

Rhodium-diphosphine complex bound to activated carbon An effective catalyst for the hydroformylation of 1-octene

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Received 9 September 2003; received in revised form 9 September 2003; accepted 12 December 2003

Abstract

A rhodium(I) diphosphine complex has been anchored on an activated carbon by means of a covalent bond and then it has been tested as catalyst for the hydroformylation of 1-octene. The heterogenization procedure includes the functionalization of the carbon surface to create acid chloride groups where an esterification reaction with the hydroxyl end of a diphosphine ligand (HONP) can take place. Two strategies have been followed: route I: ligand anchorage followed by complex formation (using the $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ complex as precursor) and route II: synthesis of the rhodium diphosphine complex $[\text{Rh}(\text{HONP})(\text{COD})]\text{Cl}$ followed by anchorage on the functionalized carbon support. The solid samples, functionalized activated carbon and anchored complexes, have been characterized by XPS and ^{31}P NMR. The two synthetic routes render catalysts that are active, selective and stable enough to be used in consecutive catalytic runs. The catalyst prepared by route II shows an outstanding behaviour, being fully active and with almost constant selectivity to the linear aldehyde in four consecutive catalytic runs.

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Keywords: Immobilization; Covalent bond; Activated carbon; Hydroformylation; Rh complex

1. Introduction

The hydroformylation of olefins (known as the oxo process) is one of the most important industrial processes using transition metal complexes as homogeneous catalysts. To overcome the disadvantages of the homogeneous process, mainly related with the recovery of the metal complex from the reaction media, some alternatives to support the metal complexes are in use or under investigation [1–18]. With basis on the work of Arhancet et al. [5], dealing with supported aqueous-phase catalysts (SAPCs), two-phase catalysis has already achieved industrial-scale importance in hydroformylation [4]. However, to avoid solubility limitations and to exploit the advantages of heterogeneous catalysis, there is great interest in the development of so-called immobilized metal complex catalysts. These are transition metal complexes heterogenised on various supports by physical adsorption or chemical anchoring.

The main problems related with heterogenisation on solid supports are the leaching of the metal complex under reaction conditions and the decrease in catalytic activity with respect to the homogeneous process. Thus, for example, Balué and Bayón [12] reported that a rhodium thiolate binuclear catalyst supported on a cationic resin is much slower than the homogeneous catalyst with the same molecular structure. And more recently, Bryant and Kilner [17] found that the overall yield in the hydroformylation of 1-hexene is reduced by supporting rhodium catalysts in nafion, and many of the systems investigated suffer an important leaching process [17].

It must be remembered that leaching under hydroformylation conditions usually takes place by substitution of the π -bonding ligands (like PR_3 , dienes, etc.) by CO, with the formation of metal carbonyls that wash out easily from the support [1]. Because of that, a robust anchorage is required for supported complexes used as hydroformylation catalysts.

In a previous work [13], the complex $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ was heterogenized on activated carbons by ion exchange. The catalysts showed catalytic properties similar to those

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of the homogeneous complex in the first run, but leaching was close to 50%. With an oxidized support, the resistance against leaching was slightly improved but the induction time was higher. This anchorage was considered not effective enough because leaching of the complex was high, and the catalytic activity decreased dramatically in consecutive runs.

A new strategy is reported in this paper: the development of a system with the Rh complex anchored to the support by a covalent bond [14]. To achieve this goal, the carbon surface must be functionalized and a ligand with a suitable functional group has to be used. The procedure described in this work includes the formation of carboxylic acid groups followed by their transformation into acid chlorides. These are good nucleophilic groups where ligands containing the hydroxyl functionality can be fixed through an esterification reaction. This heterogenisation procedure resembles the one used to anchor complexes on the SiO₂ surface [19] and it is also related to the one reported by Pugin [20] and more recently by Stanger et al. [21]. In the case of activated carbon, Silva et al. [22] have functionalized the support with acid chloride groups and immobilised amine nickel complexes via an amide bond. The characterisation of these catalysts shows that the anchoring was successful, but no activity tests were reported [22].

