Rhodium(I) Complex with Hexylamine and Chloride Ligands, Catalytically Active in the Selective Hydrogenation of 1-Heptyne

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A rhodium(I) complex containing chloro and hexylamine was obtained. This species shows catalytic activity for the 1-heptyne semihydrogenation under at mild conditions (303 K and 150 kPa) in homogeneous as well as heterogeneous systems using γ-alumina as support. Fourier transform infrared (FTIR) spectra indicate that the hexylamine molecule is one of the ligands present in the complex species. On the other hand, the analysis of the results of X-ray photoelectron spectroscopy (XPS) and elemental composition suggest that the complex is tetracoordinated with an empirical formula $[RhCl(NH_2(CH_2)_5CH_3)_3]$, and that it attaches to the support and is not destroyed under reaction conditions. The absence of complex leaching from the supported catalyst was verified by XPS, atomic absorption analysis for Rh in solution, and catalyst reuse tests. When supported, the complex shows higher activity and selectivity than it does when it is unsupported, and also higher activity than the classic Lindlar catalyst used as a reference; this fact may be attributed, at least in part, to electronic and geometric effects.

1. Introduction

There is widespread agreement in the literature regarding the academic and industrial importance of hydrogenation reactions.[1−3] This is due to the utility of many products obtained via this type of reactions, such as some biologically active compounds. Hydrogenation of alkynes is particularly relevant, with the premise of avoiding overhydrogenation to simple bonds.

In this respect, the Lindlar catalyst, consisting of metallic Pd on calcium carbonate support modified with lead(II) acetate, has become, in the past decade, a reference catalyst for the hydrogenation of unsaturated systems. Many other metallic and bimetallic catalysts,[4−9] as well as catalysts based on complex species, have been studied in homogeneous[10] and heterogeneous systems.[11,12] The latter have some advantages over homogeneous systems, namely easy separation from fluid media, the possibility of continuous operation,[13] and the avoidance of costly purification stages.

Research activity has progressively tended to work under milder conditions of pressure and temperature, and to achieve higher activities and selectivities, especially in the cases of catalysts based on transition metal complexes.[14−17] A major part of the effort has been devoted to the semihydrogenation of short chain alkynes such as ethyne,[13,18] with few works related to longer chain alkynes.

Our previous work has covered aspects related to the use of transition metal complexes, unsupported or supported on alumina or active carbon, as catalysts in the selective hydrogenation of double and triple bonds of cyclic and linear hydrocarbons.[19−26] The present work is aimed at preparing a rhodium complex with chloride and hexylamine as ligands, to be anchored on γ-alumina and evaluated as a catalyst in the semihydrogenation of 1-heptyne, a relatively high molecular weight alkyne presenting a terminal triple bond. Comparison with the same complex in homogeneous conditions is also addressed. Data for the Lindlar catalyst at the same hydrogenation conditions are used as a reference. The possibility of reusing the supported catalyst is also evaluated.

2. Experimental Section

2.1. Preparation and Purification of the Complex. The Rh−chloride−hexylamine complex was obtained by reaction of $RhCl_3$ (Aldrich, Catalog No. 30786-6) with hexylamine (Aldrich, Catalog No. 21970-3; $CH_3(CH_2)_5NH_2$, HA) in toluene under an Ar atmosphere, at 353 K, with $HA/RhCl_3 = 6$ mol/mol.

The purification was made by column chromatography, with silica gel as the stationary phase and chloroform−methanol (5/1 vol/vol) as the solvent. All of the aliquots were analyzed for excess HA by means of plate chromatography, and then HA-free fractions were collected and evaporated in a rotary evaporator to obtain a yellow-brown solid.

2.2. Complex Heterogenization. A 0.3 wt % Rh heterogeneous catalyst was prepared by the incipient wetness technique[21] on Ketjen CK 300 γ-alumina (cylinders of 1.5 mm diameter, BET surface area 180 m^2 g^{-1}, pore volume 0.52 mL g^{-1}), previously calcined in air at 773 K for 3 h. The Rh complex was dissolved in a mixture of chloroform−methanol (5/1 vol/vol) to impregnate 0.075 g of γ-alumina.

