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THE WILKINSON COMPLEX AS A HETEROGENEOUS CATALYST IN THE PARTIAL HYDROGENATION OF 1-HEPTYNE. REGENERATION OF THE COMPLEX

Edgardo Cagnola[a,*], Domingo Liprandi[a], José Paredes[a], Nicolás Carrara[a,b] and Mónica Quiroga[a,b]
[a]Departamento de Química, Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, 3000 Santa Fe, Argentina
[b]Instituto de Investigaciones en Catálisis y Petroquímica, Facultad de Ingeniería Química, Universidad Nacional del Litoral, CONICET, Santiago del Estero 2654, 3000 Santa Fe, Argentina

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The Wilkinson complex was tested as a catalyst in the partial hydrogenation of 1-heptyne, a medium chain alkyne, at a temperature of T = 303 K and hydrogen pressure PH_2 = 150 kPa. The tests were performed in homogeneous system as well as heterogeneous system, supporting the complex on i) γ-Al_2O_3 and ii) a commercial carbonaceous material, RX3. Characterization by means of XPS and FTIR revealed that the anchored complex did not lose its chemical identity, being the catalytically active species. The Wilkinson complex on RX3 showed better conversions and selectivities, higher than the Lindlar catalyst, used as a reference. Additionally, it was proposed a method to recover Rh as a metal from the remaining solutions, and from it regenerate the complex to be reused from it.

Keywords: Wilkinson complex; partial hydrogenation; heterogeneous catalyst; complex regeneration.

INTRODUCTION

From the academic and industrial standpoints, partial hydrogenation reactions of alkynes have a great importance, as many of the products obtained are useful in the synthesis of natural fine chemicals, such as biologically active compounds.[1] In this respect, the Lindlar catalyst ($Pd/CaCO_3$ modified with $Pb(OAc)_2$) proved to be useful for the hydrogenation of almost any triple bond to double bond, or reduction of doubly substituted acetylenes giving cis olefins.[2] Alternatively, along the years, the use of transition metal complexes has become increasingly important as catalysts for such reactions, both in homogeneous and heterogeneous systems.[3-7] One of the most used complexes is $[RhCl(PPh_3)_3]$, usually called as Wilkinson catalyst.[8] This complex is useful in the catalytic hydrogenation of a variety of alkenes under mild conditions of pressure and temperature, essentially in homogeneous phase.[9-14] In a previous work by our group,[15] the Wilkinson catalyst was supported on γ-Al_2O_3 and tested as a heterogeneous system in the hydrogenation of cyclohexene, showing a high activity as well as an important resistance to sulfur-containing poisoning substances.

However, less information has been published on the use of this catalyst in the partial hydrogenation of alkynes.[16] While these catalytic processes conducted in homogeneous phase exhibit high conversions and selectivities, they have the disadvantage, due to both economic and environmental reasons, that the complex has to be recovered from the system after the reaction in order to obtain pure nontoxic products and to recycle the catalyst, thereby minimizing the environmental contamination by heavy metals. In this regard, numerous attempts, with limited success, have been carried out to reduce the amount of complex used and to improve the process of removing and recycling it.[14]

Regarding publications on the selective hydrogenation of alkynes, most of the literature has been engaged so far in the investigation of the partial hydrogenation of acetylene using palladium catalysts, with very few references to the partial hydrogenation of medium chain alkynes.[17-23]

The aims of this work are: a) to provide results on the performance of Wilkinson complex as catalyst in the partial hydrogenation of 1-heptyne, a medium chain alkyne, in homogeneous and heterogeneous systems, using γ-Al_2O_3 and a commercial carbonaceous material named RX3 as supports, and b) to propose a method for recovering the expensive metal (Rh) and from this one regenerate $[RhCl(PPh_3)_3]$ for reusing. Additionally, in the catalytic tests, the Lindlar catalyst was used as reference.

EXPERIMENTAL

Catalytic Systems: commercial Wilkinson complex and Lindlar catalyst, and regenerated Wilkinson complex

The commercial complex $[RhCl(PPh_3)_3]$ and the Lindlar catalyst were purchased from Aldrich (Catalog No. 20503-6 and 20573-7, respectively).

