Long-chain-amine metal complexes as hydrogenation catalysts. Heterogenisation on activated carbon

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The catalytic activity of [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] (named [Pd(TDA)]) and [$RhCl(NH_2(CH_2)_{12}CH_3)_3$] (named [Rh(TDA)]) complexes for the hydrogenation of cyclohexene has been analysed both in homogeneous phase and heterogenised on activated carbon. The [Rh(TDA)] complex has been found to be more active than the [Pd(TDA)], both homogeneous and heterogenised. Experimental and modelled results indicate that these complexes follow a similar reaction mechanism, but with different rates. A clear positive effect of the carbon support has been found in the case of the complex [Rh(TDA)], which has been related to the anchorage of the aliphatic chains of the amine ligands on the activated carbon pores. Experiments in consecutive catalytic runs show that the heterogenised complexes can be used several times giving an acceptable conversion level.

KEY WORDS: amine Pd and Rh complexes; heterogenisation; activated carbon; catalytic hydrogenation

1. Introduction

The field of hydrogenation reactions has been traditionally dominated by heterogeneous metal catalysts [1]. However, for the past few decades soluble metal complexes have also emerged as essential tools in laboratory-scale synthesis as well as in the manufacturing of fine chemicals. Homogeneous hydrogenation catalysts offer advantages, mostly related to selectivity. Besides, for homogeneous catalysts the mechanism of action has been elucidated in many cases [1–5].

One of the major drawbacks of homogeneous systems is the catalyst recycling. Heterogenisation on solid supports could be a way to solve the problem and give those systems a broader industrial scope. Several materials have been used as supports and they are usually classified as organic (macroreticular/macro-porous polymers) and inorganic (silica, alumina, zeolites, clays) supports [6]. Carbon is not clearly included in any of these groups and despite its recognised outstanding properties as catalysts support [7], research on the heterogenisation of metal complexes using carbon materials is relatively scarce [8–14].

In previous works [11–14], the heterogenisation of [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] and [$RhCl(NH_2(CH_2)_{12}CH_3)_3$] complexes on activated carbon has been reported. The obtained results reveal that the complexes are effectively anchored on activated carbon [11–14] and that the heterogenised catalysts show the same or higher catalytic activity (in the hydrogenation of cyclohexene) than the unsupported and alumina-supported complexes [11–13]. In addition, they do not leach from the carbon support under reaction conditions.

In the present paper, the catalytic behaviour of [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] and [$RhCl(NH_2(CH_2)_{12}CH_3)_3$] complexes in the cyclohexene hydrogenation has been studied both in homogeneous phase and after being supported on activated carbon (heterogenised). The objective is to analyse and compare the catalytic activity of both complexes and to explain the effect of the heterogenisation in the catalytic activity.

2. Experimental

2.1. Preparation of catalysts

The procedure used to synthesise the [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] and [$RhCl(NH_2(CH_2)_{12}CH_3)_3$] complexes has been previously reported [14,15]. For the sake of simplicity, the complexes [$PdCl_2(NH_2(CH_2)_{12}CH_3)_2$] and [$RhCl(NH_2(CH_2)_{12}CH_3)_3$] will be referred to as [Pd(TDA)] and [Rh(TDA)], respectively.

The carbon support used is a commercial activated carbon (NORIT) named GF-45. Heterogenisation was carried out by means of the incipient wetness technique. A solution of the metal complex in toluene or carbon tetrachloride (for [Pd(TDA)] and [Rh(TDA)], respectively) with the appropriated concentration to obtain a metal content of 0.3 wt%, was used for impregnation. The impregnated samples were dried in air overnight at 348 K.