2.3. Complex and Catalyst Characterization. 2.3.1. Complex Elemental Composition. The elemental composition was evaluated for the pure complex and for the supported one as well. Determinations were made for rhodium, chlorine, and nitrogen, according to standard methods.[27−30]

2.3.2. X-ray Photoelectron Spectroscopy (XPS). To characterize the pure complex, two kinds of data were obtained by XPS on a Shimadzu ESCA 750 electron spectrometer coupled to a Shimadzu ESCAPAC 760 data system: (a) the binding energies corresponding to Rh $3d_{5/2}$, N $1s_{1/2}$, and Cl $2p_{3/2}$ and (b) the superficial atomic ratios N/Rh and Cl/Rh, to determine the complex minimum formula. Likewise, to investigate if such variables kept their values, the same analyses were performed

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for the supported complex before and after reaction. Additionally, the superficial atomic ratio Rh/Al was obtained, to detect a possible support-to-solution complex transfer. The Pd $3d_{5/2}$ binding energy was also determined for the Lindlar catalyst. In all cases the C 1s line was taken as an internal standard at 285.0 eV, to correct deviations caused by electronic charges of the samples. The samples were introduced into the sample holder following the operational procedures described in the literature,[31] to ensure that there were no modifications of the electronic states of the species analyzed. No electronic modifications occurred on exposure of the samples to the atmosphere for different periods. The atomic ratios were determined by comparing the areas under the peaks after background subtractions and corrections due to differences in escape depths and in photoionization cross sections.[32]

2.3.3. Fourier Transform Infrared Spectroscopy (FTIR). The characteristic IR group frequencies corresponding to hexylamine[33] were used to determine whether this molecule was part of the obtained compound as a ligand. The spectra of the pure complex and that of hexylamine were determined by FTIR in the $4600-200$ cm^{-1} range in a Shimadzu 8101/8101 M 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$_2$ (or dry air) atmosphere. The solid 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 nonsaturated spectra.

2.4. Catalytic Evaluation. The catalytic evaluation was performed for the selective hydrogenation of 1-heptyne to 1-heptene, using 100 mL of a 0.15 M solution of 1-heptyne (Fluka, Catalog No. 51950) in toluene (EM Science, Catalog No. TX0735-5). The reaction was carried out in a PTFE-coated batch stainless steel stirred tank reactor, with a stirring speed of 600 rpm. The following three systems were used as catalysts: (a) the alumina-supported Rh complex (0.3 wt % Rh, 0.075 g), (b) the Rh complex in homogeneous condition, and (c) the Lindlar catalyst (Aldrich, Catalog No. 20573-7). In all three cases the same 1-heptyne/metal ratio (6.95×10^3 mol/mol) was used.

Every catalytic test was carried out in triplicate, at optimum values of temperature and pressure determined in the same way as previously reported:[23] $P = 150$ kPa, $T = 303$ K, with a relative experimental error of about 3%.

The possibility of diffusional limitations was also investigated. Experiments revealed a constancy of the activity above 500 rpm, thus indicating the absence of external diffusional limitations at the rotary speed selected (600 rpm). On the other hand, to ensure also the absence of intraparticle mass-transfer limitations, the heterogenized complex catalyst was crushed up to one-fourth the original size of the commercial γ-Al$_2$O$_3$ used as the support. Runs executed with the crushed complex catalyst exhibited the same conversion as that corresponding to the noncrushed catalyst; this fact provided evidence that internal diffusional limitations were absent from our experiments.[34,35]

The analyses of reactants and products were made by gas chromatography using a flame ionization detector and a CP Sill 88 capillary column.