The regenerated Wilkinson complex was obtained by carrying out the following stages:

i) Recovery of the Wilkinson complex from the remaining solution of the partial hydrogenation reaction in homogeneous system.
ii) Obtainment of rhodium metal by programmed thermal treatment with the aim of destroying not only the original complex (by removal of phosphine), but also the remaining substances of the catalytic reaction.[24-25] This process had an efficiency higher than 60%.
iii) Transformation of the recovered metallic rhodium in rhodium(III) chloride by reaction with HCl.[24-26]
iv) Preparation of the Wilkinson complex by reaction between rhodium(III) chloride and triphenylphosphine.[8] This stage showed a yield of 80%.
v) Purification of the obtained complex by dissolving it in chloroform, and subsequent evaporation of the solvent.

Wilkinson complex immobilization

The commercial Wilkinson complex and the regenerated one were supported on pellets of: γ-Al_2O_3 Ketjen CK 300 (previously

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*e-mail: ecagnola@fiq.unl.edu.ar

calcined at 773 K for 3 h) and RX3, a commercial carbon from NORIT, by means of the incipient wetness technique.[27] To make this, the complex was dissolved in chloroform in a suitable concentration to obtain a catalyst containing 0.3 wt% of Rh. Then, the solvent was let to evaporate in a desiccator at 298 K until a constant mass was attained.

These supports present the following features: a) γ-Al_2O_3, pellets of 1.5 mm diameter, BET specific surface area of 180 m^2xg^{-1}, and b) RX3, pellets of 2.3 mm diameter, BET surface area of 1,411 m^2xg^{-1}.

Wilkinson Complex Characterization

X-Ray photoelectron spectroscopy (XPS)

By means of this technique atomic electronic states and atomic ratios were evaluated. The data collected were: a) for the commercial Wilkinson complex, pure and immobilized on both supports (fresh and after reaction): binding energies Rh $3d_{5/2}$, Cl $2p_{3/2}$ and P $2p_{3/2}$ and atomic ratios Cl/Rh, P/Rh and Rh/Z (where Z = Al or C); b) for the Lindlar catalyst: binding energies Pd $3d_{5/2}$, Pb $4f_{7/2}$ and Ca $2p_{3/2}$, and atomic ratios Pd/Pb and Pd/Ca. In order to correct possible deviations caused by electronic charges on the samples, the C1s binding energy was taken as an internal standard at 285.0 eV.[27] The substances were introduced into the equipment following a procedure described by other authors[28] to ensure that there were no changes in the electronic state of the species under study.[29] Either way, exposure of the samples to air for various lengths of time confirmed that there were no electronic modifications. Determinations of the surface atomic ratios were made by comparing the areas under the peaks following standard methodologies.[30,31]

Fourier Transform Infrared Spectroscopy (FTIR)

Both the commercial Wilkinson complex and the regenerated one were analyzed by FTIR in the range of 4000 - 625 cm^{-1} using a single beam Shimadzu 8101/8101M equipment provided with an optical Michelson interferometer and two chambers for improving the quality of the spectra. The first one has a pyroelectric detector made of highly sensitive LiTaO, and the second one has an MCT (Mercury Cadmium Telluride) detector with the possibility of working in an atmosphere of N_2.[32] All of the samples were dried at 353 K and examined in potassium bromide discs with a concentration in the range of 0.5 to 1 wt% to ensure non-saturated spectra.

UV/Vis Spectroscopy

Also, the commercial and the regenerated Wilkinson complex were characterized by UV/Vis Spectroscopy using a double beam λ 20 Perkin Elmer equipment in the range of 300-900 nm. Spectra in terms of absorbance were obtained, using chloroform as solvent in such a way to get the same concentration for the species.

Support characterization

The porosity of the supports was determined by physical adsorption of nitrogen (77 K) and carbon dioxide (273 K). This type of adsorption is useful for calculating specific surface areas and pore volumes. The use of both adsorbates (N_2 and CO_2) allows estimating the volume distribution of those pores with a diameter up to 7.5 nm.[33] The volume of micropores having a diameter less than 0.7 nm (V_{micro}) can be obtained applying the Dubinin-Raduskevich equation to the CO_2 adsorption isotherm at 273 K. On the other hand, the volume of supermicropores (V_{sm}) with diameters between 0.7 and 2 nm is calculated by subtracting V_{micro} from the volume calculated by applying the method of Dubinin-Raduskevich to the N_2 adsorption isotherm at 77 K.[33] Additionally, the volume of mesopores with diameters between 2 and 7.5 nm was determined from the N_2 adsorption isotherm at 77 K. In connection to this, the volume of gas adsorbed between 0.2 and 0.7 relative pressure corresponds to the range of mesopores. The volume of macropores (V_{macro}) and part of the volume of mesopores (with diameters between 7.5 and 50 nm) were evaluated by the technique of mercury porosimetry using a Carlo Erba 2000 equipment. This one may reach a maximum pressure of 196 MPa, which allows estimating the volume of pores with a diameter larger than 7.5 nm. Furthermore, the sum of the mesopore volume determined from the N_2 adsorption isotherm and by mercury porosimetry gives the total volume of mesopores (V_{meso}).[33] Finally, the specific surface area can be evaluated by applying the B.E.T. (Brunauer-Emmett-Teller) equation to the nitrogen adsorption isotherm at 77 K.

