

[Rh(μ -Cl)(COD)]₂ supported on activated carbons for the hydroformylation of 1-octene: effects of support surface chemistry and solvent

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Abstract

The [Rh(μ -Cl)(COD)]₂ complex has been heterogenised on activated carbon and used as catalysts for the hydroformylation of 1-octene. The objective is to achieve the effective anchorage of the complex on the carbon surface, keeping or improving the catalytic properties of the complex in the homogeneous process. The effects of surface chemistry of the activated carbon and the solvent used as reaction media (hexane, acetone or methanol) on the activity and selectivity to linear products (alcohols and aldehydes) and on the lixiviation of the complex from support, using different methods of catalyst recovering, are investigated. Gas adsorption, temperature-programmed desorption (TPD), immersion calorimetry and XPS techniques were used for characterisation. Catalytic activity at 353 K and a total pressure of 5 MPa (H₂:CO ratio 1:1) was carried out in a stainless steel stirred tank reactor. Obtained results show that the heterogenised complex shows a conversion level higher or similar to that of the homogeneous complex and with a higher selectivity to the linear products. Complex lixiviation depends on the support, the solvent and the method used to recover the catalyst from the reactor. The catalyst prepared with the functionalised activated carbon, where the anchorage takes place by ion-exchange, is more stable and active in further catalytic runs using the proper recovering method. © 2001 Elsevier Science B.V. All rights reserved.

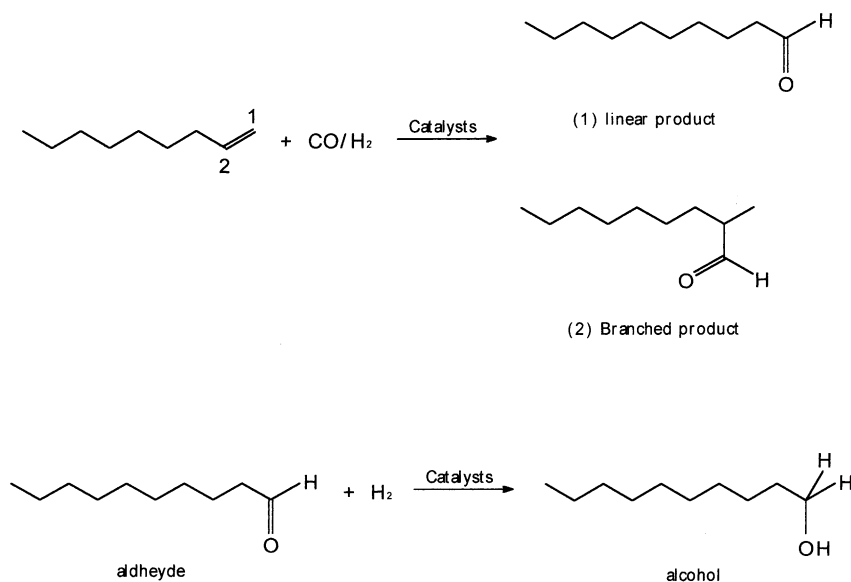
Keywords: Activated carbon; [Rh(μ -Cl)(COD)]₂; Heterogenisation; Hydroformylation; Solvents

1. Introduction

The hydroformylation (named also oxo process or carboxylation) of olefins is one of the most important industrial processes using transition metal complexes as homogeneous catalysts. Rhodium complexes are the most efficient catalysts for this reaction in terms of both activity and selectivity [1–3]. The products of hydroformylation can be aldehydes and/or alcohols,

in linear (n) or branched (i) forms, depending on the catalytic system. Scheme 1 shows these possibilities for the hydroformylation of 1-octene [4]. At industry, most of the aldehydes produced are further hydrogenated to alcohols or oxidised to carboxylic acids. The linear products are more desirable and long-chain alcohols are useful for many applications [1]. The main related industrial processes are in order of importance: the esterification of alcohols with phthalic anhydride to produce dialkyl phthalate plasticizers, that are primarily used for polyvinyl chloride plastics, production of detergents and surfactants, and the production of solvents, lubricants, and chemical intermediates [2].

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Scheme 1.

Some alternatives to the homogeneous reaction have been used and many other are under investigation. The main objective is to maintain the activity and selectivity of the homogeneous catalysis but facilitating the recovery of the metal complex from the reaction media, that supposes an important economical advantage [5,6].

At industrial scale, water-soluble catalysts (named supported liquid-phase catalysts, SLPCs) have been applied in the hydroformylation of propene, but this approach is less efficient for higher molecular weight alkenes [7]. This process uses two phases, one aqueous phase containing the catalyst and the water-soluble promoter (water is used as “catalyst support”) and the organic phases consisting of the reactant and products (Kuntz, 1987). The process developed by Mitsubishi for the manufacture of higher aldehydes and alcohols, like nonanal (from 1-octene), using rhodium catalysts is highly complex and needs a final distillation (Onoda, 1993). Many studies at laboratory scale used this type of systems for hydroformylation as an alternative to the homogeneous reaction [7–10].

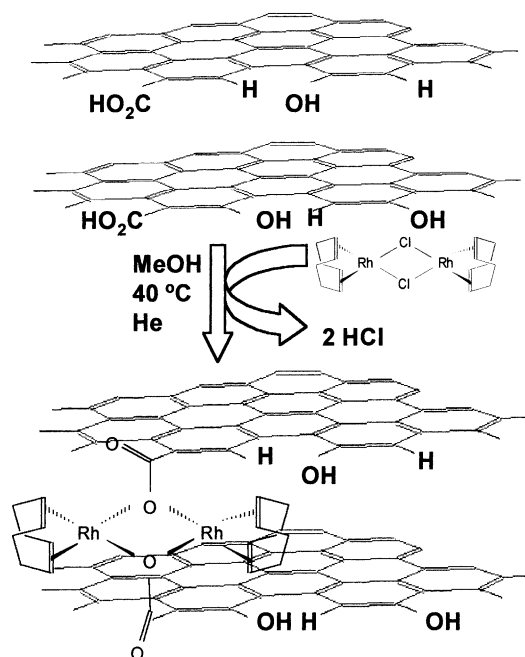
An interesting system was developed by Arhancet et al. [11] supporting water-soluble catalysts (SLPCs) on a hydrophilic support, like silica or aluminiumphosphate (in this case, they are named supported

aqueous-phase catalysts, SAPCs). These catalysts consist of a water-soluble complex dissolved in a film of water which is supported on a high surface area hydrophilic solid.