2.5. Complex Leaching. To evaluate the possibility of complex leaching during the supported complex evaluation, two experiments were performed to complement the XPS information (section 2.3.2). On one hand the remaining solution from
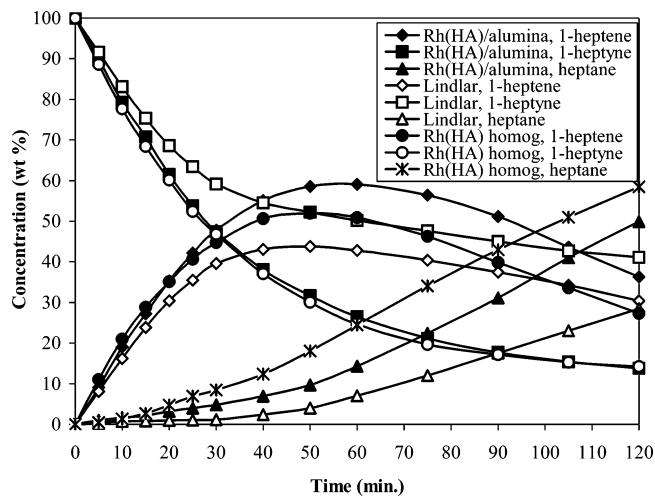

Figure 1. Reaction profiles for: alumina-supported complex, unsupported complex, and Lindlar catalyst. $P_{H_2} = 150$ kPa; $T = 303$ K.
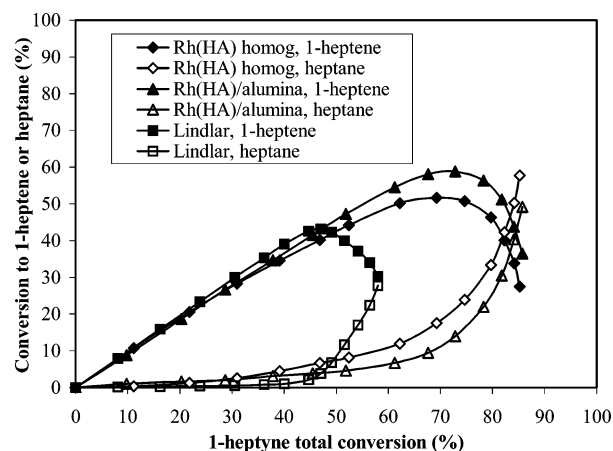

Figure 2. Conversion to 1-heptene and to heptane vs 1-heptyne total conversion for alumina-supported complex, unsupported complex, and Lindlar catalyst.

the heterogeneous run was analyzed for rhodium by atomic absorption spectroscopy. On the other hand, three successive additional runs were performed with the same catalyst used initially, for the same reaction and operative conditions (catalyst reuse tests).

3. Results

Figure 1 is a plot of the weight percentage (on a solvent-free basis) of 1-heptyne, 1-heptene, and heptane vs time, corresponding to the runs in which the Lindlar catalyst, the supported complex, and the unsupported complex were used. Typical profiles for a consecutive reaction alkyne−alkene−alkane were attained in all cases.

The conversions of 1-heptyne to 1-heptene and to heptane vs total 1-heptyne conversion are shown in Figure 2.

The selectivity to 1-heptene is another important aspect to be taken into account. It is presented in Figure 3 as a function of total 1-heptyne conversion. As a consequence of the decreasing conversion of 1-heptyne to 1-heptene beyond the maxima shown in Figure 2 and the increasing heptane production, the selectivity also undergoes a noticeable diminishment.