Catalytic evaluation

The selective hydrogenation of 1-heptyne to 1-heptene was evaluated using 100 mL of a 0.15 mol L^{-1} 1-heptyne solution (Fluka, Cat No. 51950) in toluene (EM Science, Cat No. TX 0735-5). The reaction was carried out at T = 303 K, PH_2 = 150 kPa and a stirring speed of 600 rpm for 120 min in a stainless steel semi-continuous stirred tank reactor coated with polytetrafluoroethylene (PTFE) to prevent contamination of the reaction solution with ions from the reactor material. In every case the mass of the complex (supported or not) was $2x10^{-3}$ g. All of the reactions, regardless of the catalyst used, in homogeneous or heterogeneous phase, were carried out with a molar ratio 1-heptyne/Rh equal to $6.85x10^3$ mol/mol.

The detection of possible diffusion limitations, during the catalytic tests, was taken into account according to procedures described in the literature.[34,35] External diffusion limitations were examined by performing the hydrogenation reaction with variation of the stirring speed in the range of 180-1400 rpm. The constancy of conversion and selectivity verified above 500 rpm showed that this kind of limitation did not occur at the selected rotational speed. On the other hand, possible limitations due to intraparticle mass transfer were evaluated by crushing the heterogenized complex catalyst to approximately one fourth the original size, and using this sample to carry out the reaction. The values of conversion and selectivity, equal to those obtained with the uncrushed catalyst, permitted to establish that such limitation was also absent at the selected operational conditions. Last but not least, the catalyst cylinders were weighed before and after the reaction. The difference in mass of the cylinders of the catalysts was not significant within the experimental error of the analytical balance method employed, which indicates no mass loss. Consequently, it can be considered that the effect of attrition was absent or insignificant, so that it did not play an important role in relation to a possible limitation of mass transfer by loss of material.

All of the catalytic evaluations were performed in triplicate, with an experimental error not higher than 3%. Reactants and products were analyzed by gas chromatography using a FID detector and a CP Sill 88 capillary column.

Study of Supported Complex Washing / “Leaching” effect

The possible washing of the complex during the heterogeneous hydrogenation runs by the action of the operational conditions, i.e., composition of the liquid phase in contact with the catalyst, temperature (303 K) and pressure (150 kPa), was assessed in two ways: a) by analyzing the presence of rhodium in the residual solutions, using the technique of Atomic Absorption Spectroscopy, and b) by comparing the surface atomic ratios Rh/Z (Z = Al or C, for γ-Al_2O_3 or RX3, respectively) obtained by XPS before and after the reaction.

Table 1. XPS results: Binding Energies (eV) and Superficial Atomic Ratios (at/at) for the commercial Wilkinson catalyst

Wilkinson Complex	Condition	Rh $3d_{5/2}$ (eV)	P $2p_{3/2}$ (eV)	Cl $2p_{3/2}$ (eV)	P/Rh (at/at)	Cl/Rh (at/at)	Rh/Al (at/at)	Rh/C (at/at)
Homogeneous	---	307.2	130.1	198.3	3.01	1.02	-	-
On γ-Al_2O_3	Fresh	307.3	130.2	198.2	3.00	1.00	0.093	-
	Used	307.2	130.2	198.1	2.99	1.01	0.093	-
On RX3	Fresh	307.2	130.1	198.2	3.00	1.00	-	0.100
	Used	307.2	130.2	198.2	2.99	0.99	-	0.100

RESULTS

Wilkinson Complex Characterization

X-Ray photoelectron spectroscopy (XPS)

Table 1 shows the results obtained by XPS for the commercial Wilkinson complex in different conditions, emphasizing that they were replicated within acceptable experimental error, by the regenerated Wilkinson complex (not reported in Table 1).

