electronic enrichment on the Rh central atom.

Besides, the TDA ligand presents another remarkable feature related to the dispersion forces, which in turn are relevant in the adsorption processes and in the interaction with the solvent. The former aspect allows the complex anchoring on the γ -alumina support. On the other hand, the latter is linked to the square complexes dissociative mechanism when the TDA molecule is released because of the trans-effect and simultaneously stabilized through the solvation process. In this respect, the longer the hydrocarbon chain, the stronger the dispersion forces and its interaction with the solvent media.

Finally, long amine hydrocarbon chains present more flexibility to adopt different conformational configurations, an important fact, as TDA is the part of the complex involved in the adsorption process (see last paragraph in Section 4.2 above).

4.4.3. Heterogeneous condition

γ -Alumina is widely used in catalysis as a support not only for metals but also for other species such as metal complexes. Under the pre-treatment conditions (see Section 2.3. Complex heterogenization) it presents predominantly Lewis acid sites, which in the context of this work, interact with the $[\text{RhCl}(\text{TDA})_3]$ complex via a portion of the TDA ligand by dispersion forces, as previously stated. In order to illustrate this situation, Fig. 7 shows a schematic representation (not drawn to scale) of the complex anchored on the support.

In this adsorption model, as there is no interaction between the central atom and the support, the complex C_{2v} local point

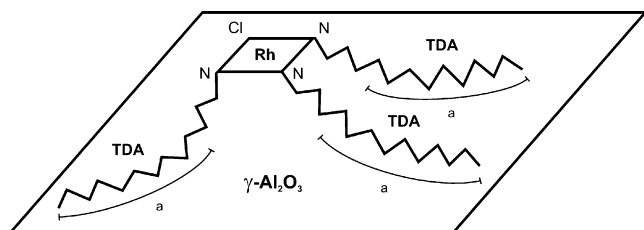


Fig. 7. $[\text{RhCl}(\text{TDA})_3]$ anchored on $\gamma\text{-Al}_2\text{O}_3$ – “a” indicates the TDA carbon chain portion involved in the adsorption process.

symmetry is preserved. Thus, the considerations made about the HOMO and LUMO frontier orbitals for the pure complex (Section 4.4.1) still apply. In particular, the complex LUMO orbital receives electron density from the substrate molecule, what means to activate 1-heptyne for the semihydrogenation reaction. In addition, there could be some extra 1-heptyne molecules activated by their possible electron-donating interaction with the acidic Lewis sites of the support. This fact makes the reactant concentration around the supported complex catalyst higher than in bulk solution. Such an argument could explain the high activity and selectivity of this catalytic system.

Complex compounds, acting as catalysts, can be interpreted as a metallic element (Rh in this case) “conditioned” by a coordination sphere to regulate its selectivity maintaining, at the same time, a high activity performance. This idea of “metal conditioning” was already used by H. Lindlar when he tailored his well-known catalyst in the 50 decade [53].

Last but not least, the fact that the optimum catalyst system is a heterogeneous one has a practical-economic advantage: the easy and cheap way in which the catalyst is removed from the remaining solution avoiding the main product contamination with a heavy metal compound.

4.5. Supported complexes state after catalytic evaluation

Table 2 shows the binding energies corresponding to supported Rh or Pd complexes after catalytic hydrogenation. The electronic states of the main atoms may be considered as follows: (a) according to literature values ranging from 307.3 to 308.5 eV for Rh(I) and 338.3 eV for $[\text{PdCl}_2(\text{NH}_3)_2]$ [49,50], an $n+$ state may be assigned to Rh or Pd, with n close to 1 and $n = 2$ respectively, (b) for Nitrogen, the $1s_{1/2}$ binding energies fall within the values found in the literature (ranging from 400.9 to 402 eV [49,50]), corresponding to an ammonium-like Nitrogen; this information suggests a bonding character for the N lone pair towards an electrophilic centre, in this case the Rh or Pd atom; and (c) for chlorine: -1 , as in chloride compounds (literature values: from 197.9 to 198.5 eV [49,50]) for all the cases. At the same time, from the mentioned table, the atomic ratios for the anchored complexes after catalytic hydrogenation indicate that these elements appear in the proportion Rh:Cl:N equal to 1:1:3, and Pd:Cl:N equal to 1:2:2. These results, equal to those previously obtained for the fresh anchored complex, suggest that the coordination compounds maintain their identities after being used in the hydrogenation test reaction, and that they remain adsorbed as a whole on the support surface.