In all three consecutive runs performed with the same supported catalyst, the corresponding reaction profiles obtained were almost the same as that corresponding to the fresh catalyst; the values were accurate well below the ±3% experimental error affecting the catalytic tests.
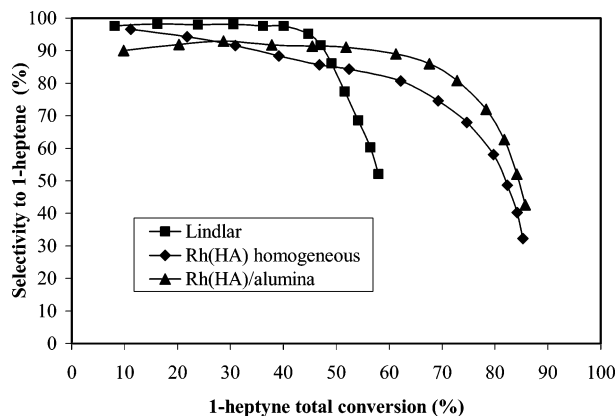
Figure 3. Selectivity to 1-heptene as a function of 1-heptyne total conversion for alumina-supported complex, unsupported complex, and Lindlar catalyst.
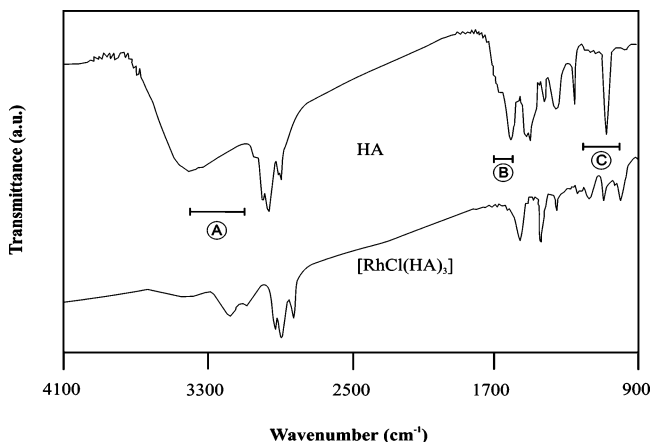

Figure 4. FTIR spectra for hexylamine (HA) and the rhodium complex. (A) NH_2 "stretching" (3600−3100 cm^{-1}); (B) NH_2 "bending" (1700−1600 cm^{-1}); (C) CN "stretching" (1200−1000 cm^{-1}).

Table 1. Elemental Composition Values Obtained for the Pure Complex and for the Fresh Supported Complex

	composition (wt %)			atomic ratios (atom/atom)	
species	Rh	Cl	N	Cl/Rh	N/Rh
pure complex	57.28	20.28	22.44	1.03	2.88
supported complex	0.30	0.11	0.10	1.0	3.1

Figure 4 shows the respective FTIR spectra of the hexylamine ligand and the pure complex, in the range 4100−900 cm^{-1}. The spectrum of hexylamine shows, at high frequencies, the following characteristic peaks of a primary aliphatic amine:[33] NH_2 "stretching" (3600−3100 cm^{-1}) (A), CH "stretching" (3000−2800 cm^{-1}), NH_2 "bending" (1700−1600 cm^{-1}) (B), CH "bending" (1500−1300 cm^{-1}), and CN "stretching" (1200−1000 cm^{-1}) (C). The labels "A", "B", and "C" denote ranges associated with the nitrogen atom in hexylamine and are taken as references for comparative purposes (see Discussion section).

The elemental composition values obtained for the pure complex and for the supported complex are shown in Table 1 on a weight percentage basis.

Table 2 shows the Rh $3d_{5/2}$, N $1s_{1/2}$, and Cl $2p_{3/2}$ peak binding energies (BEs) and the N/Rh and Cl/Rh atomic ratios for the pure complex and the supported complex before and after reaction. The Rh/Al atomic ratios for the supported complex before and after reaction are also reported. For the Lindlar catalyst, the Pd $3d_{5/2}$ binding energy found was 337.2 eV.

Gas chromatographic analyses revealed that 1-heptyne, 1-heptene, and heptane were the only solutes found for the

different catalytic systems. In addition, no rhodium was detected by atomic absorption spectroscopy in the remaining solutions from the heterogeneous run.

4. Discussion

As Figure 1 shows, throughout the reaction higher concentrations of 1-heptene were obtained for both supported complex and unsupported Rh complex than those obtained for the classic Lindlar catalyst under the same operational conditions. The highest 1-heptene concentration corresponded to the supported complex.

According to Figure 2, at low values of 1-heptyne total conversion, up to ca. 45%, the unsupported complex, the supported complex, and the Lindlar catalyst show very similar conversions to 1-heptene and to heptane. From that point on, the heterogeneous system is more active than its homogeneous counterpart, a fact attributable, at least in part, to electronic and geometric effects. Also, both systems are more active than the Lindlar catalyst. For the supported complex, the conversion to 1-heptene reaches a maximum of 59% at a total conversion of 73%; this value is higher than the corresponding one for the unsupported complex, namely 52% at a total conversion of 69%. After these maxima, both cases exhibit a steep decrease in the conversion to 1-heptene and a marked increase in the conversion to heptane. As a consequence, the selectivity also undergoes a noticeable diminishment.