In the present work, the heterogenised catalysts have been characterized by XPS and solid state ³¹P NMR and, what is essential in this kind of investigation, they have been tested under reaction conditions, specifically for the hydroformylation of 1-octene. The study of the catalytic properties includes the determination of total conversion and selectivity, and the analysis of the reutilization in consecutive catalytic runs.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Functionalization of the carbon support

A commercial activated carbon, GF-45 from NORIT, was used as support. This activated carbon, in pelletised form (about 0.5 mm \varnothing and 5 mm length), has a surface area of 1700 m²/g and the following pore-volume distribution: micropore ($\varnothing < 0.7$ nm) = 0.34 cm³/g, supermicropore (0.7 nm $< \varnothing < 2.0$ nm) = 0.50 cm³/g, mesopore (2.0 nm $< \varnothing < 50$ nm) = 0.45 cm³/g, and macropore (50 nm $< \varnothing$) = 0.40 cm³/g.

The support functionalization includes two steps: oxidation and chlorination. Oxidation was carried out by treatment with a solution of HNO₃ 35 wt.% (5 ml/g) at 80 °C until dryness. The oxidised carbon was extensively washed with deionised water until the total elimination of nitrates, and dried in oven at 100 °C overnight. With this treatment, a significant proportion of carboxylic groups are formed on the carbon surface [23]. The oxidised activated carbon is named GF-N. The chlorination step was performed with

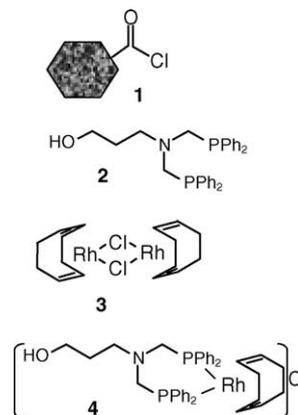


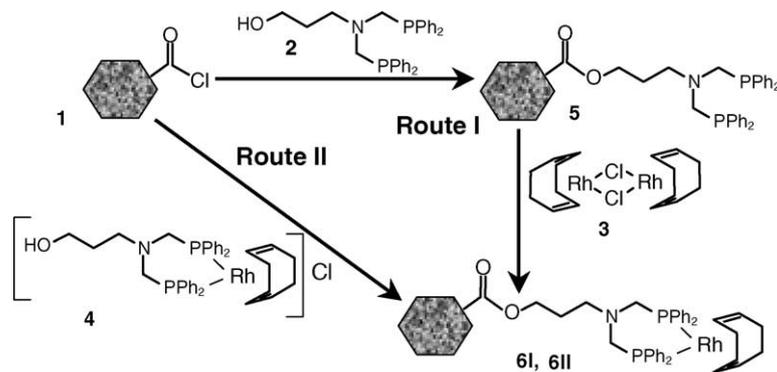
Plate 1. Schematic representation of some species involved in this work.

SOCl₂. About 1 g of carbon GF-N was then introduced in a Schlenk tube with 0.5 ml of SOCl₂ in 20 ml of degassed CH₂Cl₂ and treated at 80 °C under N₂ for 2 h. The sample was washed three times with degassed CH₂Cl₂ and dried under vacuum at 40 °C. The chlorinated activated carbon is named GF-Cl (**1**, see Plate 1).