Furthermore, the following values were obtained from XPS for the Lindlar catalyst: a) deconvolution of the spectrum reveals two peaks for Pd $3d_{5/2}$ and Pb $4f_{7/2,}$ with values at 335.2 eV (69% at/at) and 336.9 eV (31% at/at) for Pd, and 136.8 eV (20% at/at) and 138.6 eV (80% at/at) for Pb, b) Ca $2p_{3/2}$, 346.8 eV, c) Pd/Pb = 0.7 at/at, and d) Pd/Ca = 0.24 at/at.

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 1 shows the transmittance infrared spectra for a) the commercial Wilkinson complex and b) the regenerated one, both in the range of 4000-625 cm^{-1}.

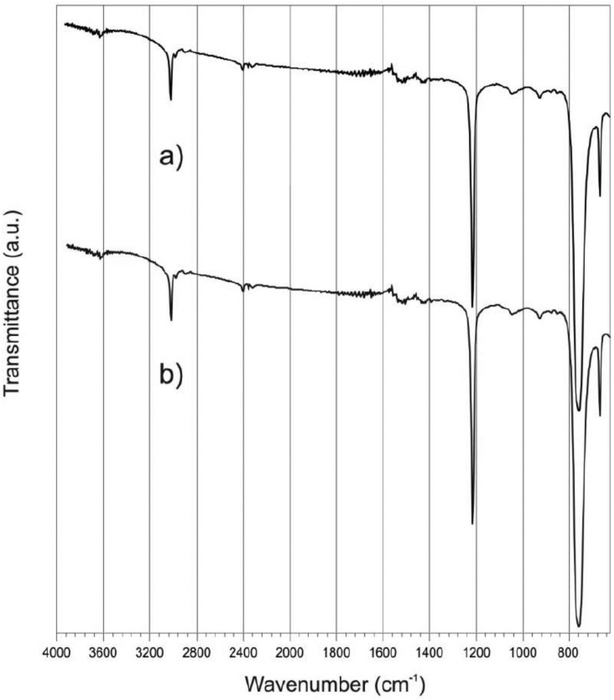

Figure 1. *FTIR spectra of: a) commercial Wilkinson complex and b) regenerated Wilkinson complex*

UV/Vis Spectroscopy

Figure 2 depicts the UV/Vis absorbance spectra for a) the commercial Wilkinson complex and b) the regenerated one in the range of 300-900 nm.

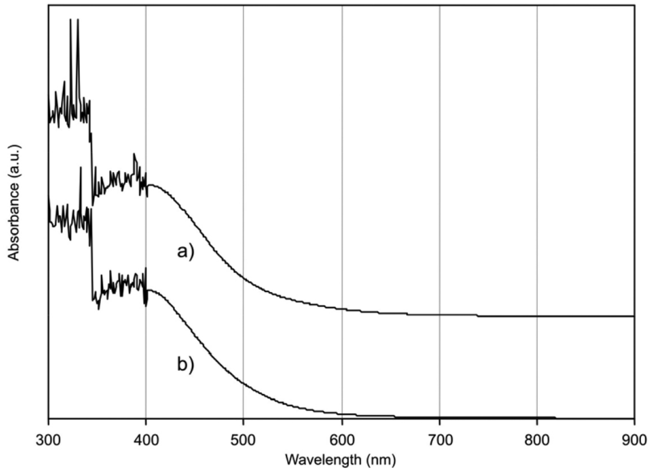

Figure 2. *UV/Vis spectra of: a) commercial Wilkinson complex and b) regenerated Wilkinson complex*

Support characterization

In Table 2, the BET specific surface area and the pore size distribution are detailed for the supports γ-Al_2O_3 and RX3.