4.6. Complex leaching evaluation

4.6.1. XPS analysis

From Table 2, the constancy of the M/Al atomic ratio values (M = Rh or Pd) for each supported complex before and after catalytic evaluation for both ligands (TDA or HA), may be used as an argument that there is no complex leaching at all during the catalytic runs.

4.6.2. Atomic Absorption analysis

The absence of M (Rh or Pd) in the liquid phase after each catalytic reaction for the heterogeneous systems, allows to say that no leaching of the corresponding complexes is produced.

In conclusion the analysis of the results of both techniques assures that: (a) each complex may be regarded as the catalytically active species, or they are converted to the actual active ones during the catalytic cycle or process, and (b) the mass of each complex keeps being the same in all the catalytic runs. Both factors provide a uniform basis for carrying out a comparative analysis of activity and selectivity values for all of the involved systems.

5. Conclusions

Experimental results reported in this paper show that it is possible to semihydrogenate 1-heptyne using $[\text{RhCl}(\text{TDA})_3]$, $[\text{RhCl}(\text{HA})_3]$, $[\text{PdCl}_2(\text{TDA})_2]$ and $[\text{PdCl}_2(\text{HA})_2]$ as catalysts in homo/heterogeneous conditions with a very good general performance. All of them are better than the Lindlar catalyst, with the exception of homogeneous $[\text{PdCl}_2(\text{HA})_2]$. As determined by FTIR, XPS and Atomic Absorption, the active catalytic species in each case is the complex itself, with a minimum formula as shown above.

Tetracoordinated electron-rich transition elements, as well as the presence and the relative quantity of a good electron-donating ligand such as a primary amine, specially those having a long-chain hydrocarbon substituent and the heterogeneous condition, contribute to obtain a catalytic system with a high activity and selectivity performance. According to this, the optimum catalytic system turns out to be: $[\text{RhCl}(\text{TDA})_3]/\text{Al}_2\text{O}_3$ in this case. This behaviour may be explained in terms of electronic and geometrical effects.