2.1.2. Synthesis and characterization of the HONP ligand and the Rh diphosphine complex

The synthesis of the ligand HONP (**2**, Plate 1) was performed in a Schlenk system, with basis on the procedure described in the literature [6]. A mixture of formaldehyde (37 wt.% in water, 0.6 ml, 8.0 mmol) and diphenylphosphane (1.2 ml in 5 ml methanol, 6.8 mmol) was heated at 70 °C for 30 min under inert atmosphere. The reaction mixture was cooled to room temperature and treated with 0.25 ml of HO(CH₂)₂NH₂ (3.3 mmol). After 30 min, the solution was heated at 70 °C overnight, and then it was cooled down to room temperature. The product was concentrated and dried in vacuum for 6 h, resulting in a pale yellow oil-like substance. It was characterised by ¹H, ¹³C and ³¹P NMR [6,19]. ³¹P (300 MHz, CDCl₃): -27.2 ppm. ¹H NMR (300 MHz, CDCl₃): 1.58 (q, 2H, methylene, *J*_{H-H} = 5.9 Hz), 3.04 (t, 2H, -CH₂-NR₂, *J*_{H-H} = 6.0 Hz), 3.52 (t, 2H, -CH₂OH, *J*_{H-H} = 5.9 Hz), 3.67 (m, 4H, RN-(CH₂-PR₃)₂), 7.33 (m, 12H, phenyl), 7.45 (m, 8H, phenyl). ¹³C (300 MHz, CDCl₃): 28.4 (C-CH₂-C), 54.0 (N-CH₂-P, ¹*J*_{P-C} = 19.5 Hz), 58.4 (CH₂-N, ³*J*_{P-C} = 6.5 Hz), 61.1 (CH₂-OH), 128.2 (*o*-phenyl, ²*J*_{P-C} = 7.0 Hz), 132.6 (*m*-phenyl, ³*J*_{P-C} = 3.9 Hz), 132.9 (*p*-phenyl), 137.2 (P-C (phenyl), ¹*J*_{P-C} = 12.2 Hz). The NMR spectra also showed a small amount of HOCH₂P(Ph)₂ (³¹P peak: -10.5 ppm) and monophosphinated amine HO(CH₂)₃NH(CH₂P(C₆H₅)₂) (³¹P peak: -24.2 ppm).

The rhodium complex [Rh(HONP)(COD)]Cl (**4**) was synthesized inside the Schlenk apparatus as follows: 11.8 mg of complex [Rh(μ-Cl)(COD)]₂ (**3**) (abbreviated as Rh(COD)) (24 μmol) was added to a solution of 32.9 mg of the synthesized HONP ligand (**2**) in 20 ml MeOH (molar ratio 1:2). The mixture was stirred in N₂ at room temperature



Scheme 1. Synthetic routes to obtain the Rh complex covalently bounded to the activated carbon surface.

for 2 h. A dark-red solution, different from the pale-yellow solution of Rh(COD) (3), was obtained. The synthesized complex was characterized by ^{31}P and ^1H NMR [6,19]: ^{31}P (300 MHz, CDCl_3): 8.3 ppm. ^1H NMR (300 MHz, CDCl_3): 1.35 (2H, methylene), 2.12 (8H, methylene COD), 2.98 (2H, $-\text{CH}_2-\text{NR}_2$), 3.18 (2H, $-\text{CH}_2\text{OH}$), 3.63 (4H, $\text{RN}-(\text{CH}_2-\text{PR}_3)_2$), 7.06–7.70 (24H, phenyl and $\text{H}-\text{C}=\text{C}$ COD).

2.1.3. Anchorage on the carbon support

Heterogenised catalysts were prepared by the formation of a covalent bond, via an esterification reaction, between the acid chloride groups of the carbon surface and the $-\text{OH}$ functional group of ligand HONP (2). Scheme 1 shows the two different anchoring strategies followed:

- Route I: The ligand HONP (2) is bonded to the support GF-Cl (1) and later the diphosphine Rh complex is formed through reaction with Rh(COD) (3).
- Route II: The rhodium diphosphine complex $[\text{Rh}(\text{HONP})(\text{COD})]\text{Cl}$ (4), previously synthesized, is bonded to the support GF-Cl (1) through the HONP ligand (2).

