Efficient hydrogenation of alkenes using a highly active and reusable immobilised Ru complex on AlPO$_4$

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ABSTRACT

The homogeneous ruthenium complex [Ru^{II}Cl$_2$(bpea)(PPh$_3$)], where bpea = N,N-bis-(2-pyridylmethyl)ethylamine, has been immobilised on an amorphous AlPO$_4$ support through phosphamide bonds that are comparatively more stable than organosilane bonds. The catalyst was characterised by means of UV–vis and DRIFT and its activity was compared to that of the homogeneous complex in the liquid-phase hydrogenation of a range of alkenes. The heterogenized catalyst exhibited very good activities and excellent reusabilities (up to 25 runs) in the hydrogenation reaction.

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1. Introduction

The immobilisation of homogeneous metal coordination complexes is a very useful methodology in organic synthesis. A great deal of interest has been devoted to the preparation of such heterogenized complexes over the last few years due to their ease of separation from the reaction mixture and minimal product contamination caused by metal leaching [1–5] as well as to their efficient recyclability without a significant loss in activity [6]. In particular, Rh, Ir and Ru complexes have been widely employed in hydrogenations [7]. Several supports have been employed for the immobilisation of various homogeneous complexes including polymeric organic and inorganic supports [8–14]. Following the solid-phase synthesis studies introduced by Merrifield and co-workers [15,16] the majority of the work in this area has focused on polymer-supported catalysts. Nevertheless, the immobilisation of a homogeneous catalyst on an insoluble polymer support renders heterogenized materials with reduced stability that affects the reusability of the catalysts, mainly due to their swelling and deformation [17–19]. Inorganic supports are

particularly suitable as supports owing to their high physical strength, chemical inertness and stability (in terms of swelling and deformation) in organic solvents. Such advantageous properties will facilitate the application of the materials in reactions at higher temperatures and their use in continuous flow reactions.

Much work is currently devoted to the development of an adequate methodology to anchor homogeneous complexes onto inorganic supports [20–24]. Covalent immobilisation is possibly the most convenient but also challenging way of immobilisation to perform on such supports [23,25–27]. Micelle templated silicas (MTS) featuring an unique porous distribution and high thermal and mechanical stability can be easily functionalised by direct grafting of the functional organosilane groups on their surfaces [20–24,28–33]. However, polar solvents including water or alcohols and high temperatures can promote the hydrolysis of the grafted moieties.

This methodology can be improved via the formation of more stable and hydrolysis-resistant organic–inorganic hybrid bonds through the phosphamide bond in AlPO$_4$ materials. The high stability of the phosphamide or phosphoester bonds plays a crucial role in some biomolecules including the RNA and DNA structures. We have recently reported the feasibility of the anchoring of ruthenium complexes in AlPO$_4$ [34,35] following a methodology that was also reported for the immobilisation of enzymes on amorphous AlPO$_4$
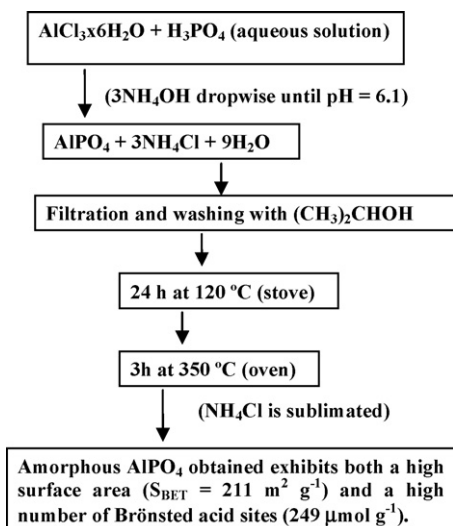
Scheme 1. Synthesis of the amorphous AlPO$_4$ support.

[36,37]. This amorphous material is completely isostructural with silica exhibiting parallel polymorphic transformations [38,39].

2. Experimental

2.1. Materials preparation

AlPO$_4$ can be easily prepared by means of a sol–gel protocol as previously reported [34–41]. Materials have high surface area and density of Brönsted acid sites making them particularly suitable as metal supports and heterogeneous catalysts in different organic synthesis reactions [40,41]. The amorphous AlPO$_4$ (Al/P = 1) employed as support was prepared according to the general methodology outlined in Scheme 1 [34–41].