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2.2. Catalytic activity measurements

Determinations of catalytic activity were carried out in a 300 ml batch stainless-steel stirred tank reactor (Autoclave Engineers) operated at 353 K, with a stirring velocity of 600 rpm. A hydrogen pressure of 10 bar and a 5 vol% solution of cyclohexene in toluene or hexane (100 ml solution, corresponding to an olefin concentration of 0.49 mol/l) were used as reactants. The reaction was carried out for 3 h. Measurements were performed with the unsupported complexes [Pd(TDA)], [Rh(TDA)], and the Wilkinson's catalyst for comparative purposes (homogeneous) and with the heterogenised samples [Pd(TDA)]/GF-45 and [Rh(TDA)]/GF-45, both with a 0.3 wt% metal loading. In the latter case, 0.2 g of catalyst was employed. In the homogeneous experiments, a similar quantity of the metal complex present in the heterogeneous tests was dissolved in the solution of cyclohexene in toluene, having a final concentration of 60 μmol/l. To check the stability of the heterogenised complexes, they have been used in three successive catalytic tests. That is, after a 3 h run, the catalyst was removed from the liquid phase by filtration. It was allowed to dry in air overnight ($T = 348$ K) and used the following day in a new catalytic run. This process was repeated to have three consecutive catalytic runs.

Reactants and products were analysed using a HP-6890 chromatograph equiped with a FID detector and a HP-1 capillary column. The catalytic activity was expressed as conversion percentage.

3. Results and discussion

3.1. Characterisation of catalysts

Data on the characterisation of the activated carbon, pure complexes and heterogenised samples have been previously reported [13,14]. The most significant information can be summarised as follows. The stoichiometry of the synthesised complexes was confirmed with the aid of XPS, TG and elemental analysis (C, H, N) determinations [14]. The IR analysis shows that the Pd complex is the *trans* isomer [15]. Comparison of pore volume in the activated carbon and the heterogenised samples allows one to assume the adsorption of both metal complexes, [Pd(TDA)] and [Rh(TDA)], in the entrance of pores with sizes near to the thickness of the aliphatic chain of the amine ligand [13,14]. XPS data showed that complexes [Pd(TDA)] and [Rh(TDA)] do not change their chemical state upon heterogenisation [13,14].

3.2. Catalytic activity

3.2.1. Homogeneous [Pd(TDA)] and [Rh(TDA)]

The precise mechanism of the catalytic homogeneous hydrogenation has been the subject of much speculation and controversy. However, in the case of olefin hydrogenation, some steps, that constitute the basic catalytic cycle, seem to be widely accepted [2–4].

Due to the similar nature of the $[RhCl(NH_2(CH_2)_{12}CH_3)_3]$ complex and the Wilkinson's catalyst, it will be assumed that the reaction mechanism for the hydrogenation of cyclohexene with [Rh(TDA)] and with [Pd(TDA)] is similar to that corresponding to the Wilkinson's catalyst [2–4].

Making a notorious simplification of the reaction mechanism, the hydrogenation of cyclohexene can be interpreted in terms of the following equation:

$$C_6H_{10} + H_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_{12} \tag{1}$$

in which the indicated reversibility must correspond to one or more of the steps involved in the reaction pathway and it does not necessarily imply inhibition by the product. Constants k_1 and k_2 are apparent rate constants.

According to equation (1), the variation in the concentration of cyclohexane (in mol/l) with time could be calculated by the expression

$$\frac{d[C_6H_{12}]}{dt} = k_1 P_{H_2}[C_6H_{10}] - k_2[C_6H_{12}]. \tag{2}$$

Based on equation (2), the process has been modelled to fit the experimental data and the apparent rate constants, k_1 and k_2, for the reaction with [Pd(TDA)] and [Rh(TDA)] have been estimated. The Solver tool in the Microsoft Excel software has been used for calculations. The modelling was based on minimising the sum of squares of residuals (SSR), that is, the difference (residual) between the calculated (according to the model) and experimental data

$$\mathrm{SSR} = \sum \left([C_6H_{12}]_{\mathrm{exp}} - [C_6H_{12}]_{\mathrm{calc}}\right)^2. \tag{3}$$

Figure 1 shows the experimental and calculated data for cyclohexane formation using catalysts [Pd(TDA)] and [Rh(TDA)]. As can be observed, calculated values fit the experimental data reasonably well. The maximum conversion found with [Rh(TDA)], about 24%, is reached in the first 60 min reaction time. In the case of [Pd(TDA)], however, such a conversion is not reached even after 180 min. Calculated data have been plotted for a reaction time longer than 180 min and this plot indicates that, in the case of the [Pd(TDA)] catalyst, the concentration of cyclohexane also levels-off, at the same value as for [Rh(TDA)] (24% conversion), but after 600 min.