The maximum conversion attained with the Lindlar catalyst under the same operational conditions is even lower, with a maximum conversion to 1-heptene of 43% at a total conversion of 47% and then also undergoing a sharp decrease.

The supported complex shows, in Figure 3, good selectivity values above 90% up to a total conversion of ca. 60%, but then the selectivity begins to decrease, keeping a value over 80% up to 73% total conversion; after that, it decreases rapidly, as stated above. On the other hand, the unsupported complex exhibits a high initial selectivity, ca. 96%, but decreases monotonically without showing a plateau. The Lindlar catalyst shows initially an almost constant high selectivity of around 97−98%, but beyond 45% total 1-heptyne conversion it undergoes an abrupt decrease, reaching a final value of 52% at a total conversion of 58%. Thus, the Lindlar catalyst presents a slightly higher selectivity, but the supported complex keeps a high value over a wider range of total conversion.

The values of yield and selectivity given above for the Rh(I)−HA complex, unsupported or supported, are better than those of the Pd(II)−HA complex, [PdCl$_2$(HA)$_2$], previously reported by us,[25] for the same reaction and under the same conditions. However, when the comparison is made with the Pd(II)−TDA complex,[23] [PdCl$_2$(TDA)$_2$] (TDA = tridecylamine), considering the complexes supported on γ-Al$_2$O$_3$, it is seen that the Pd system presents a yield only some 10−12% higher and a selectivity only some 5−6% higher. Thus, the performance of the Rh−HA complex may be considered as intermediate between Pd−HA and Pd−TDA, especially when the analysis is made for the supported catalysts, which have in general a better behavior than the unsupported systems.

The peaks in the pure complex FTIR spectrum (see Figure 4) globally agree with those corresponding to pure hexylamine, as reported in the Results section, and with those reported in the literature. Anyhow, differences are found in some frequencies, particularly those labeled A, B and C, associated with the nitrogen atom environment in the complex. They show a slight shift to lower frequencies with respect to pure hexylamine because of the interaction with the metal atom via the nitrogen

Table 2. XPS Binding Energies and Atomic Ratios for the Pure Rhodium Complex and for the Same Complex Supported on γ-Al$_2$O$_3$ Before and After Catalytic Evaluation

condition	Rh 3d$_{5/2}$ (eV)	N 1s$_{1/2}$ (eV)	Cl 2p$_{3/2}$ (eV)	N/Rh (atom/atom)	Cl/Rh (atom/atom)	Rh/Al (atom/atom)
pure complex	307.1	402.0	198.1	3.00	1.02	
supported complex, fresh	307.1	402.0	198.0	3.00	1.00	0.053
supported complex, after reaction	307.1	402.1	198.1	2.99	1.02	0.053

lone pair. This suggests that hexylamine is present as a ligand in the complex species.

According to the data given in Table 1, the atomic ratios for Rh, Cl, and N in the pure complex and in the supported complex may be expressed as Rh/Cl/N = 1/1/3.

Taking into account the Rh 3d$_{5/2}$ binding energy, the electronic state of Rh in the complex, formally represented with oxidation number I, may actually be regarded as $n+$, with n between 0 and 1, according to the literature.[36] This shows that Rh in the complex is an electron-rich center. The N 1s$_{1/2}$ binding energy presents a shift to higher values with respect to reported data on N in amines;[36] this shift may be attributed to the fact that N is bonded to the metal center, thus making N more positive than it is in the free amine. The Cl 2p$_{3/2}$ peak corresponds, in every case, to chlorine as chloride ligand.[36]

Because hexylamine is present as a ligand (as suggested by FTIR analysis), and the atomic ratios from XPS analyses, reported in Table 2, are N/Rh $\cong$ 3 and Cl/Rh $\cong$ 1, it is possible to assign a minimum formula [RhCl(NH$_2$(CH$_2$)$_5$CH$_3$)$_3$] to the complex. The same conclusion about atomic ratios can be drawn from the elemental analysis for the pure complex and for the supported complex as well, in agreement with the analysis made by XPS. According to these results, the rhodium complex may be considered tetracoordinated.