Another alternative consists of the development of different procedures for the heterogenisation of metal complexes on a solid support. To enhance the anchorage, support functionalisation (using phosphine, amine, silanol or sulphur groups) [12–15], and ion-exchange processes (with ion-exchange resins, clays, zeolites, etc. as supports) have been used [5,16–18]. The main problems related with the heterogenisation on solid supports are the lixiviation of the metal complex and the decrease in activity. Lixiviation under hydroformylation conditions usually takes place by substitution of the π -bonding ligands (like PR_3 , dienes, etc.) by CO, forming carbonyls that wash out easily from the support [4,5].

The $[\text{Rh}(\mu\text{-Cl})(\text{COD})_2]$ complex is a well-known, air stable, active catalyst for the hydroformylation of olefins [7]. It has been used in homogeneous phase and also supported on clay materials by ion-exchange [19] with the objective of increasing the regioselectivity to linear products.

The present paper deals with the heterogenisation of the complex $[\text{Rh}(\mu\text{-Cl})(\text{COD})_2]$ (named here



Scheme 2.

Rh(COD)) on activated carbon and the study of its catalytic properties (activity and selectivity). The main objective is to improve the anchorage of the Rh complex under reaction conditions in order to obtain a stable heterogeneised complex which shows a good conversion and selectivity to the linear products. Activated carbon has been selected as support, because it has a large surface area and the surface chemistry can be modified [20]. Attention is focused on the effect of the support surface chemistry on the anchorage of the complex by ion-exchange. To favour the ion-exchange, the carbon surface has been oxidised to create surface oxygen complexes [21]. The expected ion-exchange process is presented in Scheme 2.

The influence of solvents, used as reaction media, on the activity and selectivity of the hydroformylation reaction is well known [2,22,23]. The use of alcohols (ethanol or methanol) favours the direct formation of alcohol products, while the use of acetone or non-polar solvents favours the formation of aldehyde products. In this work, the hydroformylation of 1-octene was studied using three different solvents (methanol, acetone and hexane). The effect of the support/solvent interaction in the catalytic performance and in the lixiviation of the heterogeneised rhodium complex has been also investigated. Besides, the recovery of the catalyst for further uses has been analysed.

The final objective of the study is to find the catalytic system (heterogeneised catalyst and solvent) for which the best relation between good catalytic properties and low complex lixiviation is obtained.

2. Experimental

2.1. Preparation of samples

The supports used were a commercial activated carbon ROX-0.8 (from NORIT), and carbon ROX-N prepared from ROX-0.8 by oxidation with a solution of HNO₃ 35 wt.% at 80°C until dryness [24].

The heterogeneisation process was carried using a methanol solution of the complex and contacting with the activated carbon at room temperature under He atmosphere. The solution contained the amount of the Rh(COD) complex equivalent to 1 wt.% Rh in the heterogeneised catalysts (named Rh/ROX-N and Rh/ROX-0.8). Finally, the heterogeneised samples were filtered and dried at 373 K in air atmosphere. The adsorption of the metal complex on the carbon surface was followed by measuring the variation in the conductivity of the solution as HCl was being formed (see Scheme 2). With appropriated calibrations and a blank experiment with the support, conductivity measurements allowed the quantification of the exchanged complex.

2.2. Characterisation of samples

The activated carbons ROX-N and ROX-0.8 were characterised in a previous work [25]. The textural properties (surface area and pore volume) were obtained from N₂ and CO₂ adsorption isotherms at 77 and 273 K, respectively. The use of both adsorptives (N₂ and CO₂) allows the estimation of the pore volume distribution of pores with diameter up to about 7.5 nm [26]. TPD (temperature-programmed desorption) experiments were used to study the carbon surface chemistry by analysing the evolution of CO and CO₂ originated from the decomposition of oxygen groups present on the carbon surface [21]. The experiments were carried out heating the samples

in a He flow (60 ml/min) at 20 K/min up to 1173 K. Gases were analysed with a mass spectrometer (VG Quadrupoles)

The interaction of the different solvents used (hexane, acetone and methanol) with the supports was analysed by measuring enthalpies of immersion. The experiments were done in a Tian-Calvet type calorimeter (C80D, Setaram) with 0.1 g of degassed samples and 7 ml of liquid solvent at 303 K. The experimental procedure is well described in the literature [27].

To study the location of the Rh complex on the carbon surface, the heterogenised samples were also characterised by gas adsorption (N_2 at 77 K and CO_2 at 273 K). By comparison with the textural properties of supports, the location of the complex molecules in a certain range of pores can be suggested [25].

The rhodium content in fresh and used catalysts was measured using the method described in the literature [14]. It consists of the extraction of Rh from the catalysts 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 was dissolved in water and treated with a solution of $SnCl_2$ in HCl 2 M. The resulting solution was heated until formation of a dark red complex, and finally diluted to a total volume of 25 ml with HCl 2 M. The determination of Rh concentration in the solution was performed by UV–VIS absorption at 475 nm.

XPS was used to know the electronic state of rhodium and the atomic ratio Rh/Cl in the heterogenised samples. The XPS spectra have been obtained with a VG-Microtech Multilab electron spectrometer, using the Mg $K\alpha$ (1253.6 eV) radiation of twin anode in the constant analyser energy mode with pass energy of 50 eV. Pressure of the analysis chamber was maintained at 5×10^{-10} mbar. 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. The BE and KE values were obtained using the Peak-fit Programme implemented in the control software of the spectrometer.