Estimated values of apparent kinetic constants k_1 and k_2 (equation (1)) are presented below ($P_{H_2} = 10$ bar):

- for [Pd(TDA)]:

$$k_1 = 0.00013\ \mathrm{s}^{-1}\,\mathrm{bar}^{-1} \quad \text{and} \quad k_2 = 0.00410\ \mathrm{s}^{-1},$$
$$\frac{k_1 P_{H_2}}{k_2} = 0.32;$$

- for [Rh(TDA)]:

$$k_1 = 0.00068\ \mathrm{s}^{-1}\,\mathrm{bar}^{-1} \quad \text{and} \quad k_2 = 0.02130\ \mathrm{s}^{-1},$$
$$\frac{k_1 P_{H_2}}{k_2} = 0.32.$$

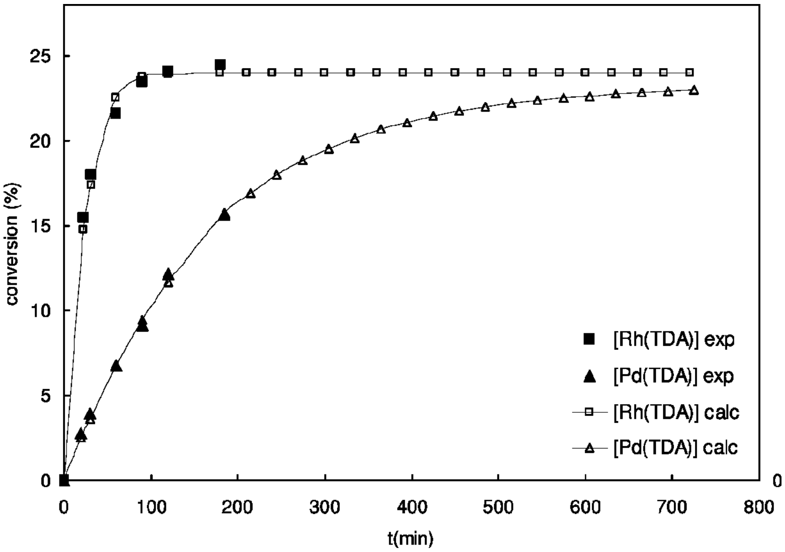

Figure 1. Experimental and calculated curves of cyclohexene conversion (%) in homogeneous phase for [Pd(TDA)] and [Rh(TDA)] complexes. The model used for calculation is explained in the text.

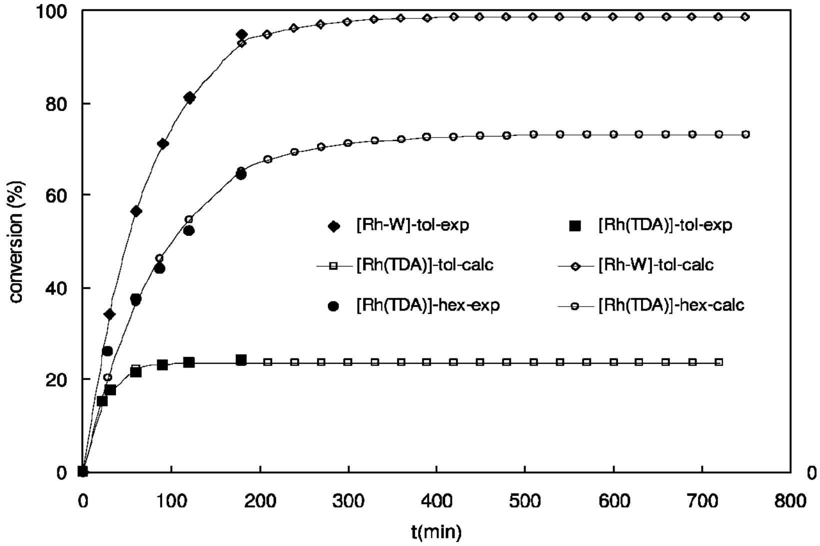

Figure 2. Effect of solvent in cyclohexene conversion (%) in homogeneous systems. Experimental and calculated conversion *versus* time curves for [Rh(TDA)] in toluene and in hexane, and for the Wilkinson's complex in toluene. The model used for calculation is explained in the text.