Table 2. B.E.T. Specific Area and Pore Size Distribution of the supports

Support	S_{BET} (m^2xg^{-1})	V_{micro} ($mLxg^{-1}$) [<0.7 nm]	$V_{supermicro}$ ($mLxg^{-1}$) [0.7-2 nm]	V_{meso} ($mLxg^{-1}$) [2-7.5 nm]	V_{macro} ($mLxg^{-1}$) [7.5-50 nm]
γ-Al_2O_3	180	0.048	0.030	0.487	0.094
RX3	1.411	0.356	0.333	0.098	0.430

Catalytic evaluation

Commercial Wilkinson complex

The results from the catalytic evaluations are shown in Figures 3 to 5 for the partial hydrogenation of 1-heptyne, obtained with the Lindlar and the commercial Wilkinson catalysts, in homogeneous and heterogeneous systems on γ-Al_2O_3 and on RX3. Figure 3 shows the mass percentages of 1-heptyne, 1-heptene and n-heptane, on a solvent-free basis, as a function of time. In this Figure, a solvent-free basis is required to show the reactant and products concentrations because of the low initial substrate molar concentration (M = 0.15 and V= 100 mL).

On the other hand, Figure 4 shows the conversion of 1-heptyne to 1-heptene and the conversion of 1-heptyne to n-heptane, with respect to the 1-heptyne total conversion (X_T).

Finally, Figure 5 plots the selectivity to 1-heptene as a function of 1-heptyne total conversion.

Table 3 exhibits the maximum values of conversion to 1-heptene (X_e), with the corresponding data of 1-heptyne total conversion (X_T) and selectivities to 1-heptene (S_e) and n-heptane (S_n) for the different catalysts.

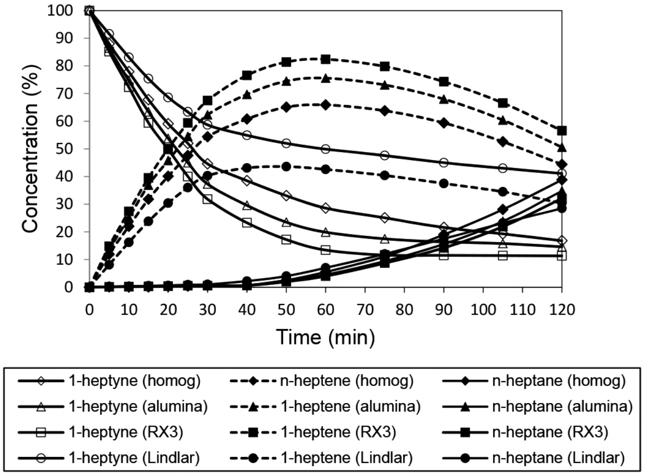

Figure 3. *Concentration profiles of reactants and products as a function of time for the commercial Wilkinson complex in homogeneous and heterogeneous systems, and for the Lindlar catalyst*

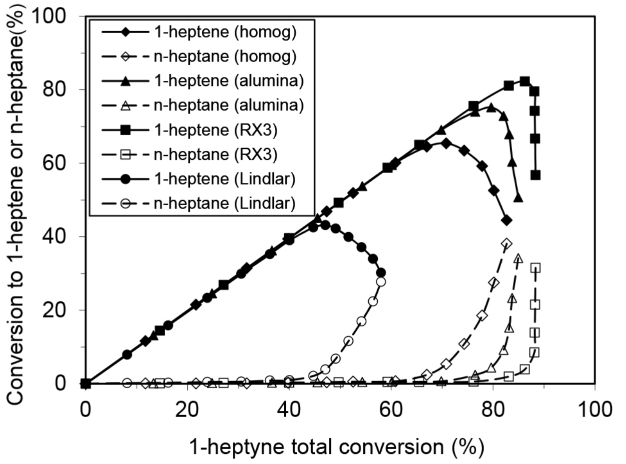

Figure 4. *Conversion of 1-heptyne to 1-heptene (solid lines) and conversion of 1-heptyne to n-heptane (dashed lines) as a function of 1-heptyne total conversion, for the commercial Wilkinson complex in homogeneous and heterogeneous systems, and for the Lindlar catalyst*

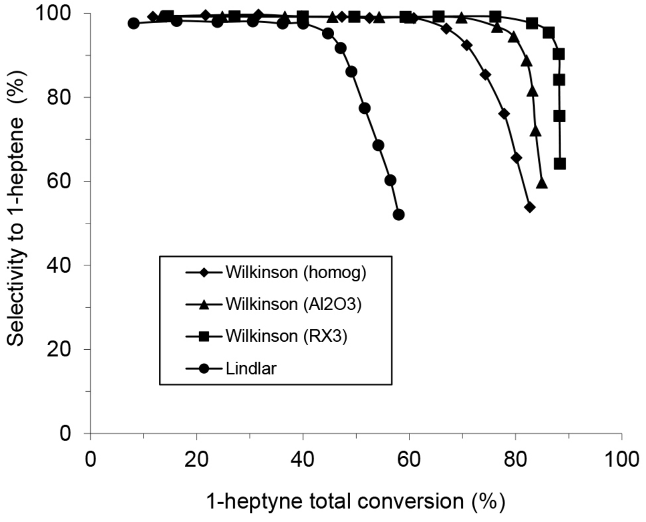

Figure 5. *Selectivity to 1-heptene as a function of 1-heptyne total conversion, for the commercial Wilkinson complex in homogeneous and heterogeneous systems, and for the Lindlar catalyst*