The anchorage of ligand HONP on the carbon support (route I in Scheme 1) was carried out inside a Schlenk tube by adding 0.118 g of HONP ligand dissolved in degassed CH_2Cl_2 to 1 g of sample GF-Cl (1). The slurry was stirred and heated to reflux (at 70°C) under N_2 for 1 h. Afterwards, it was cooled to room temperature and dried at 70°C for 4 h under vacuum. The ligand grafted-support is named GF-ONP (5). To synthesize the supported Rh complex, about 1 g of the dried GF-ONP (5) support was added to a solution of Rh(COD) (3) in methanol of the appropriated concentration to obtain a catalyst with 1 wt.% Rh ($97.2 \mu\text{mol/g}$). The slurry was stirred under inert atmosphere at room temperature for 2 h. Then, the solution was removed with a syringe and the catalyst was dried inside the Schlenk tube ($T \sim 50^\circ\text{C}$). The catalyst thus prepared is named Rh(COD)/GF-ONP (6I).

The procedure used to anchor the complex $[\text{Rh}(\text{HONP})(\text{COD})]\text{Cl}$ (4) on GF-Cl (1) (route II, Scheme 1) is

similar to the one described above. In this case, a solution of the complex, in degassed methanol, with the appropriated concentration to obtain a catalyst with 1 wt.% Rh was employed. The catalyst prepared by route II is named Rh(ONP)/GF-Cl (6II).

2.2. Characterisation by XPS and solid state ^{31}P NMR

The XPS spectra were obtained with a VG-Microtech Multilab electron spectrometer, using Mg $\text{K}\alpha$ (1253.6 eV) radiation. The binding energy was adjusted by setting the C 1s transition at 284.6 eV. The accuracy of BE and KE values was ± 0.2 and ± 0.3 eV, respectively.

Analysis by solid state ^{31}P NMR was carried out in a Bruker 200 MHz equipment. Samples GF-ONP(5), Rh(COD)/GF-ONP (6I) and Rh(ONP)/GF-Cl (6II) were analysed by this technique.

2.3. Determination of Rh content

The rhodium content in fresh and used catalysts was determined using the method described in the literature [12]. It consists of the extraction of Rh from the catalyst with a hot concentrated solution of HCl and HNO_3 . The filtrate is further heated to dryness, treated with concentrated HCl, and heated again to dryness. The residue is dissolved in water and treated with a solution of SnCl_2 in HCl 2 M. The resulting solution is heated until a dark red complex is formed, and finally diluted with HCl 2 M to a total volume of 25 ml. The determination of the concentration of rhodium in the solution was performed by UV-Vis absorption at 475 nm.

2.4. Catalytic activity measurements

Catalytic activity experiments were run in a stainless steel stirred tank reactor. The hydroformylation of 1-octene was carried out at 80°C and a total pressure of 4 MPa (with a $\text{H}_2:\text{CO}$ ratio of 1:1) using a solution (10 ml) of 5 vol.% 1-octene in hexane (3 mmol) and 50 mg of the heterogeneous catalyst ($4.9 \mu\text{mol}_{\text{Rh}}$ for catalysts with 1 wt.% Rh). For the homogeneous reference test, the metal complex Rh(COD) (3) in a similar amount (in mole Rh) to that present in the

heterogeneous catalysts was dissolved in the liquid phase. The reaction was carried out for 7 h. Then, the reactor was depressurized and allowed to cool to room temperature. With the purpose of testing the reutilization of the catalyst, it was recovered from the reaction media by removing the solution with the aid of a syringe and washed three times with hexane (also by removing the solution with a syringe). Afterwards, a new catalytic run was performed. Catalytic activity and selectivity were determined by ^1H NMR spectroscopy of the resultant concentrate solution.

3. Results and discussion

3.1. XPS analysis

Table 1 shows the binding energies of Rh 3d_{5/2}, P 2p, N 1s, Cl 2p and O 1s in samples GF-45, GF-N, GF-Cl (1), GF-ONP (5), Rh(COD)/GF-ONP (6I) and Rh(ONP)/GF-Cl (6II). Table 2 includes the Rh, P, Cl, N and O atomic ratios referred to C.