The constancy of the above-reported atomic ratios for the pure complex and supported complex, before and after reaction, can also be noted. In addition, the Rh/Al ratio obtained for the supported complex, remained practically unchanged after the reaction, revealing that no complex transfer from the support to the solution had occurred. The absence of complex leaching was also confirmed by the absorption spectroscopic analysis, by means of which no Rh was detected in the remaining solutions. Additionally, the same conclusion can be extracted from the catalytic constant performance over four successive cycles. These results permit the assumption that the complex did not lose its chemical identity and remained strongly attached to the support. It can thus be suggested that it is the active catalytic species, or is a precursor of it.

The activity of Rh(I) complexes is usually attributed, on one hand, to the fact that the most important oxidation states for rhodium, I and III, are separated by two units;[37−39] this allows the oxidative addition of dihydrogen to give dihydride intermediate species which are considered essential in the catalytic cycle. An electron-rich metal center such as the Rh atom in this complex, as confirmed by XPS, or, in general, central metal atoms in low oxidation states, may facilitate the dihydrogen molecule bond breaking because of the interaction of a filled metal d orbital with the empty σ antibonding H$_2$ molecular orbital, thus weakening the H−H bond.[39,40] Moreover, basic ligands such as amines tend to donate electron density to the metal atom to which they are bonded. Thus in this complex, despite the electron-withdrawing effect of the chloride ligand, there are three electron-donating hexylamine ligands that contribute to increase the central metal atom's electron density. These features may be also important in the performance of the heterogenized complex. In addition, the acidic Lewis sites on the γ-alumina support could explain the better behavior of the anchored complex. An increase of the substrate concentration

around the active species on the support (with respect to that of the bulk solution) is expected because of an acid/base Lewis interaction between the γ-alumina acidic sites and the 1-heptyne triple bond basic sites.

5. Conclusions

A complex compound of Rh(I) with chloride and hexylamine as ligands was obtained, with a suggested minimum formula [RhCl(NH$_2$(CH$_2$)$_5$CH$_3$)$_3$], as indicated by FTIR, XPS, and elemental composition techniques, that anchored on γ-alumina could be used as a heterogeneous catalyst in the semihydrogenation of 1-heptyne under mild conditions. It shows good selectivity to the corresponding alkene, and a higher alkene yield than the classic Lindlar catalyst does, at the same operative conditions. Furthermore, the complex presents better activity and selectivity when supported than it does in the homogeneous condition, probably owing, at least in part, to electronic and geometric effects. This performance adds to the advantages that heterogeneous systems have over their homogeneous counterparts, for example easy separation from the reaction media and the possibility of continuous operation. The supported catalyst showed also the possibility of being reused at least three times. In all cases, no complex leaching from the support was detected, as verified by means of XPS, atomic absorption analysis for Rh in solution, and catalyst reuse tests.

Literature Cited

(1) Chen, B.; Dingerdissen, U.; Krauter, J. G. E.; Lansink Rotgerink, H. G. J.; Möbus, K.; Ostgard, D. J.; Panster, P.; Riermeierd, T. H.; Seebald, S.; Tackec, T.; Trauthweine, H. New developments in hydrogenation catalysis particularly in synthesis of fine and intermediate chemicals. *Appl. Catal. A: Gen.* **2005**, *280*, 17.

(2) Molnár, Á.; Sárkány, A.; Varga, M. Hydrogenation of carbon-carbon multiple bonds: chemio-, regio- and stereo-selectivity. *J. Mol. Catal. A: Chem.* **2001**, *173*, 185.

(3) Park, J. W.; Chung, Y. M.; Suh, Y. W.; Rhee, H. K. Partial hydrogenation of 1,3-cyclooctadiene catalyzed by palladium-complex catalysts inmobilized on silica. *Catal. Today* **2004**, *93−95*, 445.