Table 3. Maximum conversion of 1-heptyne to 1-heptene and the corresponding values of 1-heptyne total conversion and selectivities to 1-heptene and to n-heptane

Catalyst	X_e (%)	X_T (%)	S_e (%)	S_n (%)
$[RhCl(PPh_3)_3]$/RX3	82	86	95.4	4.6
$[RhCl(PPh_3)_3]$/ γ-Al_2O_3	75	80	93.8	6.2
$[RhCl(PPh_3)_3]$ homogeneous	65	71	91.6	8.4
Lindlar	43	47	91.5	8.5

Regenerated Wilkinson complex

Additionally, Figure 6 shows the mass concentration profiles on a solvent-free basis, corresponding to 1-heptyne, 1-heptene and n-heptane, obtained as a function of time during the selective hydrogenation of 1-heptyne, with the regenerated Wilkinson complex in homogeneous and heterogeneous systems on γ-Al_2O_3 or RX3.

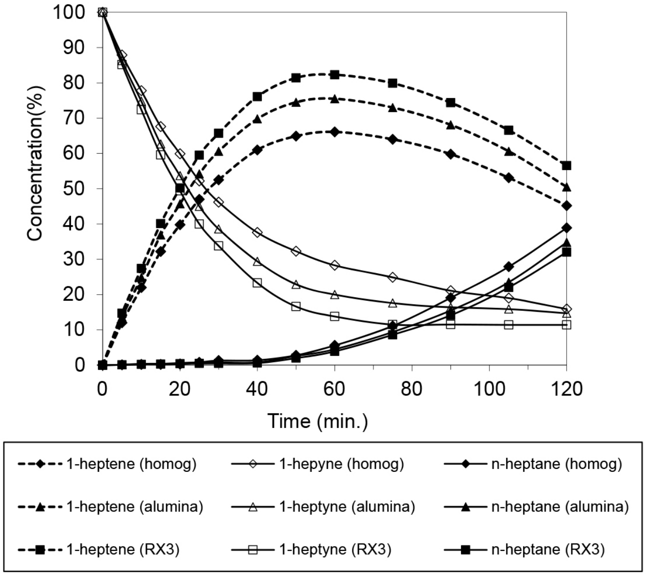

Figure 6. *Concentration profiles of reactants and products as a function of time for the regenerated Wilkinson complex in homogeneous and heterogeneous systems*

DISCUSSION

Lindlar catalyst characterization

The binding energies determined for the Lindlar catalyst permit to conclude that: a) Pd $3d_{5/2}$ peaks indicate the presence of Pd^0 (69% at/at) and Pd^{n+} (31% at/at) with 0 <n <+2[36], b) Pb $4f_{7/2}$ peaks provide evidence of the existence of Pb^0 (20% at/at) and Pb^{2+} in $Pb(OAc)_2$ (80% at/at)[36], and c) Ca $2p_{3/2}$ peak may correspond to Ca^{2+} in $CaCO_3$.[36]

Wilkinson Complex Characterization

X-Ray photoelectron spectroscopy(XPS)

For the commercial Wilkinson complex and for the pure regenerated one, the binding energies obtained by XPS were: Rh $3d_{5/2}$: 307.2 eV, P $2p_{3/2}$: 130.1 eV and Cl $2p_{3/2}$: 198.3 eV. These values are associated, respectively, to rhodium as Rh(I), to phosphorus in a phosphine, and to chlorine in the form of chloride,[29,36] in agreement with the expected theoretical electronic states for the complex under study. The atomic ratios (at/at) were: P/Rh: 3.01 and Cl/Rh: 1.02, corresponding to the minimum theoretical stoichiometry of the Wilkinson complex: $[RhCl(PPh_3)_3]$.