The methodology to heterogenize the ruthenium complex on the AlPO$_4$ is summarised in Scheme 2. The activation of the AlPO$_4$ surface was performed through the formation of strong hybrid phosphamide bonds [34–37] via microwave-assisted reaction of the Brönsted sites with ethylenediamine (Step 1) as follows: in a flask of 100 mL, 30 g support, 80 mL diethyl ether and 4 mL ethylenediamine (Merck, 99%), were stirred for an hour at room temperature. Diethyl ether was then removed by slight heating in a water bath and the product was subsequently heated at 100 °C for 90 min. The flask was eventually placed in a domestic microwave oven and microwaved for 10 min (190 W, 5 min and 380 W, 5 min) to ensure reaction completion. Upon reaction cooling, the unreacted ethylenediamine was removed washing with 100 mL of ethanol (3 times) and then the product was vacuum dried and separated.

The functionalisation step (Step 2) was then performed through reaction of the terminal amino group with 2-picolyl chloride to obtain the N-tridentate ligand N,N-bis(2-pyridylmethyl)ethylamine (bpea). This step is carried out in a 250 mL flask with 30 g of AlPO$_4$-ethylenediamine with a solution of 4.5 g of 2-picolyl chloride (Aldrich, 98%) in 50 mL ethanol (96%, Aldrich) and a variable amount of ethanol (about 60 mL) to achieve incipient wetness conditions. The reaction was carried for half an hour at room temperature. The temperature was then increased to 80–90 °C and 2 mL of a solution of 2.5 g NaOH in 15 mL of water were added every 10 min (90 min total reaction time). During the reaction, an intense pink color appeared that changes to weak red upon reaction completion. At that point, the product is filtered and washed 3 times with 100 mL of ethanol to remove the excess of 2-picolyl chloride.

The immobilised [Ru^{II}Cl$_2$(bpea)(PPh$_3$)] complex can be obtained in situ through the addition of RuCl$_3$ and triphenylphosphine (PPh$_3$) (Step 3) as follows: 8 g of functionalised and activated AlPO$_4$ were stirred with 0.4 g of RuCl$_3$ (1 h) in a flask containing 10 mL of ethanol. 0.118 g LiCl and 0192 mL triethylamine were then added to the mixture under argon atmosphere, stirring the solution for 30 min. 0.869 g triphenylphosphine were eventually added and the resultant mixture was heated under reflux conditions for 2 h. Upon cooling, the final product was filtered off, washed twice with 2 portions of 30 mL of methanol and subsequently dried prior its characterisation and testing of its catalytic activity.
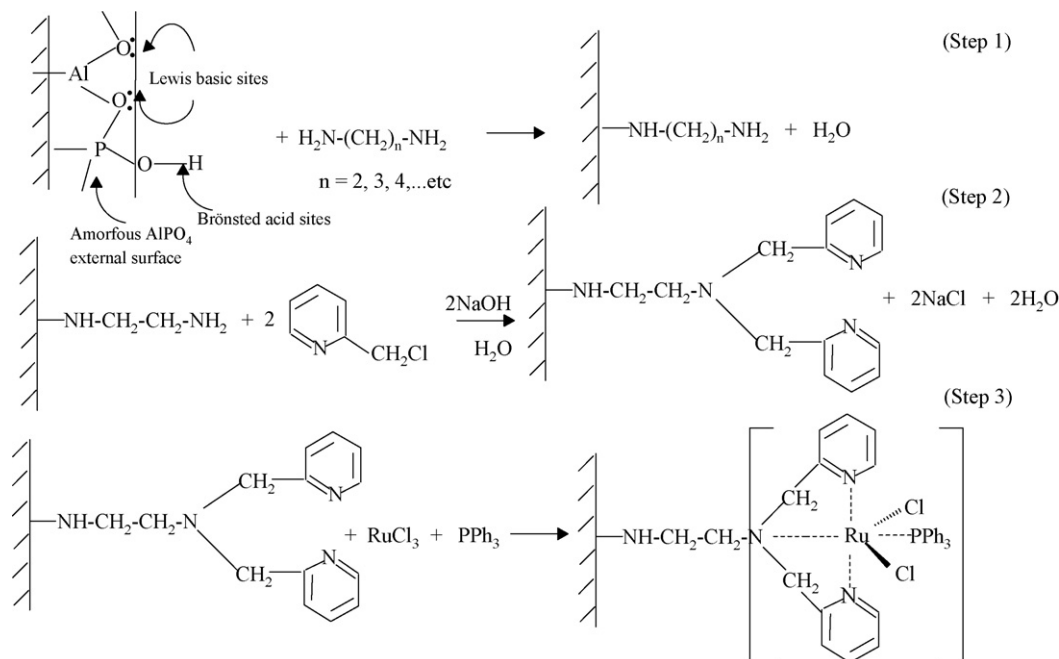
Scheme 2. General scheme for covalent immobilisation of the homogeneous [Ru^{II}Cl$_2$(bpea)(PPh$_3$)] complex. Support functionalisation of amorphous AlPO$_4$ by microwave heating with ethylenediamine (Step 1) and post-synthetic activation with 2-picolyl chloride (Step 2). Synthesis of the Ru complex (Step 3).