These results suggest that both complexes follow a similar reaction pathway, but there are factors that make kinetics noticeably different.

The Rh(I) complexes owe their catalytic activity to the facile oxidation to rhodium(III) species [16]. In contrast, for palladium(II) complexes, oxidative and reductive steps usually take place by transformation of Pd(II) to Pd(0) species and the reciprocal [17], although the formation of an intermediate dihydride of Pd(IV) during the hydrogenation of cyclohexene with a polymer-bound Pd(II) complex [18] has been reported.

Evidence on the dependency of the initial reaction rate on the formation of the hydride or of the π-complex intermediates has not been found, but considering the red-ox properties of Pd and Rh, it is likely that the differences in the behaviour of these catalysts are related to the formation of the hydride intermediate. The initial reaction rate is higher for the [Rh(TDA)] complex, possibly due to the facile oxidation of rhodium(I).

The results shown in figure 1 indicate that after a certain number of catalytic cycles, the reaction is inhibited, with both [Pd(TDA)] and [Rh(TDA)] complexes. Solvent competition for the coordination positions has been considered as an explanation of this phenomenon.

In order to clarify this point, the following two tests have been carried out: (i) reaction using the [Rh(TDA)] complex with hexane instead of toluene as solvent and (ii) reaction using the Wilkinson's catalyst (abbreviated here as [Rh-W]) in toluene. Experimental and calculated data for these tests, expressed as conversion *versus* time curves), are plotted in figure 2. For the sake of comparison, the results obtained for [Rh(TDA)] in toluene have also been included.

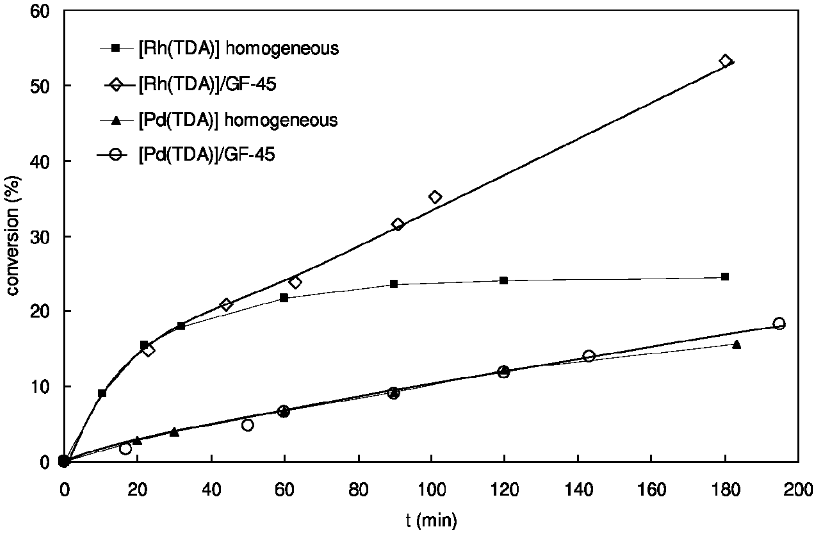

Figure 3. Catalytic activity, as % of cyclohexene conversion, with [Pd(TDA)] and [Rh(TDA)] complexes heterogenised on an activated carbon and in homogeneous phase.

The data in figure 2 indicate an important effect of the solvent used. That is, when the reaction with [Rh(TDA)] is carried out in hexane, inhibition is not observed during a 3 h trial. This could be explained considering that toluene bonds to the metal in a stronger way than hexane and because of this, removal of solvent molecules from the coordination sphere of Rh is more difficult. In addition, toluene can compete with the olefin for the metal coordination position.

As expected, with the [Rh-W] catalyst in toluene, conversion is higher than with the [Rh(TDA)] complex (about 95% conversion is reached) and it is observed that it does not level-off in the three hours of reaction time. This result shows that phosphines are ligands that perform better than the long-chain-amine ligand TDA, in a similar complex.