2.3. Hydroformylation experiments

Catalytic activity was determined in a 300 ml stainless steel stirred tank reactor (made by Autoclave Engineers) operated at 353 K and with a stirring velocity

of 600 rpm. The hydroformylation of 1-octene was carried out at a total pressure of 5 MPa (with $H_2:CO$ ratio of 1:1) in a solution of 5 vol.% of the olefin in the different solvents (100 ml). In all cases, 0.1 g of heterogeneous catalyst was used. In the homogeneous experiments, a similar amount of the metal complex present in the heterogeneous tests was dissolved in the liquid phase. The hydroformylation reaction was carried out for 7 h. Reactants and products were chromatographically analysed using a HP-6890 equipment with a FID detector and a HP-1 capillary column.

2.4. Study of lixiviation

The lixiviation of the anchored complex was analysed by measuring the Rh content in the fresh and used catalysts.

After reaction, two procedures were used to recover the catalyst: (A) pressure release at the reaction temperature and filtering in air to remove the solid catalyst; (B) replacement of the reaction atmosphere by He (keeping the pressure) and cooling down the reactor to room temperature under stirring; then successive washing of the catalyst with the solvent, preventing the contact with air.

In addition, the specific effect of the solvent in the lixiviation was measured with the following experiment. The heterogenised sample and 100 ml of the reactant solution with the selected solvent were introduced in the tank reactor. The system was pressurised to 5 MPa with He and the temperature was raised to 80°C. In this way, the sample was submitted to conditions similar to those of reaction but avoiding the presence of H_2 and CO. In this experiment, the system was maintained under the mentioned conditions for 24 h. Afterwards, the Rh content in the catalyst was measured.

3. Results

3.1. Characterisation of heterogenised samples

The Rh content measured in the heterogenised samples is very close to 1 wt.%, indicating that the entire complex in the solution has been adsorbed on the carbon surface.

Table 1
Porosity of supports and catalysts and surface chemistry of supports

Sample	Porosity			Temperature-programmed desorption ($\mu\text{mol/g}$)	
	S_{BET} (m^2/g)	V_{m}^{a} (cm^3/g)	V_{sm}^{b} (cm^3/g)	CO	CO ₂
ROX-0.8	934	0.365	0.093	88	168
Rh/ROX-0.8	888	0.338	0.068	–	–
ROX-N	958	0.399	0.065	1485	638
Rh/ROX-N	792	0.272	0.077	–	–

^a Micropore volume ($\text{\AA} < 0.7 \text{ nm}$).

^b Supermicropore volume ($0.7 < \text{\AA} < 2 \text{ nm}$).

Table 1 shows the estimated specific surface area and pore volume data of supports and heterogenised samples. As can be observed, both supports show similar specific surface area and pore size distribution. A comparison of the textural properties of the heterogenised sample and the corresponding support shows that, depending on the carbon, the complex is located in a different range of pores. The noticeable lower micropore volume of sample Rh/ROX-N compared to that of support ROX-N indicates that in this carbon, the complex is mainly located in the very narrow pores. With the heterogenised sample Rh/ROX-0.8, both micro- and supermicropore volumes slightly de-

crease. It means that in this case, the complex is probably more externally located.

The amount of surface oxygen groups of supports ROX-N and ROX-0.8, estimated by the CO and CO₂ evolved in TPD experiments (Table 1), are in accordance with previous results [24,28]. These data show that the oxidising treatment with HNO₃ produces a large amount of surface oxygen complexes, with a large proportion of carboxylic-type groups that decompose to give CO₂ under a heat treatment [28].

As indicated in Section 2, the adsorption of the Rh complex on the carbon support has been followed by conductivity. The method is based on the variation of

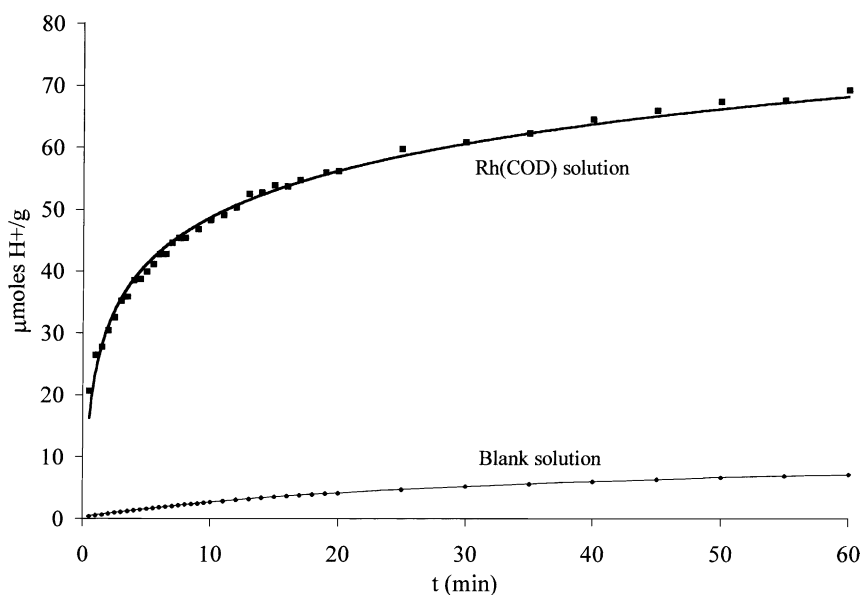


Fig. 1. Variation of the solution conductivity during the heterogenisation of the Rh(COD) complex on support ROX-N and blank experiment with the support.

Table 2
Calculated percentage of Rh exchanged and XPS data

Sample	Rh exchanged (%)	Binding energy (eV)		Rh/Cl ratio
		Rh 3d _{5/2}	Cl 2p	
Rh(COD)	–	308.34	198.58	0.89
Rh/ROX-0.8	6.7	308.6	198.2	0.84
Rh/ROX-N	63.6	309.5	198.2	0.92

the conductivity of the solution with the presence of H⁺ and Cl⁻ ions (H⁺ principally, due to the higher conductivity presented in solutions [29]) which originate from the carbon surface and the complex, respectively. Fig. 1 shows, as an example, the variation of conductivity with time during the heterogeneisation process of the Rh(COD) complex in methanol solution on ROX-N and the blank experiment with the support, using methanol as liquid phase. Results for the heterogeneisation on carbon ROX-0.8 are very similar to those corresponding to the blank. The calculations based on the conductivity data, and considering that the ion-exchange takes place with the stoichiometry shown in Scheme 2, give the percentage of complex exchanged included in Table 2. The extent of exchange is about 10 times larger in the oxidised carbon than in the original one. These data suggest that on ROX-N, the complex is mainly anchored by ion-exchange, while on the unfunctionalised support, ROX-0.8, the complex is retained by an adsorption mechanism.