In addition, Table 1 shows that the peaks Rh $3d_{5/2,}$ P $2p_{3/2}$ and Cl $2p_{3/2}$ and the atomic ratios P/Rh and Cl/Rh measured for the complex supported on γ-Al_2O_3 or RX3, fresh and after reaction, are essentially the same as those corresponding to the pure complex. These results suggest, on the one hand, that the Wilkinson complex coordination sphere remains unchanged even after being heterogenized and used, thus preserving its minimum formula $[RhCl(PPh_3)_3]$, and on the other hand, that the anchoring complex on the support occurs in a kind of "table type" way, in which the square arrangement of the central atom (rhodium) and the donor atoms (chlorine and phosphorus) would be the "top" without direct interaction with the surface of γ-Al_2O_3 or RX3, while the "legs" would be the aromatic phenyl rings in contact with the support via physicochemical interactions. This pictorial description of the immobilization implies that the Rh atom is free enough to get involved in favorable interactions through its HOMO and LUMO molecular orbitals. The former can provide electron density to the dihydrogen antibonding orbital, facilitating the cleavage of H-H bond and, according to the proposed mechanism for Wilkinson complex catalytic action, leading to the formation of hydride complexes; on the other hand, the LUMO orbital can receive electron density from the π bonds of the alkyne, rendering both carbon atoms available for C-H bond formation.

Fourier Transform Infrared Spectroscopy (FTIR)

From inspection of Figure 1, it can be stated that:

a) The peaks present in the range of 4000-625 cm^{-1} are associated to the characteristic frequencies of triphenylphosphine in the Wilkinson complex.[37] In particular, those located in the range between 1500 and 840 cm^{-1} correspond to the phenyl ring attached to the phosphorous atom (P-ϕ). Anyhow, a slight shift to lower frequencies with respect to the pure ligand[37] is observed, meaning an interaction between the phosphorous lone pair and the rhodium atom.
b) The spectrum of the Wilkinson complex regenerated after metal recovery coincides with that of the commercial complex.

UV/Vis Spectroscopy

As shown in Figure 2, the UV/Vis spectra of the Wilkinson complex, commercial and regenerated, dissolved in chloroform, were found to be identical to each other within the range of tested wavelengths.

In both cases, the peaks in the visible zone, Figure 2, correspond to electronic transitions between ground and excited states (terms)[38] for the species. They are linked to the bonds amongst Rh and three trisphenylphosfine ligands arranged in a square planar geometry which can be interpreted through the Angular Overlap Model.[38] Their presence and positions justified the red-violet color of the commercial and synthesized Wilkinson complex.

Feasibility of Wilkinson Complex Regeneration

From evaluation of the results obtained for the commercial Wilkinson complex and the regenerated one with XPS, FTIR and UV/Vis techniques discussed in the previous paragraphs, it is reasonable to conclude that the selected method of regeneration is appropriate to recover rhodium and prepare the Wilkinson complex from wastes collected after the homogeneous catalytic evaluations.

Support characterization

According to the information exhibited in Table 2, it can be noted that RX3 BET specific surface area is 7.84 times higher than that of γ-Al_2O_3. Furthermore, it can be considered that γ-Al_2O_3 is essentially a mesoporous support, while RX3 is a material with a structure covering a range of micro, supermicro and macropores.

Catalytic evaluation

Commercial Wilkinson complex

Figure 3 shows, in all cases, typical profiles corresponding to consecutive reactions, namely: alkyne → alkene → alkane. As can be seen, 1-heptene is the predominant product, followed by the generation of n-heptane due to the occurrence of over-hydrogenation. For the commercial Wilkinson complex, homogeneous or heterogeneous, the only product obtained until 40 minutes is 1-heptene, and only from that time the production of n-heptane (unwanted product) becomes apparent, while for the Lindlar catalyst, alkane detection is already observed after 30 min of reaction. It can also be noted that, throughout the reaction, the 1-heptene higher concentrations are obtained using the commercial Wilkinson complex supported on RX3, followed then by the complex anchored on γ-Al_2O_3, the homogeneous system and finally the Lindlar catalyst.

On the other hand, from the data of Figure 4, it can be seen that the commercial Wilkinson complex, homogeneous and supported, for $X_T \leq$ ca. 40%, shows 1-heptene conversions similar to those of the Lindlar catalyst, and no production of n-heptane is detected. It can also be noted that the catalyst systems exhibit their respective maximum conversions to 1-heptene at different values of X_T, and beyond the maximum, the production of 1-heptene, in all of the cases, declines steeply, with a simultaneous and important increase in the conversion to n-heptane.