The original activated carbon GF-45 contains organic and inorganic phosphorous. They are probably related with the carbon precursor material and the procedure used for the activation (with phosphoric acid). It contains, as well, organic nitrogen, chloride anions and oxygen, mainly as OH and C=O (signals (1) and (2), respectively, in Table 1).

As a consequence of the oxidising treatment with nitric acid (sample GF-N), organic nitrogen and chloride anions are removed, but inorganic nitrogen (as nitrate) is introduced. As shown in Table 2, phosphorous has been also partially removed by treatment with HNO₃, and oxygen groups have been extensively formed. The binding energies observed for oxygen (Table 1) shift to slightly higher values probably because new oxygen groups like carboxylic acids, esters, anhydrides or lactones have been formed [24].

Treatment with SOCl₂ (sample GF-Cl (1)) results in a substantial increase of organic chlorine (Tables 1 and 2). A decrease in the O/C ratio confirms the substitution of OH groups originally in GF-N by Cl in GF-Cl.

The analysis of sample GF-ONP (5) shows the expected increase in P/C and N/C ratios due to the ligand bonded to the carbon surface. The decrease in the Cl/C ratio is a consequence of the esterification reaction. It must be noted that the XPS analysis of sample GF-ONP (5) was conducted in an air exposed sample, and for that reason, the O/C ratio could be affected by the reaction of chlorine groups with air.

In the case of the catalyst Rh(COD)/GF-ONP (6I), the XPS results (Table 1) reveal that rhodium is Rh(I) but with a binding energy higher than in the pure Rh(COD) complex [13] (308.4 eV). According to the literature [25], it has been assigned to Rh bonded to phosphine, indicating that the expected anchored complex was formed. Chloride

Table 1
XPS data. Binding energies (in eV)

	GF-45	GF-N	GF-Cl	GF-ONP	Rh(COD)/GF-ONP	Rh(ONP)/GF-Cl
Rh	–	–	–	–	309.0	309.0
P						
Org	133.1	132.9	132.8	132.4	132.4	132.1
Inorg	134.7	134.0	134.1	133.6	133.6	133.6
N						
Org	398.6/400.6	–	400.0	399.7	399.6/401.3	400.0
Inorg	–	405.8	405.7	405.8	405.8	405.8
Cl						
Inorg	197.8	–	–	–	198.0	197.7
Org	–	–	199.8	199.9	199.9	199.8
O						
(1)	530.9	531.5	531.7	531.4	531.5	531.6
(2)	532.4	533.0	533.4	533.1	533.2	533.2

Table 2
XPS data. Atomic ratio

	GF-45	GF-N	GF-Cl	GF-ONP	Rh(COD)/GF-ONP	Rh(ONP)/GF-Cl
Rh/C	–	–	–	–	0.0048	0.0026
P/C	0.0118	0.0031	0.0033	0.0101	0.0116	0.0043
Cl/C	0.0025	–	0.0213	0.0103	0.0210	0.0100
N/C	0.0050	0.0204	0.0258	0.0263	0.0254	0.0232
O/C	0.1604	0.2432	0.1999	0.2361	0.2427	0.2456

introduced with the Rh(COD) complex is also detected (signal at about 198 eV) and, as a consequence, the ratio Cl/C increases (Table 2). This chloride must be adsorbed on the carbon surface.

For catalyst Rh(ONP)/GF-Cl (**6II**), very similar features to those indicated above have been found. The ratio Rh/C is lower in this case. This can be due in part to a lower amount of complex (0.72 wt.% Rh in sample Rh(ONP)/GF-Cl compared to 0.86 wt.% Rh in sample Rh(COD)/GF-ONP) and it can also be related to a deeper location of the complex in the carbon porosity. The higher value of the P/C ratio in sample Rh(COD)/GF-ONP is also expected because the amount of diphosphine ligand present in carbon GF-ONP is higher than the corresponding to the stoichiometry of the metal complex. In relation to the location of the Rh complex, it could be also considered that the presence of an excess of phosphine ligands on the carbon surface might hinder the penetration of the complex in the carbon porosity.