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References

- [1] J.G. Ulan, W.F. Maier, *J. Org. Chem.* 52 (1987) 3132–3142.
- [2] B. Chen, U. Dingerdissen, J.C.E. Krauter, H.G.J. Lansink Rotgerik, K. Mobus, D.J. Ostgard, P. Panster, T.H. Riermeier, S. Seebald, T. Tacke, H. Trauthwein, *Appl. Catal. A: Gen.* 280 (2005) 17–46.
- [3] B. Coq, F. Figueras, *J. Mol. Catal. A: Chem.* 173 (1–2) (2001) 117–134.
- [4] D. Lennon, R. Marshall, G. Webb, S.D. Jackson, *Stud. Surf. Sci. Catal.* 130 (2000) 245–250.
- [5] N. Marín-Astorga, G. Pecchi, J.L.G. Fierro, P. Reyes, *J. Mol. Catal. A: Chem.* 231 (2005) 67–74.
- [6] T.A. Nijhuis, G. van Koten, J.A. Moulijn, *Appl. Catal. A: Gen.* 238 (2003) 259–271.
- [7] T. Nozoe, K. Tanimoto, T. Takemitsu, T. Kitamura, T. Harada, T. Osawa, O. Takayasu, *Solid State Ion.* 141–142 (2001) 695–700.
- [8] M.P.R. Spee, J. Boersma, M.D. Meijer, M.Q. Slaght, G. van Koten, J.W. Geus, *J. Org. Chem.* 66 (5) (2001) 1647–1656.
- [9] S. Ziegler, J. Theis, D. Fritsch, *J. Membr. Sci.* 187 (2001) 71–84.
- [10] M. Costa, P. Pelagatti, C. Pelizzi, D. Rogolino, *J. Mol. Catal. A: Chem.* 178 (2002) 21–26.
- [11] E. de Wolf, A.L. Spek, B.W.M. Kuipers, A.P. Philipse, J.D. Meeldijk, P.H.H. Bomans, P.M. Frederik, B.J. Deelman, G. van Koten, *Tetrahedron* 58 (2002) 3911–3922.
- [12] D. Edvrand, K. Groison, Y. Mugnier, P.D. Harvey, *Inorg. Chem.* 43 (2004) 790–796.
- [13] P. Frediani, C. Giannelli, A. Salvini, S. Ianelli, *J. Organomet. Chem.* 667 (2003) 197–208.
- [14] J.M. Kerr, C.J. Suckling, *Tetrahedron Lett.* 29 (N 43) (1988) 5545–5548.
- [15] J.W. Park, Y.M. Chung, Y.W. Suh, H.K. Rhee, *Catal. Today* 93–95 (2004) 445–450.
- [16] P.K. Santra, P. Sagar, *J. Mol. Catal. A: Chem.* 197 (1–2) (2003) 37–50.
- [17] V.M. Frolov, *Plat. Met. Rev.* 40 (1) (1996) 8–18.
- [18] A.M. Trzeciak, J.J. Ziolkowski, Z. Jaworska-Galas, W. Mista, J. Wrzyszczyk, *J. Mol. Catal.* 88 (1994) 13–21.
- [19] D. Chatterjee, H.C. Bajaj, S.B. Halligudi, K.N. Bhatt, *J. Mol. Catal.* 84 (1) (1993) L1–L5.
- [20] P.C. L'Argentière, D.A. Liprandi, D.V. Marconetti, N.S. Figoli, *J. Mol. Catal. A: Chem.* 118 (1997) 341–348.
- [21] P.C. L'Argentière, E.A. Cagnola, D.A. Liprandi, M.C. Román-Martines, C. Salinas-Martinez de Lecea, *Appl. Catal. A: Gen.* 172 (1998) 41–48.
- [22] P.C. L'Argentière, E.A. Cagnola, M.G. Cañón, D.A. Liprandi, D.V. Marconetti, *J. Chem. Technol. Biotechnol.* 71 (1998) 285–290.
- [23] M.E. Quiroga, E.A. Cagnola, D.A. Liprandi, P.C. L'Argentière, *J. Mol. Catal. A: Chem.* 149 (1999) 147–152.
- [24] D.A. Liprandi, M.E. Quiroga, E.A. Cagnola, P.C. L'Argentière, *Ind. Eng. Chem. Res.* 41 (2002) 4906–4910.
- [25] E.A. Cagnola, M.E. Quiroga, D.A. Liprandi, P.C. L'Argentière, *Appl. Catal. A: Gen.* 274 (2004) 205–212.
- [26] C.A. Hamilton, S.D. Jackson, G.J. Kelly, R. Spence, D. Bruin, *Appl. Catal. A: Gen.* 237 (2002) 201–209.
- [27] B.C. Gates, *Catalytic Chemistry*, Wiley, 1992, p. 79.
- [28] J.C. Bailar, et al. (Eds.), *Comprehensive Inorganic Chemistry*, vol. 3, 1975, p. 1234.
- [29] D.F. Shriver, P.W. Atkins, C.H. Langford, *Inorg. Chem.*, third ed., WH Freeman and Co, 1994, p. 258.
- [30] P.C. L'Argentière, E.A. Cagnola, M.E. Quiroga, D.A. Liprandi, *Appl. Catal. A: Gen.* 226 (2002) 253–263.
- [31] I.M. Kolthoff, E.B. Sandell, E.J. Meehan, S. Bruckenstein, *Quantitative Chemical Analysis*, fourth ed., Interscience Publishers, New York, 1969.
- [32] S.N. Anderson, F. Basolo, *Inorg. Synth.* 7 (1963) 214.
- [33] A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longmans, Green and Co, London, 1951.
- [34] S. Livingstone, in: J.C. Bailar, Jr., H.J. Emeléus, R. Nyholm, A.F. Trotman-Dickenson (Eds.), *The Chemistry of Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum*, *Comprehensive Inorganic Chemistry*, Pergamon Press, Oxford, 1973.
- [35] X.L. Seoane, P.C. L'Argentière, N.S. Figoli, A. Arcoya, *Catal. Lett.* 16 (1992) 129–135.
- [36] G.M. Cherkashin, L.P. Shuikina, O.P. Parenago, V.M. Frolov, *Translated from Kinetika i Kataliz* 26 (5) (1985) 1110–1114.
- [37] Z. Dobrovolná, P. Kacer, L. Cerveny, *J. Mol. Catal. A: Chem.* 130 (1998) 279–284.
- [38] B.M. Choudary, M. Lakshmi Kantam, N. Mahender Reddy, K. Koteswara Rao, Y. Haritha, V. Bhaskar, F. Figueras, A. Tuel, *Appl. Catal. A: Gen.* 181 (1999) 139–144.
- [39] S. Chandrasekhar, C. Narsihmulu, G. Chandrashekar, T. Shyamsunder, *Tetrahedron Lett.* 45 (11) (2004) 2421–2423.
- [40] F.A. Holland, F.S. Chapman, *Liquid Mixing and Processing in Stirred Tanks*, Reinhold, New York, 1976, Chapter 5.
- [41] J.F. Le Page, *Catalyse de Contact*, Editions Technip, Paris, 1978, Chapter 2.
- [42] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, fourth ed., Wiley, New York, 1986, Parts I and III.