XPS results are also shown in Table 2. The binding energy data show that the electronic state of Rh in Rh/ROX-0.8 sample is quite similar to that in the original complex. In sample Rh/ROX-N, however, the binding energy of Rh 3d is displaced to higher values, which correspond to Rh(I) bonded to oxygen [30]. There is no variation in the binding energy of chlorine, and the Rh/Cl ratio in the heterogeneised samples is similar to that in the pure complex.

3.2. Catalytic activity

Figs. 2–4 show the conversion versus time curves for the homogeneous catalyst and the two heterogeneised samples using hexane, acetone and methanol, respectively, as reaction media. Each figure includes the conversion to linear and branched forms of the main product (aldehyde or alcohol). In all cases, it

is observed that linear products are formed earlier, but conversion levels-off at a certain time. This is due to the isomerisation of 1-octene to internal double bounds [31]. Conversion to branched products, however, follows an increasing trend with time.

In hexane and acetone, only aldehydes are produced, while in methanol, alcohols are the main products. This is in agreement with previously reported results [2]. The use of methanol as solvent is interesting because, in general, alcohols are regarded as more desirable products.

In hexane (Fig. 2), the three catalysts behave in a similar way but at different rates. After 7 h reaction time, conversion is high and similar for the homogeneous and the Rh/ROX-0.8 catalyst, and lower for sample Rh/ROX-N. With Rh/ROX-0.8, the process at the beginning of experiment is faster than with the homogeneous catalyst, while with the Rh/ROX-N it is slower with a clear delay of about 0.5 h.

In acetone (Fig. 3), the Rh/ROX-0.8 and the homogeneous catalysts show quite similar behaviour, with an induction time close to 0.5 h, while conversion on Rh/ROX-N is noticeably delayed (about 2 h). Furthermore, in this last case the reaction is slower.

In methanol (Fig. 4), alcohols are main products (selectivity above 90%) and the three catalysts behave more similarly. For the three catalysts, there is a clear difference between the rate of formation of linear and branched products. Compared with the reaction in other solvents, conversion to linear products is always higher. Something to remark is that conversion to the linear alcohol is lower with the homogeneous catalyst than with the heterogeneous samples, while conversion to the branched alcohol is similar in the three cases.

Table 3 summarises the results of activity and selectivity to hydroformylation products, without considering the isomerisation products. The included data are the conversion (in %) at 7 and 2 h, selectivity to

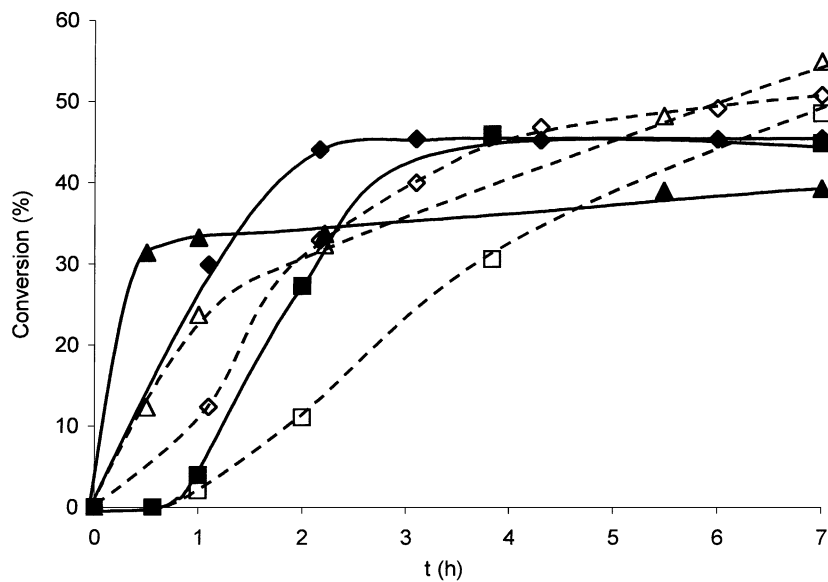


Fig. 2. Conversion vs. time in hexane as reaction media. Circle: homogeneous Rh(COD); square: Rh/ROX-N; triangle: Rh/ROX-0.8. Full symbols for the linear product and empty symbols for the branched ones.

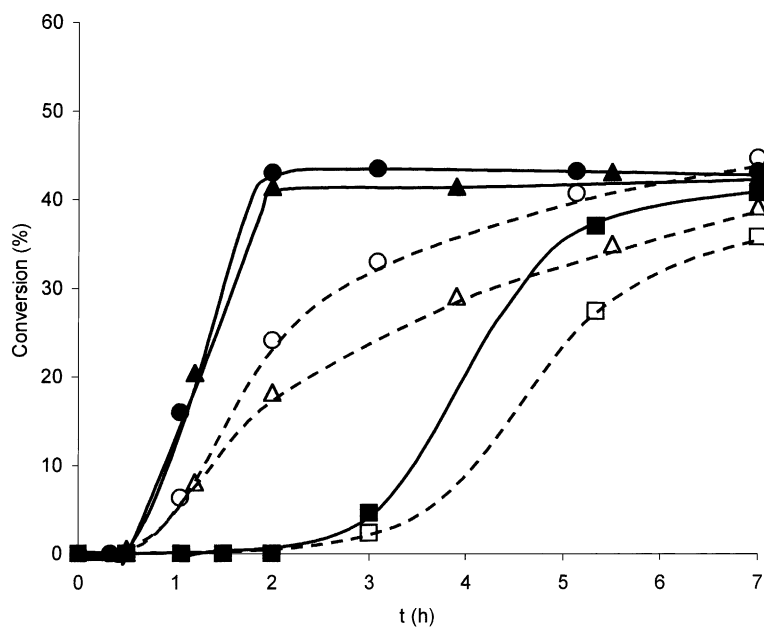


Fig. 3. Conversion vs. time in acetone as reaction media. Circle: homogeneous Rh(COD); square: Rh/ROX-N; triangle: Rh/ROX-0.8. Full symbols for the linear product and empty symbols for the branched ones.