3.2. Solid state ^{31}P NMR analysis

The ^{31}P NMR spectra of sample GF-ONP (**5**) and also of catalyst Rh(COD)/GF-ONP (**6I**) reveal partial oxidation of the phosphine ($\delta = 31$ ppm) [18]. A second analysis carried on a GF-ONP sample, handled with care to avoid exposition to air and sealed under inert atmosphere for the analysis, reveals as well the oxidized form of the phosphine, meaning that the phosphine group of the ligand anchored to the support is not stable. It seems that oxidation is due to the interaction with the carbon support, maybe related to its extensive surface oxidation. On the other hand, in catalyst Rh(ONP)/GF-Cl (**6II**), the state of P ($\delta = 25$ ppm) corresponds to a phosphine bonded to the metal [18]. That is, when the ligand HONP forms the complex with rhodium, the phosphine group is stabilised against oxidation.

3.3. Catalytic activity

Fig. 1 shows the catalytic activity results obtained with catalysts Rh(COD)/GF-ONP (**6I**) and Rh(ONP)/GF-Cl (**6II**)

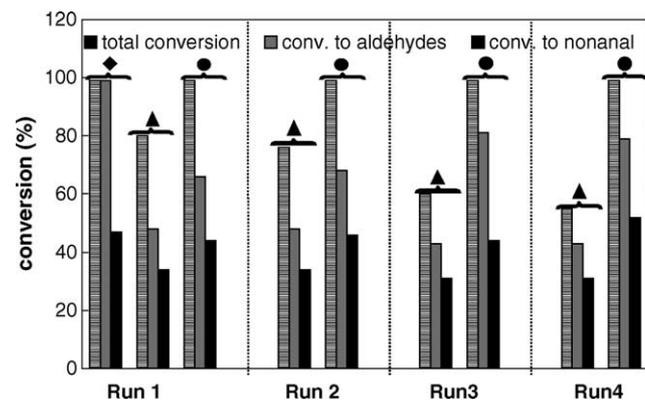


Fig. 1. Catalytic activity of catalysts: homogeneous (◆) Rh(COD) (**2**), (▲) Rh(COD)/GF-ONP (**6I**) and (●) Rh(ONP)/GF-Cl (**6II**).

in four consecutive catalytic runs. For comparative purposes, data corresponding to the Rh(COD) complex (**3**) in homogeneous phase have been also included. Results of the total conversion of 1-octene, the conversion to aldehydes (nonanal and 2-methyloctanal) and the conversion to the linear aldehyde (nonanal) are presented. The difference between the total conversion and conversion to aldehydes corresponds to the isomerisation products, mainly 2-octene.

In the first run, total conversion is very high for the three catalysts investigated. However, while the homogeneous Rh(COD) catalyst produces only the aldehydes, with the heterogenised catalysts a noticeable amount of 2-octene is obtained. Considering that the phosphine ligands are usually employed to decrease isomerization [1], it was not expected that complex [Rh(HONP)(COD)]Cl (**4**) would be more active than Rh(COD) for the isomerization reaction. This suggests that the anchorage of the complex could have some influence in the selectivity. The conversion to nonanal with catalysts Rh(COD) (homogeneous) and Rh(COD)/GF-ONP (**6I**) and Rh(ONP)/GF-Cl (**6II**) is 47.4, 33.9 and 44.0%, respectively (with L/B ratio: 0.9, 2.4 and 2.0, respectively). It means that although the heterogenised catalysts are less selective to aldehydes in front of isomerization, the conversion to the linear aldehyde is comparable to that obtained with the homogeneous catalyst.