(4) Volpe, M. A.; Rodríguez, P.; Gígola, C. E. Preparation of Pd/Pb/ α-Al$_2$O$_3$ catalysts for selective hydrogenation using PbBu$_4$: the role of metal-support boundary atoms and the formation of a stable surface complex. *Catal. Lett.* **1999**, *61*, 27.

(5) Coq, B.; Figueras, F. Bimetallic palladium catalysts: influence of the co-metal on the catalyst performance, *J. Mol. Catal. A: Chem.* **2001**, *173* (1−2), 117.

(6) Nijhuis, T. A.; van Koten, G.; Moulijn, J. A. Optimized palladium catalyst systems for selective liquid-phase hydrogenation of functionalized alkynes. *Appl. Catal. A: Gen.* **2003**, *238*, 259.

(7) Marín-Astorga, N.; Pecchi, G.; Fierro, J. L. G.; Reyes, P. Alkynes hydrogenation over Pd-supported catalysts. *Catal. Lett.* **2003**, *91* (1−2), 115.

(8) Mastalir, Á.; Király, Z.; Berger, F. Comparative study of size-quantized Pd-montmorillonite catalysts in liquid-phase semihydrogenation of alkynes. *Appl. Catal. A: Gen.* **2004**, *269*, 161.

(9) Chen, L.; Li, Ch.-J. Facile and selective copper-palladium catalyzed addition of terminal alkynes to activated alkynes in water. *Tetrahedron Lett.* **2004**, *45*, 2771.

(10) Atencio, R.; Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. Synthesis, reactivity and catalytic activity of [RuH(η^1-OCMe$_2$)(CO)$_2$-(PPr$^i_3$)$_2$]BF$_4$. *J. Chem. Soc., Dalton Trans.: Inorg. Chem.* **1995**, *13*, 2171.

(11) Ulan, J. G.; Maier, W. F.; Smith, D. A. Rational design of a heterogeneous Pd catalyst for the selective hydrogenation of alkynes. *J. Org. Chem.* **1987**, *52*, 3132.

(12) Mallat, T.; Baiker, A. Selectivity enhancement in heterogeneous catalysis induced by reaction modifiers. *Appl. Catal. A: Gen.* **2000**, *200*, 3.

(13) Lennon, D.; Marshall, R.; Webb, G.; Jackson, S. D. The effects of hydrogen concentration on propyne hydrogenation over a carbon supported palladium catalyst studied under continuous flow condition. *Stud. Surf. Sci. Catal.* **2000**, *130*, 245.

(14) Kerr, J. M.; Suckling, C. J. Selective hydrogenation by novel palladium (II) complexes. *Tetrahedron Lett.* **1988**, *29*, 5545.

(15) Trzeciak, A. M.; Ziólkowski, J. J.; Jaworska-Galas, Z.; Mista, W.; Wrzyszcz, J. Homogeneous and alumina supported rhodium complex catalyzed hydrogenation. *J. Mol. Catal.* **1994**, *88*, 13.

(16) Frolov, V. M. Platinum metals complex catalysts for liquid-phase hydrogenations. *Platinum Met. Rev.* **1997**, *40* (1), 8.

(17) Costa, M.; Pelagatti, P.; Pelizzi, C.; Rogolino, D. Catalytic activity of palladium (II) complexes with tridentate nitrogen ligands in the hydrogenation of alkenes and alkynes. *J. Mol. Catal. A: Gen.* **2002**, *178*, 21.

(18) Hamilton, C. A.; Jackson, S. D.; Kelly, G. J.; Spence, R.; de Bruin, D. Competitive reactions in alkyne hydrogenation. *Appl. Catal. A: Gen.* **2002**, *237*, 201.

(19) L'Argentière, P. C.; Liprandi, D.; Cagnola, E. A.; Fígoli, N. S. [PdCl$_2$(NH$_2$(CH$_2$)$_{12}$CH$_3$)$_2$] supported on γ-Al$_2$O$_3$ as catalyst for selective hydrogenation. *Catal. Lett.* **1997**, *44*, 101.