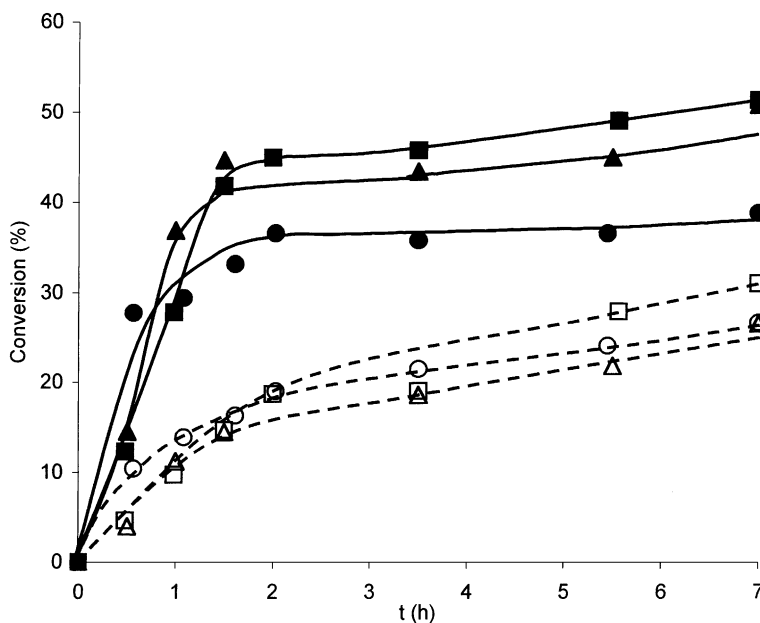


Fig. 4. Conversion vs. time in methanol as reaction media. Circle: homogeneous Rh(COD); square: Rh/ROX-N; triangle: Rh/ROX-0.8. Full symbols for the linear product and empty symbols for the branched ones.

aldehydes or alcohols (at 2 h), and the corresponding selectivity to linear products, expressed as n/i (linear/branched) ratio. At 2 h, the catalysts present good conversion to the linear products with high n/i ratio.

Total conversion after 7 h reaction time is high in all cases (between 65 and 96%), but some differences are observed depending on the solvent and the catalysts used. At 2 h, the activity and the selectivity also depend

Table 3
Catalytic activity, selectivity and complex lixiviation

Sample	Solvent	Conversion ^a (%)		Aldehydes		Alcohols		Rh loss (R) ^c (%)	Rh loss (S) ^d (%)
		At 7 h	At 2 h	Selectivity ^{a,b} (%)	n/i^b	Selectivity ^{a,b} (%)	n/i^b		
Rh(COD)	Hexane	96	77	100	1.34	0	–	–	–
	Acetone	88	67	100	1.78	0	–	–	–
	Methanol	65	55	0	–	100	1.92	–	–
Rh/ROX-0.8	Hexane	95	76	100	1.04	0	–	58	67
	Acetone	82	59	100	2.27	0	–	83	60
	Methanol	80	65	9	0.35	91	3.08	83	55
Rh/ROX-N	Hexane	93	38	100	2.45	0	–	48 (13) ^e	0
	Acetone	76	0	0	–	0	–	83	28
	Methanol	84	64	0	–	100	2.4	56	0

^a Conversions and selectivity expressed relative to hydroformylation products, without considering the isomerisation products.

^b Results at 2 h reaction time; using the recovering method (A): filtered in hot and dry air.

^c After 7 h of reaction time; using the recovering method (A): filtered in hot and dry air.

^d After 24 h under conditions similar to those of reaction but without H₂ and CO.

^e Using method (B) for recovery.

on the catalytic system. These differences must be related to the state of the complex in the different catalysts and to the interaction of the solvents with the carbon support. In general, it is found that the n/i ratio at 2 h is higher for the heterogenised samples than for the homogeneous catalyst.

In hexane, at 2 h reaction time, although with a lower conversion, the catalyst Rh/ROX-N shows the highest selectivity to the linear product. With the homogeneous complex, an intermediate value is found and catalyst Rh/ROX-0.8 shows the lowest n/i ratio. However, in this last case, it must be considered that the optimum n/i ratio was reached about 1.5 h earlier.

At 2 h of reaction in acetone, the homogeneous catalyst presents slightly higher conversion but lower selectivity to the linear aldehyde (n/i ratio) than catalyst Rh/ROX-0.8. As shown in Fig. 3, catalyst Rh/ROX-N needs more than 2 h to start the reaction.

The catalytic results obtained using methanol as solvent are qualitatively different from those described before for the other solvents. Conversions with the heterogenised samples are higher than those with the homogeneous Rh(COD) complex, and the selectivity to the linear alcohol is also higher. Sample Rh/ROX-0.8 presents a production of aldehydes of around 9%, mainly in the branched form (Table 3). This sample also presents the highest selectivity to the linear alcohol.

3.3. Lixiviation and interaction of the solvents with supports and heterogenised samples

Using process (A) for recovering the catalyst, after 7 h reaction time, the heterogenised samples show a certain degree of complex leaching. The remaining Rh has been determined and the lixiviation has been expressed as percentage of Rh removed from the carbon. These data are included in Table 3. As can be observed, the lixiviation of the complex under reaction conditions varies between 48 and 83% depending on the sample and the solvent. In order to analyse the effect of the solvent itself in the lixiviation process, the heterogenised samples have been kept in conditions similar to those of reaction, but without presence of H_2 and CO for 24 h (see Section 2.4), and the remaining Rh has been determined. Results have been also expressed as Rh loss (in %), and they are included in Table 3 (Rh loss (S)).