Calculated data shown in figure 2 indicate that, according to the model presented in equations (1) and (2), a 99% conversion could be reached after 300 min with the [Rh-W] catalyst, and at the same reaction time, the [Rh(TDA)] complex in hexane would show a conversion of *ca.* 73%. The estimated rate constants are

- for [Rh(TDA)] in hexane:

$$k_1 = 0.00072\ \mathrm{s}^{-1}\,\mathrm{bar}^{-1} \quad \text{and} \quad k_2 = 0.00250\ \mathrm{s}^{-1},$$
$$\frac{k_1 P_{\mathrm{H}_2}}{k_2} = 2.9;$$

- for [Rh-W] in toluene:

$$k_1 = 0.00115\ \mathrm{s}^{-1}\,\mathrm{bar}^{-1} \quad \text{and} \quad k_2 = 0.00000\ \mathrm{s}^{-1}.$$

Comparing these data with those obtained for the [Rh(TDA)] catalyst in toluene ($k_1 = 0.00068\ \mathrm{s}^{-1}\,\mathrm{bar}^{-1}$ and $k_2 = 0.02130\ \mathrm{s}^{-1}$), it can be concluded that inhibition, related to k_2, decreases when hexane is used instead of toluene as reaction medium. In the case of the [Rh-W] catalyst no inhibition is observed, being able of reaching a 100% conversion. Although using hexane instead of toluene improves the performance of [Rh(TDA)], reaction is still inhibited after a certain number of catalytic cycles.

3.2.2. Heterogenised [Pd(TDA)] and [Rh(TDA)]

The conversion *versus* time curves obtained with the heterogenised [Pd(TDA)] and [Rh(TDA)] complexes are plotted in figure 3. For a better comparison, data corresponding to the homogeneous process have also been included. It is important to point out that no leaching of the complexes was observed under reaction conditions [11–14].

In the case of the [Rh(TDA)] complex, the effect of heterogenisation on conversion is very important. At a reaction time below 60 min the homogeneous and the heterogenised catalysts had similar conversion values. But, at longer reaction times, the supported catalyst reached a noticeable higher conversion. This behaviour indicates a positive effect of the carbon support. For the heterogenised [Pd(TDA)] catalyst, conversion values, in the reaction conditions used, are similar to those obtained with the unsupported complex; that is, in the interval of reaction time studied, both samples showed a conversion that increases almost linearly with time at a similar rate. However, in the homogeneous process it has been found that the conversion with the [Pd(TDA)] complex becomes close to that of [Rh(TDA)] after approximately 600 min of reaction time. That is, it is possible that the positive effect of the carbon support on [Pd(TDA)] catalyst could be observed after a longer reaction time.

XPS data showed that heterogenisation does not modify the electronic state, nor the coordination sphere of Pd and Rh [13,14] in the complexes. Therefore, it is considered that in the heterogenised samples, the reaction mechanism must essentially consist of the same steps as in the homogeneous process. In fact, Yu *et al.* [19] reported that the mechanism of hydrogenation on polymer-anchored amine palladium complexes involves the formation of a Pd–H bond by heterolysis of molecular hydrogen and the equilibrium formation of a π-olefin complex with subsequent insertion of the olefin into a

