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COMMUNICATION

Preparation of rhodium–phyllosilicate catalysts without leaching in liquid-phase 1-hexene hydrogenation

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Rhodium catalysts have been prepared on palygorskite and montmorillonite (clay) supports by reduction with hydrogen (1 atmosphere) at room temperature of a cationic organometallic rhodium compound anchored to the support. The activity of these catalysts for the hydrogenation of liquid-phase 1-hexene remains constant with increase of prehydrogenation time and with re-use for several runs. No rhodium leaching is observed.

Keywords: Rhodium, phyllosilicates, palygorskite, montmorillonite, clays, catalyst preparation, 1-hexene hydrogenation, leaching

INTRODUCTION

One method of immobilizing homogeneous catalysts and/or obtaining metallic particles with maximum dispersion is to prepare an organometallic complex anchored to a support.[1–4] Phyllosilicates, such as palygorskite and montmorillonite, have various properties which make them suitable for supports, viz. large specific surfaces, good adsorption capacities and, as can be deduced from their crystalline structure, a homogeneous distribution of active surface centres.[5] In effect, sheet phyllosilicates have been used for immobilizing homogeneous catalysts and the resulting heterogeneous catalysts have proven to be active in hydrogenation and even more selective than their homogeneous counterparts.[6] Sheet silicates themselves have been used as catalysts in organic synthesis.[7]

Here we report on the use of phyllosilicates as supports for rhodium catalysts. These catalysts were prepared by reduction at room temperature of a cationic organometallic rhodium norbornadiene compound anchored on palygorskite and montmorillonite supports. The rhodium compound was reduced with molecular hydrogen in acetone solution at atmospheric pressure. The preparation of the catalysts is summarized in the reactions shown in Scheme 1 from $[Rh(nbd)(Me_2CO)_x]ClO_4$. This was prepared from $[RhCl(nbd)]_2$ in acetone using $AgClO_4$ giving an acetone solution of $[Rh(nbd)(Me_2Co)_x]ClO_4$. Not all of the rhodium complex binds to the support. After these two reactions the corresponding solids are filtered off. The proportion of the rhodium bound is shown in Table 1. When all of the rhodium is bound to the support the resultant percentage is stated as one. When silica is used as a support the rhodium compound and metallic rhodium leached from the support. However, with clay as support neither the rhodium compound nor metallic rhodium was leached under the conditions studied.

Note that Rh(I)/support is used to designate the precursor, and does not indicate that supported rhodium is necessarily in the oxidation state I.

A *cationic* rhodium compound, $[Rh(nbd)(Me_2CO)_x]^+$ with prechlorateanion, which is easily reduced, was chosen in order to avoid leaching[8] of the metal (the clay structure is *negatively* charged). The rhodium compound itself could be reduced under mild conditions. In this context, Oro *et al.*[9] have described the synthesis of stable cationic rhodium(I) compounds with oxygen donor ligands which are reducible in a polar medium.

The catalysts which we prepared are active for 1-hexene hydrogenation and their activity remains constant during several runs without rhodium leaching. The interaction between the rhodium and the support

$$\underset{0.1\ \text{mmol}}{[\text{Rh(nbd)Me}_2\text{CO})_x]^+} + \underset{1\ \text{g}}{\text{support}} \xrightarrow[24\ \text{h}]{\text{Me}_2\text{CO, Ar}} \text{Rh(I)/support} \qquad [1]$$

$$\text{Rh(I)/support} + \text{H}_2 \xrightarrow[t\ \text{h}]{\text{Me}_2\text{CO}} \text{Rh/support} \qquad [2]$$

Table 1 Hydrogenation of 1-hexene by rhodium/support catalysts[a]

Support	Rh (%)	Catalyst (mg)	Rate of hydrogen uptake ($molH_2$(mol Rh)$^{-1}$min^{-1}) First run[b]	Third run[b]
SiO_2	0.65	344	21	0
SiO_2-400	0.65	344	9	0
Mont.	1	210	24	24
Paly.	0.85	257	31	31
Paly.-150	0.95	211	45	45
Paly.-400	0.95	211	53	53

[a] Reaction conditions: 1-hexene, 2 mmol; catalyst, 0.02 mmol; volume of acetone solution, 15 cm^3; temperature, 20°C; P_{H_2}, 1 atm. Initial hydrogenation rates are given (at constant 20% conversion) and were obtained from hydrogen uptake under these conditions. [b] Variation in values is ±1.5 mol H_2 (mol Rh)$^{-1}$ min^{-1}.

is determined by the concentration and type of surface hydroxyl group,[10,11] which is determined, in turn, by the water content of the support. In order to study the influence of the water content, the palygorskite was heated in a vacuum at different temperatures (150 and 400°C) before anchoring. This procedure makes it possible to control the water content better than with calcination, because the material is cooled in a vacuum. The temperature at which the support is heated before anchoring influences both the induction time (*t*) and the activity of the catalyst in 1-hexene hydrogenation. Table 1 shows that in all cases the activity of these catalysts remains constant with increasing prehydrogenation time period since the catalyst suspension is put in contact with hydrogen until the substrate, 1-hexene, is injected, and with reuse during several runs. The filtrate solutions after the hydrogenation experiments were analysed for the rhodium compound using UV–visible spectroscopy at a λ_{max} of 382 nm. No absorption was observed and this is taken as an indication that no rhodium had leached from the support.

In order to determine whether the lack of leaching is due to the preparation method or to the support itself, we performed analogous preparations using an 'Aerosil' (SiO_2) support to avoid any contribution of heterogeneity in the preparation of the catalysts. As occurred in the case of the catalyst with phyllosilicate supports, the induction time varies with the temperature at which the support was heated before anchoring, i.e. with the water content during the reduction process. However, (unlike the catalysts on phyllosilicate supports) the hydrogenation activity of catalysts on silica decreases with increasing prehydrogenation time and with re-use. This is probably due to rhodium agglomeration and leaching (we have seen metallic rhodium on the walls of the reaction flask and the filtrate solution of the catalyst preparation presents some absorption by UV–visible spectroscopy of the rhodium compound indicative of the weak rhodium–silica interaction. This result is in general agreement with those described for carbonyl clusters on silica and other supports.[11]

The lack of leaching when the support is a phyllosilicate indicates that there is a good interaction between the rhodium and phyllosilicate. This is consistent with XPS results, in which the intensity of the rhodium 3*d* orbital energy level is to be constant for precursors and catalysts. This fact may be due to the distribution of the negative charge[12,13] on the palygorskite fibres which would force the rhodium to relatively fixed positions in order to maintain electroneutrality, thus preventing its migration and leaching. These are the first catalysts prepared by reduction at room temperature of an organometallic compound anchored on phyllosilicate supports. They illustrate the potential of phyllosilicates as models for studying metal–support interactions from the perspective of some type of ionic interaction rather than as a van der Waals interaction. This type of interaction makes them better at avoiding metal migration and resulting agglomeration and/or leaching. In the preparation of heterogeneous catalysts it seems interesting to use not only an organometallic compound,[1] but also a support which provides the possibility of such ionic interactions. The analogy between phyllosilicates and ionic solutions[14] may provide another bridge between heterogeneous and homogeneous catalysis.

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