Table 4

Heat of adsorption measurements by immersion calorimetry of different solvents in the two carbon supports

	Heat of adsorption (J/g)		
	Hexane	Acetone	Methanol
ROX-0.8	155.9	129.2	122.2
ROX-N	136.5	149.4	142.1

Comparing data in columns Rh loss (R) and Rh loss (S) of Table 3, it can be observed that the effect of the solvent in lixiviation is much more pronounced in sample Rh/ROX-0.8 for which, as indicated above, the complex is only physically adsorbed. With this support, the lixiviation of the rhodium complex is higher both by effect of the solvent and under reaction conditions. The low lixiviation found for catalyst Rh/ROX-N must be related to the surface chemistry of the support that has a noticeable effect on the anchorage of the complex.

Results of immersion calorimetry give also information about the interaction of the different solvents used with the carbon supports (Table 4). In general terms, the results reflect that polar/polar and non-polar/non-polar (solvent/support) interactions are favoured. For example, a non-polar solvent, like hexane, shows the highest heat of adsorption with the unfunctionalised ROX-0.8 carbon that has a low surface polarity. Analogously, the more polar solvent, methanol, displays with carbon ROX-0.8 the lowest adsorption heat. For acetone, similar to methanol in the dielectric constant, similar results are found.

In the case of carbon ROX-N, with a large amount of surface oxygen complexes, and as a consequence a more polar surface, the tendency in the heats of adsorption is more or less the reverse of the above mentioned (see Table 4).

Comparing data of Rh loss (S) in Table 3 with the heats of adsorption (Table 4), some relation between them is observed. Using ROX-0.8 as support, the Rh loss has a direct relationship with the interaction between solvent and support. On the other hand, for the sample Rh/ROX-N, lixiviation only occurs when acetone is used as solvent; this solvent is the one that presents the highest heat of adsorption in the ROX-N carbon.

Due to experimental limitations, some authors [14,19] have to cool down the autoclave before to

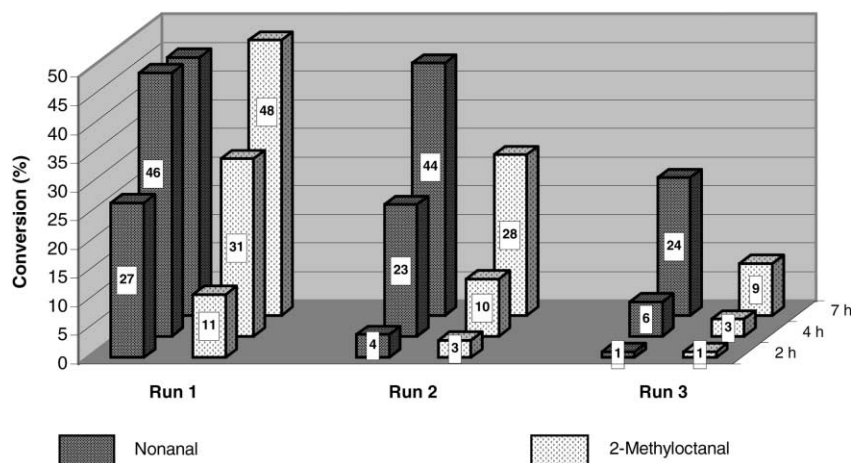


Fig. 5. Product distribution (nonanal and 2-methyloctanal) at 2, 4 and 7 h of reaction in three consecutive runs (using hexane as solvent) for Rh/ROX-N catalyst recovered by method (B).

analyse the reaction products and to recover catalyst after catalytic test. In those cases, lower lixiviation of the complex from the support is observed in comparison to our results. For that reason, the method to recover the catalyst after the reaction in hexane was modified for sample Rh/ROX-N using method (B) (described in Section 2). The Rh loss using this method, included in Table 3, is considerably lower than for method (A) of recovering.

3.4. Catalyst reutilisation

Catalyst Rh/ROX-N, used in hexane and methanol as reaction media and recovered by method (A), shows a lixiviation close to 50%. However, the samples were not active in further catalytic runs.

Catalyst Rh/ROX-N used in hexane and recovered by method (B) was found to be active in three further reaction runs. Fig. 5 presents the product distribution at 2, 4 and 7 h of reaction in the three consecutive cycles. At 2 h of reaction, there is an important decrease in activity during the second cycle. However, the differences became smaller with time and after 7 h reaction, only the production of the branched product (2-methyloctanal) is reduced with a considerable increase in selectivity to the linear product (nonanal). A third cycle was conducted with the same catalyst, the reaction became slower, at 7 h the conversion went down as can be observed in Fig. 5. It is important to

point out that the catalyst was not treated for reactivation after each cycle. This point should be studied more deeply in the future.

4. Discussion

In the heterogenisation process, the rhodium complex contained in the impregnating solution is completely adsorbed on the two carbons. However, the variations in the conductivity of the solution during impregnation indicate that the anchorage mechanism is different in each case. With the functionalised support, ROX-N, a high degree of ion-exchange is achieved, while with the original carbon, ROX-0.8, the ion-exchange hardly occurs and the rhodium complex must be physisorbed on the carbon surface (Table 2). This is consistent with the results of Rh loss in the solvent (S). The complex is washed to large extent by all the solvents in catalyst Rh/ROX-0.8, while with Rh/ROX-N, acetone is the only solvent that produces lixiviation ($\text{Rh loss (S)} = 28\%$). The amount of Rh exchanged in sample Rh/ROX-N is about 63% (see Table 2), that is, about 37% of Rh is weakly adsorbed. These results suggest that the complex lixiviated in acetone is mainly the one physically adsorbed. Acetone interacts better than the other solvents with the ROX-N carbon and is able to remove most of the physically adsorbed complex.

In addition, for sample Rh/ROX-0.8, a reverse relationship between the heat of adsorption of the different solvents on the activated carbons and the complex lixiviation by solvent effect (Rh loss (S)) has been found (Tables 3 and 4). This relationship can be explained because a better contact between solvent and support may disfavour the interaction complex/support and lixiviation is enhanced.