- [43] R.M. Silverstein, G. Clayton Basler, T.C. Morrill, *Spectrometric Identification of Organic Compounds*, fifth ed., Wiley, New York, 1991, Chapter III.
- [44] C.J. Pouchert, *The Aldrich Library of Infrared Spectra* Ed. (III), 1981, p. 1562 D.
- [45] J.A. Díaz-Auñón, M.C. Román-Martínez, C. Salinas-Martínez de Lecea, P.C. L'Argentiére, E.A. Cagnola, D.A. Liprandi, M.E. Quiroga, *J. Mol. Catal. A: Chem.* 153 (2000) 243–256.
- [46] T. Mallat, J. Petrov, S. Szabó, J. Sztatisz, *Reac. Kinet. Catal. Lett.* 29 (1985) 353–361.
- [47] R. Borade, A. Sayari, A. Adnot, S. Kaliaguine, *J. Phys. Chem.* 94 (1990) 5989–5994.
- [48] J.H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* 8 (1976) 129–137.
- [49] C.D. Wagner, W.M. Riggs, R.D. Davis, J.F. Moulder, in: G.E. Muilenberg (Ed.), *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Preirie, MN, 1978.
- [50] NIST X-ray Photoelectron Spectroscopy Database NIST Standard Reference Database 20, Version 3.4 (Web Version), National Institute of Standards and Technology, USA, 2003.
- [51] C.J. Pouchert, *The Aldrich Library of Infrared Spectra*, Ed. (III), ed. by Aldrich Chemical Company, Inc., Wisconsin, USA, 1981, pp. 163–164.
- [52] Purcell, F. Keith, C. Kotz John, *Inorganic Chemistry*, Holt-Saunders International Edition, 1977, pp. 543–545.
- [53] H. Lindlar, *Helv. Chim. Acta* 35 (2) (1952) 446–450.