Another relevant aspect to be considered is the selectivity to the desired product (1-heptene). In Figure 5, it can be seen that the Wilkinson complex, homogeneous or heterogeneous, shows very good values of selectivity, above ca. 99 %, up to a value of X_T of ca. 61%, 70% and 83% for the homogeneous complex, the complex supported on γ-Al_2O_3 and RX3, respectively. Concerning the Lindlar catalyst, it shows a high selectivity, initially almost constant and close to 97-98 %, but from 40 % of total conversion it decreases abruptly, reaching a final value of 52 % at $X_T = 58\%$.

Additionally, according to Table 3, it can be established, with respect to the production of 1- heptene, the following order of importance of the catalysts:

$[RhCl(PPh_3)_3]/RX3 > [RhCl(PPh_3)_3]/\gamma\text{-}Al_2O_3 > [RhCl(PPh_3)_3]$ homogeneous >>>Lindlar

It is worth pointing out that the maximum production of 1-heptene in each case corresponds to a selectivity value higher than 91%, comparable to that obtained with the Lindlar catalyst system, which is usually taken as a reference for the hydrogenation of alkynes.

From the results presented in Figures 3 to 5 and in Table 3, it can be concluded that with the Wilkinson complex, evaluated as catalyst in homogeneous or heterogeneous condition, high conversion and selectivity to 1-heptene are obtained, significantly exceeding the production of 1-heptene achieved with the commercial Lindlar catalyst.

The increased activity of the supported complex has been also verified in other systems.[15,16] The best performance of the heterogeneous Wilkinson catalysts may be explained considering that the reactant chemical species, via physicochemical adsorption, are more concentrated in the vicinity of the complex than in the solution. Furthermore, the alkyne undergoes a stronger interaction with the support than the alkene, thus promoting the hydrogenation of the former instead of the latter. As a result, the selectivity remains high for an important period of time until the alkyne is exhausted, after which it begins to decline.

On the other hand, the almost eight times higher specific area of RX3 with respect to γ-Al_2O_3 can explain the higher 1-heptyne total conversion obtained with the former as support.

Regenerated Wilkinson complex

The catalytic evaluations performed with the regenerated Wilkinson complex yielded concentration profiles (Figure 6), conversions and selectivities with a difference lower than the experimental error (less than 3%) with respect to the commercial catalyst $[RhCl(PPh_3)_3]$. These results and those obtained by FTIR and UV/Vis, as mentioned in the Results section, lead to the conclusion that the regeneration technique implemented is valid for recovering and synthesizing the Wilkinson complex from the residual solutions of the test reactions conducted in homogeneous system.

Last but not least, it can be concluded again that the complex $[RhCl(PPh_3)_3]$, anchored on γ-Al_2O_3 or RX3, is the catalytically active species, throughout the catalytic process. This conclusion is supported by the following facts:

a) The constancy of the surface atomic ratio Rh/Z with Z = Al or C for γ-Al_2O_3 or RX3, respectively, based on the XPS data in Table 1, for the fresh and used catalysts.
b) The lack of detection of Rh in the residual solution after the heterogeneous hydrogenations, according to the data from Atomic Absorption Spectroscopy, thus confirming that the complex was not leached from the solid and remained anchored during the whole process.

CONCLUSIONS

The results obtained demonstrate that the Wilkinson complex is the catalytically active species, presenting high activity and selectivity for the partial hydrogenation of 1-heptyne, a medium chain alkyne, both in homogeneous and heterogeneous phase. In the latter case, it was also verified that there was no effect of complex leaching by the solvent.

The catalytic behavior of $[RhCl(PPh_3)_3]$ in any condition (homogeneous or heterogeneous) exceeds that of Lindlar, at the same operational conditions. A comparison between them allows setting the following order of importance in the production of 1-heptene:

$[RhCl(PPh_3)_3]$/RX3> $[RhCl(PPh_3)_3]/\gamma$-Al_2O_3 > $[RhCl(PPh_3)_3]$ homogeneous >>>Lindlar

On the other hand, the regeneration of the Wilkinson complex, using the remaining solutions of the homogeneous runs, by means of a simple and effective technique, was proved to be possible.

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