XPS results (Table 2) show that in sample Rh/ROX-N, the electronic density on Rh atoms has changed to lower values (like those in Rh bonded to oxygen atoms in its first coordination sphere). In sample Rh/ROX-0.8, however, the electronic state of Rh is quite similar to that of the unsupported complex. These results are in accordance with the differences in the anchorage of the complex on the two different supports derived by conductivity measurements and with the expected anchorage model (see Scheme 2). In this model, the exchanged Cl^- anion was supposed to be removed from the catalyst, and accordingly a Rh/Cl ratio in the heterogeneised sample higher than 1 was expected. XPS results show, however, a Rh/Cl atomic ratio close to 1. Two possible explanations are suggested: (1) the Cl^- exchanged is strongly physisorbed on the activated carbon surface and XPS technique cannot distinguish the different states of the Cl^- anion, and (2) the dimeric complex is divided in monomers and the oxygen surface group is introduced as a ligand, without substitution of chlorine. In principle, we cannot distinguish between these two possibilities, but in both cases, the exchange with the surface implies delivery of H^+ ions to the solution, and the increase of the concentration of H^+ in the solution is clear from the conductivity measurements.

The catalytic activity results show that the solvent used has a marked effect on the selectivity to aldehydes or alcohols and to the linear or branched products (Table 3). In all the cases, the formation of linear products is faster (Figs. 2–4). This can be due to the higher steric impediment for the insertion of CO in the second C atom of the 1-octene chain compared to insertion in the first C atom [32]. However, formation of linear products (n) levels-off at a conversion value that depends on the solvent and the type of the catalyst (heterogeneous or homogeneous) (Figs. 2–4). On the other hand, the formation of branched products (i) increases continuously with time. This phenomenon can be explained considering that rhodium complexes

are active catalysts for the isomerisation of double bonds [31], and this can occur as side reaction. To decrease the isomerisation reaction, phosphines or diphosphines are usually used as ligands [31]. This effect will be studied in the future.

In hexane, the important differences between the behaviour of the two heterogeneised samples can be related to the different interactions of the solvent with the two carbon supports. The heat of adsorption of hexane on ROX-0.8 is much higher (Table 4), which means a better contact between the carbon and the solvent. In accordance with a lower interaction between hexane and the ROX-N carbon, conversion on Rh/ROX-N is delayed by about 0.5 h (see Fig. 2). This can be considered as the activation time required for an effective contact between reactants (in solution) and the catalyst that is located in the very narrow pores.

In acetone, with the Rh/ROX-N catalyst, an important delay of about 2 h at the beginning of the reaction is observed, and conversion increases more slowly than in the other solvents. Complex lixiviation is noticeable higher than in hexane, being for both supports about 83%. The high degree of lixiviation found suggests that the reaction in acetone takes place mainly in the homogeneous phase. Differences between the behaviour of samples Rh/ROX-0.8 and Rh/ROX-N can be related with the higher stability of the catalyst Rh/ROX-N (stronger anchorage), and the more internal location of the complex in the support (Table 1) that makes the complex to need some time to wash out and start the reaction. Results in acetone can be considered worse than in hexane because of the higher lixiviation and the lower conversion.

Using methanol, the selective production of alcohols by reduction of aldehydes (step 2 of Scheme 1) is observed [2,22]. Table 3 shows that at 2 h, selectivity to alcohols is 100% in homogeneous case and with the Rh/ROX-N catalyst, while with Rh/ROX-0.8 it is around 90% (but at larger reaction time aldehydes are not produced). It should be noted that in methanol, the production of traces of more internal branched alcohols is found at the end of the reaction. This is due to the hydroformylation of isomerised olefins (on the third and fourth C atom of the 1-octene chain). The isomerisation reaction is considered to be the main reason for the levelling-off in the conversion to linear products. As shown in Fig. 4, the conversion to linear alcohols in the heterogeneised samples is higher than

in the homogeneous catalyst. Rh(COD) exchanged clays produced also higher conversion than the homogeneous catalyst in the hydroformylation of vinylsilanes [19]. Data in Table 3 also show that the n/i ratio is noticeable higher when the supported samples are used.

In general, the activated carbon heterogenised catalysts show better catalytic properties than the unsupported complex. For a similar conversion level, a higher selectivity to linear product is observed. This better selectivity is probably due to the increase of steric impediments for the carboxylation on the second C atom of the 1-octene chain (see Scheme 1) when the complex is supported on activated carbons.

The different catalytic behaviours (reaction rate and selectivity) of the heterogeneous catalysts compared to the homogeneous catalyst indicates that although some lixiviation occurs, the reaction is produced not only in the homogeneous phase but also by the heterogenised complexes.

On the other hand, regarding the properties of the carbon supports, the heterogenised catalysts are more resistant to lixiviation when prepared with the functionalised activated carbon. It can be concluded that when the complex is supported by ion-exchange, lixiviation is mainly produced by formation of carbonyl intermediates under reaction conditions. But the catalyst is stable to the effect of solvents.

Results of Rh loss (S) in Table 3 show that in He atmosphere, the complex did not leach using sample Rh/ROX-N in hexane or methanol. Based on this, method (B) of catalyst recovery has been designed. After reaction, the reactor is purged with He to make possible the readsorption of the complex on support. The temperature is decreased, in continuous stirring, to favour the adsorption process. This is a consequence of the following reasons: (1) in typical adsorption mechanism the amount adsorbed is in reverse relationship with temperature; (2) the catalyst preparation (impregnation) was made at 40°C in continuous stirring and He atmosphere, and using this method the complex was totally adsorbed after 1 h (see Sections 2.1 and 3.1). Sample Rh/ROX-N in hexane has shown the lowest complex lixiviation, and it was studied using both recovering methods. Results suggest that the complex is leached under reaction conditions, but it could be readsorbed in a He atmosphere. In this way, the catalyst can be re-

covered for further uses. This is in agreement with the results of Valli and Alper [19] for Rh(COD) exchanged on clays and with Balúe and Bayón [14] using Rh(COD) derivatives exchanged on ion-exchange resins.

The complete deactivation of Rh/ROX-N recovered by method (A), even though 50% of the Rh was still in the catalyst, should be an effect of the oxidation of Rh carbonyl complexes formed on the reaction media due to exposure to air during recovery. Contrarily, using method (B) of recovering, without air exposure, the catalyst is active in further runs.