The complex leaching expressed as percentage of Rh removed from the catalyst, after the four catalytic runs, for catalysts Rh(COD)/GF-ONP and Rh(ONP)/GF-Cl is 59 and 43%, respectively. After the first catalytic run, the resulting solution shows a red wine colour. Analysis by ^{31}P NMR of this solution reveals the presence of the diphosphine ligands in the solution. This confirms that part of the complex is in solution. After subsequent catalytic runs, the resulting solution is colourless and ^{31}P NMR analysis does not reveal the presence of phosphine. This observation can be interpreted considering that part of the complex is more loosely bound to the support and is leached in the first run. The rest of the complex is effectively anchored. The gradual loss of conversion found for catalyst Rh(COD)/GF-ONP (**6I**) in the four consecutive catalytic runs may be, then, related to a progressive deactivation of the supported complex.

The differences in catalytic activity between the two heterogenised catalysts can be related to the different nature of the -ONP ligand, since as revealed by ^{31}P NMR, phosphine is partially oxidised in sample Rh(COD)/GF-ONP (**6I**).

The most relevant results are those corresponding to runs 2–4, that is, on the reutilization of the heterogenised catalysts. Both catalysts show an acceptable conversion level and selectivity in four catalytic runs. With catalyst Rh(COD)/GF-ONP (**6I**), the conversion to aldehydes and the L/B ratio remain constant. The case of catalyst Rh(ONP)/GF-Cl (**6II**) is intriguing since it not only remains fully active, but the selectivity to aldehydes increases. The TO (turnover, $\text{mol}_{\text{aldehyde}}/\text{mol}_{\text{Rh}}$ corresponding to the total reaction time) of this catalyst in the consecutive runs

are: 566, 583, 694 and 677 (calculated without considering leaching) and the L/B ratio remains close to 2.

A comparison with literature on supported systems reveals that the catalytic performance of the catalysts studied in this work is similar or better than that shown in previously published papers. Thus, for example, Bourque et al. [18], using Rh-complexed dendrimers also obtained for the hydroformylation of octene a $L/B = 2$ ratio, but the total conversion (of 2 mmol substrate) is achieved after 22 h. Nozaki et al. [11] reported the behaviour of polymer immobilized chiral phosphine–phosphite–Rh(I) complexes for the hydroformylation of styrene and they found an interesting conversion in the first run (about 80%), but it is strongly reduced in the second one. Besides the L/B ratio is <1 . More recently, Wrzyszc et al. [16] prepared Rh complexes supported on a zinc aluminate spinel and found in the hydroformylation of 1-hexene a high conversion to aldehydes (96%) with $L/R = 3$. No leaching was detected although the catalysts were not tested in a second run. Finally, Fierro et al. [15a] in their work using Rh thiolate complexes anchored on phosphinated silica for the hydroformylation of 1-heptene, obtain a 100% conversion (TO (as defined above) of about 300) and a regioselectivity higher than 60% with L/B close to 2.5. Furthermore, the catalysts do show activity after seven consecutive cycles. This brief revision on the behaviour of supported Rh complexes for olefine hydroformylation allows to state that the results of the present work show a promising perspective for the use of carbon materials as support for the anchorage of metal complexes.

4. Conclusions

A rhodium diphosphine complex was effectively anchored by covalent bonding on an activated carbon. The complex is bound to the support via an esterification reaction between a hydroxyl group in the ligand and the acid-chloride-functionalised activated carbon surface. The two synthetic routes developed for the heterogenisation (I: ligand anchorage and then, complex synthesis and II: complex synthesis followed by anchorage) give catalysts with interesting catalytic properties, with the noteworthy feature of being usable in consecutive catalytic cycles. However, it must be pointed out that the anchoring procedure that first synthesizes the Rh diphosphine catalyst (**4**) and then bonds it to the carbon surface, is particularly attractive: the resulting catalyst is fully active in four consecutive catalytic cycles with a conversion to the linear aldehyde that increases with reuse.

Acknowledgements

The authors thank project PPQ2002-01025 of the Spanish Ministry of Science and Technology for financial support, and J.A.D.A. thanks the same organism for the Ph.D. grant.

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