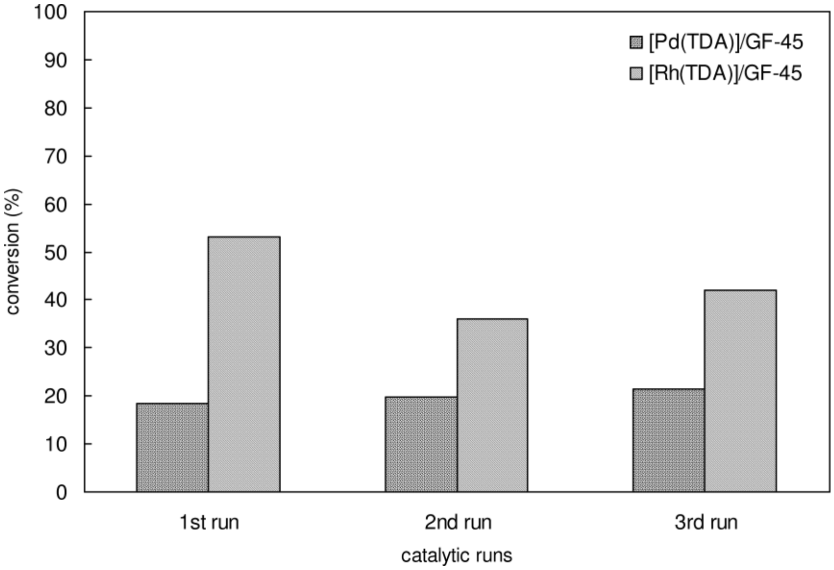

Figure 4. Catalytic activity, as % of cyclohexene conversion, of heterogenised [Pd(TDA)] and [Rh(TDA)] complexes in three successive catalytic runs (see the text for conditions).

Pd–H bond. The same authors [19] report, as well, a mechanism similar to the one reported for the Wilkinson's catalyst, for rhodium complexes (Wilkinson's type) anchored on polymers.

Our results indicate that the presence of the support has an important effect in the reaction pathway (in one or more steps). Conversion *versus* time curves obtained for the supported [Rh(TDA)] complex could be interpreted as being composed of two different stages (figure 3). One corresponding to a very fast process in the first 30 min of reaction, followed by a second slower process. It seems that the inhibition found in the homogeneous process does not take place in this case.

The reaction mechanism reported for cyclohexene hydrogenation in [$RhClL_3$] complexes [3], includes a more direct but slower reaction pathway, by which the oxidative addition of hydrogen on the original complex can also occur (without the previous substitution of a ligand L by a solvent molecule). This implies the recovery of the original form of the complex to complete the catalytic cycle; that is, the catalyst must recover the original state by accepting again a ligand L (the amine in the present case) in its coordination sphere.

Previous studies dealing with the characterisation of [Pd(TDA)] and [Rh(TDA)] complexes supported on carbon [11–14] reported that the heterogenised complex is physisorbed on the support through the aliphatic chains of the amine ligands. They are anchored on the carbon surface in a way in which the state of the metal cation is not altered with respect to the free complex. In consquence, the continuous increase in conversion observed for the heterogenised samples, instead of the levelling-off found with homogeneous catalysts (figure 3), could be explained considering the easy substitution of the outgoing bonded alkane and/or solvent molecules by an incoming amine ligand, favoured because during the catalytic cycle the amine remains adsorbed on the carbon support and, consequently, close to the metal complex. In this way, the direct pathway through the original complex might have a noticeable participation in the case of the heterogenised complexes.

A possible desorption of the complex from the support to act in homogeneous phase cannot be ruled out. However, considering that metal loading in the used samples is very close to that in the fresh ones, a readsorption process should take place during cooling down and before filtration.

In order to check the stability of the heterogenised complexes, three consecutive catalytic tests have been performed. Conversion at 180 min reaction time in the three consecutive runs is plotted in figure 4. It is clearly shown that heterogenised [Pd(TDA)] and [Rh(TDA)] complexes exhibit an acceptable stability. This means the heterogenisation on activated carbon is quite efficent because the catalysts can be reutilised several times giving interesting conversion levels.

4. Conclusions

In the homogeneous process, the [Rh(TDA)] complex is more active than the [Pd(TDA)] for the hydrogenation of cyclohexene. Experimental and model calculated results (modelling) suggest that both complexes follow a similar mechanism but with different kinetics. Conversion on [Pd(TDA)] is delayed with respect to that on [Rh(TDA)] by about 600 min. Differences are mainly related to the redox properties of the metal. The inhibition of the reaction observed with homogeneous [Rh(TDA)] and [Pd(TDA)] complexes can be attributed to solvent effects and, mainly, to the nature of the complex (type of ligands in this case).

In the heterogenised form, [Rh(TDA)] is also more active than [Pd(TDA)]. A clear positive effect of the carbon support has been found; probably as a consequence of the anchorage of the amine ligands (by means of the long aliphatic chain) on the carbon surface. It means that the ligand remains close to the metal during the catalytic cycle and because of that, reincorporation of the ligand to the coordination sphere and restoration of the active species, is favoured.

The utilisation of heterogenised complexes in successive catalytic runs indicates that they show a good stability with acceptable conversion levels.

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