5. Conclusions

The heterogenisation of the Rh(COD) complex on activated carbons is largely influenced by the support surface chemistry. With the functionalised support, an ion-exchange process takes place and the complex is mainly located in the very narrow pores.

Both the interaction of the Rh(COD) complex with the carbon surface and the solvent used as reaction media determine the stability of the heterogenised samples against lixiviation. The ion-exchanged sample is more stable. The effect of the solvents seems to be related to polar interactions with the carbon surface. The highest stability is found in hexane.

The heterogenised samples show conversion levels similar or higher to those of the homogeneous complex but with a higher n/i ratio. The selectivity of the heterogenised and the homogeneous complexes is influenced by the solvents. In methanol, the catalysts are selective to alcohols.

The method for catalyst recovery is a key step to let possible further uses of the catalyst. It can be concluded that the sample Rh/ROX-N used in hexane and recovered after cooling in continuous stirring under a He atmosphere seems to be an attractive “heterogeneous” catalyst for typical homogeneous hydroformylation reactions.

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References

- [1] V.A. Likhovov, B.L. Moroz, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Vol. 5, Wiley, Weinheim, 1997, p. 2231.
- [2] J.K. McDougall, M.C. Simpson, M.J. Green, *J. Chem. Soc., Dalton Trans.* (1996) 1161.
- [3] T.A. Kainulainen, M.K. Niemelä, *J. Mol. Catal. A: Chem.* 122 (1997) 39.
- [4] R.M. Desphande, R.V. Chaudhari, *J. Mol. Catal.* 64 (1991) 143.
- [5] M. Lenarda, L. Storaro, R. Ganzerla, *J. Mol. Catal. A: Chem.* 111 (1996) 203.
- [6] V.M. Frolov, *Platinum Met. Rev.* 40 (1996) 8.
- [7] R.M. Desphande, Purwanto, H. Delmas, *Ind. Chem. Res.* 35 (1996) 3927.
- [8] P. Kalck, M. Dessoudeix, S. Schwarz, *J. Mol. Catal. A: Chem.* 143 (1999) 41.
- [9] B. Cornils, W.A. Herrmann, R.W. Eckl, *J. Mol. Catal. A: Chem.* 116 (1997) 27.
- [10] A.N. Ajjou, H. Alper, *J. Am. Chem. Soc.* 120 (1998) 1466.
- [11] J.P. Arhancet, M.E. Davis, J.S. Merola, B. Hanson, *Nature* 339 (1989) 454.
- [12] M. Iglesias-Hernández, F. Sánchez-Alonso, in: A. Corma, F.V. Melo, S. Mendioroz, J.L.G. Fierro (Eds.), *Studies in Surface Science and Catalysis* 1340, Vol. 130D, Elsevier, Amsterdam, 2000, p. 3395.
- [13] E. Lindner, T. Schneller, F. Auer, H.A. Mayer, *Angew. Chem. Int. Ed.* 38 (1999) 2154.
- [14] J. Balúe, J.C. Bayón, *J. Mol. Catal. A: Chem.* 137 (1999) 193.
- [15] K. Nozaki, F. Shibahara, Y. Itoi, E. Shirakawa, T. Ohta, H. Takaya, T. Hiyama, *Bull. Chem. Soc. Jpn.* 71 (1999) 1911.
- [16] A.M. Tzreciak, J.J. Ziolkowski, *J. Mol. Catal.* 88 (1994) 13.
- [17] A.J. Seen, A.T. Townsend, J.C. Bellis, K.J. Cavell, *J. Mol. Catal. A: Chem.* 149 (1999) 233.
- [18] R. Margalef-Catalá, P. Salagre, E. Fernández, C. Claver, *Catal. Lett.* 60 (3) (1999) 121.
- [19] V.L.K. Valli, H. Alper, *Chem. Mater.* 7 (1995) 359.
- [20] L.R. Radovik, F.R. Reinoso, in: P.A. Throver (Ed.), *Chemistry and Physics of Carbon*, Vol. 25, Marcel Dekker, New York, 1997, p. 243.
- [21] H.P. Boehm, *High Temperatures-High Pressures* 22 (1990) 275.
- [22] M. Haukka, L. Alvila, T.A. Pakkanen, *J. Mol. Catal. A: Chem.* 102 (1995) 79.
- [23] L. Gilbert, C. Mercier, in: M. Gisnet, et al. (Eds.), *Heterogeneous Catalysis and Fine Chemicals III*, Elsevier, Amsterdam, 1993.
- [24] H.E. Van Dam, H. Van Bekkum, *J. Mol. Catal.* 131 (1991) 335.
- [25] J.A. Díaz-Auñón, M.C. Román-Martínez, C. Salinas-Martínez de Lecea, P.C. L'Argentièrre, E.A. Cagnola, D.A. Liprandi, M.E. Quiroga, *J. Mol. Catal. A: Chem.* 153 (2000) 243.
- [26] F. Rodríguez-Reinoso, A. Linares-Solano, in: P.L. Walker Jr. (Ed.), *Chemistry and Physics of Carbon*, Vol. 21, Marcel Dekker, New York, 1988, p. 1.
- [27] C.G. de Salazar, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, in: K.K. Unger, et al. (Eds.), *Studies in Surface Science and Catalysis*, Vol. 128, Elsevier, Amsterdam, 2000.
- [28] M.C. Román-Martínez, D. Cazorla-Amorós, A. Linares-Solano, C. Salinas-Martínez de Lecea, *Carbon* 31 (1993) 895.
- [29] J.A. Dean, *Lange's Handbook of Chemistry*, 14th Edition, McGraw-Hill, New York, 1992.
- [30] D. Briggs, M.P. Seah, *Practical Surface Analysis*, Vol. 1, Wiley, Chichester, UK, 1993.
- [31] J. Hagen, *Industrial Catalysis. A Practical Approach*, Wiley, Weinheim, 1999, p. 17.
- [32] G.G. Stanley, in: R. Bruce King (Ed.), *Encyclopedia of Inorganic Chemistry*, Vol. 2, Wiley, Chichester, UK, 1994, p. 596.