(20) L'Argentière, P. C.; Cagnola, E. A.; Cañon, M.; Liprandi, D. A.; Marconetti, D. V. A nickel tetra-coordinated complex as catalyst in heterogeneous hydrogenation. *J. Chem. Technol. Biotechnol.* **1998**, *71*, 285.

(21) Quiroga, M. E.; Cagnola, E. A.; Liprandi, D. A.; L'Argentiére, P. C. Supported Wilkinson's complex used as a high active hydrogenation catalyst. *J. Mol. Catal. A: Chem.* **1999**, *149*, 147.

(22) Quiroga, M. E.; Cagnola, E. A.; Liprandi, D. A.; L'Argentiére, P. C. Cyclohexene hydrogenation using Group VIII metal complexes catalysts in heterogeneous and homogeneous conditions. *J. Chem. Technol. Biotechnol.* **2001**, *76*, 215.

(23) L'Argentiére, P. C.; Cagnola, E. A.; Quiroga, M. E.; Liprandi, D. A. A Palladium tetra-coordinated complex as catalyst in the selective hydrogenation of 1-heptyne. *Appl. Catal. A: Gen.* **2002**, *226*, 253.

(24) Liprandi, D.; Quiroga, M.; Cagnola, E.; L'Argentière, P. A new more sulfur resistant rhodium complex as an alternative to the traditional Wilkinson's catalyst. *Ind. Eng. Chem. Res.* **2002**, *41*, 4906.

(25) Cagnola, E.; Liprandi, D.; Quiroga, M.; L'Argentiére, P. 1-heptyne semihydrogenation catalyzed by [PdCl$_2$(NH$_2$(CH$_2$)$_5$CH$_3$)$_2$]. *React. Kinet. Catal. Lett.* **2003**, *88*, 277.

(26) Cagnola, E. A.; Quiroga, M. E.; Liprandi D. A.; L'Argentiére, P. C. Immobilized Rh, Ru, Pd and Ni complexes as catalysts in the hydrogenation of cyclohexene. *Appl. Catal. A: Gen.* **2004**, *274*, 205.

(27) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed.; Interscience Publishers: New York, 1969; p 421.

(28) Anderson, S. N.; Basolo, F. Hydrated rhodium(III) chloride, chloroamminerhodium(III) salts, and a note on the recovery of rhodium wastes. *Inorg. Synth.* **1963**, *7*, 214.

(29) Vogel, A. I. A *Text Book of Quantitative Inorganic Analysis*; Longmans, Green and Co.: London, 1951.

(30) Livingstone, S. *The Chemistry of Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum, Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Eméleús, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973.

(31) Mallat, T.; Petrov, J.; Szabó, S.; Sztatisz, J. Palladium-Cobalt Catalysts: Phase Structure and Activity in Liquid-Phase Hydrogenations. *React. Kinet. Catal. Lett.* **1985**, *29*, 353.

(32) Borade, R.; Sayari, A.; Adnot, A.; Kaliaguine, S. Characterization of Acidity in ZSM-5 Zeolites: An X-ray Photoelectron and IR Spectroscopy Study. *J. Phys. Chem.* **1990**, *94*, 5989.

(33) Silverstein, R. M.; Clayton Basler, G.; Morril, T. C. In *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991.

(34) Holland, F. H.; Chapman, F. S. *Liquid Mixing and Processing in Stirred Tanks*; Reinhold: New York, 1976.

(35) Le Page, J. F. *Catalyse de Contact*; Editions Technip: Paris, 1978.

(36) NIST X-ray Photoelectron Spectroscopy Database. *NIST Standard Reference Database 20*, Version 3.4 (Web Version); National Institue of Standards and Technology: Washington, DC, 2003.

(37) Gates, B. C. *Catalytic Chemistry*; John Wiley & Sons: New York, 1992.

(38) Bailar, J. C. *Comprehensive Inorganic Chemistry*; New York, Vol. 3, 1975; p 1234.

(39) Nakamura, A.; Tsustsui, M. *Principles and applications of homogeneous catalysis*; John Wiley & Sons: New York, 1980.

(40) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; Oxford University Press: New York, 1994.