2.2. Materials characterisation

Diffuse Reflectance Fourier-Transform Infrared (DRIFT) spectra were recorded on a Mattson Galaxy Satellite FT-IR spectrophotometer containing a MKII Golden Gate Single Reflection ATR system. Spectra were collected in the 4000–400 cm^{-1} range.

Diffuse reflectance UV–vis spectra were recorded on a Varian CAREY-1E UV–vis spectrophotometer (with 1 cm quartz cells), operating in ABS photometric mode, in the 200–800 nm range.

The Ru content was quantified by Inductively Coupled Plasma coupled with Atomic Emission Spectroscopy (ICP-AES) using a Thermo Elemental Iris Interprid instrument. 0.02 g catalyst was dissolved in acid, diluted with distilled water to 100 mL and subsequently analysed.

2.3. Catalytic experiments

In a typical liquid-phase hydrogenation, 14.6 mmol 1-hexene, 20 mL methanol, 2.5 g Ru(complex)/AlPO$_4$ were placed inside a conventional low-pressure hydrogenator (Parr Inst. Co., Mod. 3911) and heated at 50 °C for >24 h under 5 bar H$_2$. Samples were periodically withdrawn from the reaction mixture, filtered off, and analysed using a Gas Chromatograph (GC) Konik KNK-300-HRGC fitted with a chiral BETA DEX 120 (30 m × 0.25 mm × 0.25 μm) capillary column and a Flame Ionisation Detector (FID).

3. Results and discussion

The efficiency of the preparation of the immobilised complex (Scheme 2, Steps 1–3) was confirmed by Diffuse Reflectance Infrared Fourier-Transform (DRIFT) and Diffuse Reflectance Ultraviolet Visible (DRUV) experiments. The analogous homogeneous [Ru^{II}Cl$_2$(bpea)(PPh$_3$)] complex (molar weight = 661.07 g mol^{-1}) was also prepared, isolated and spectroscopically and structurally characterised [42] for comparative purposes.

New IR bands were observed in the 2800–3500 and 1500–1550 cm^{-1} range, indicating the presence of aromatic and aliphatic as well as amino groups, respectively, on the AlPO$_4$ support (Fig. 1). This suggests the successful immobilisation of the ruthenium complex on the AlPO$_4$ surface. Similarly, the high sensitivity of visible UV absorption bands let us follow the changes after every step in the immobilisation as compared to the homogeneous complex (Fig. 2). The UV–vis spectra of the immobilised catalyst (Fig. 3d) exhibited a characteristic absorption band at ca. 500 nm that can be correlated to the d$_\pi$(Ru) → π* [Cl$_2$(bpea)(PPh$_3$)] transition, in good agreement with UV bands of previously reported similar Ru complexes [43,44]. This band was slightly shifted compared to those found in the homogeneous complex centered at 400 and 485 nm, respectively (Fig. 2). Of note were also the similarities in the UV spectra of the fresh and reused catalyst (Fig. 3d and e), implying the stability of the catalyst under the reaction conditions. The quantity of Ru covalently anchored to the AlPO$_4$ was determined using ICP-AES. A 1.51 wt% Ru was found in the catalyst. The immobilisation efficiency was approximately 62% of the theoretical quantity of Ru (2.4 wt.%) employed in the synthesis of the complex.

The activities (turnover frequencies-TOF- and turnover numbers-TON-) of both homogeneous and heterogenized ruthenium complexes were then compared in the liquid-phase hydrogenation of 1-hexene using a conventional low-pressure hydrogenator as previously reported [34,35]. Results are summarised in Fig. 4 and Table 1. As expected, the conversions in the materials increased with increasing quantities of heterogenized catalyst. An optimum concentration equal or higher than 0.7 M substrate (equivalent to 14 mmol) and 2.5 g catalyst (equivalent to 0.374 mmol complex or 0.057 mg Ru) provided the higher reaction rate values (Fig. 4).
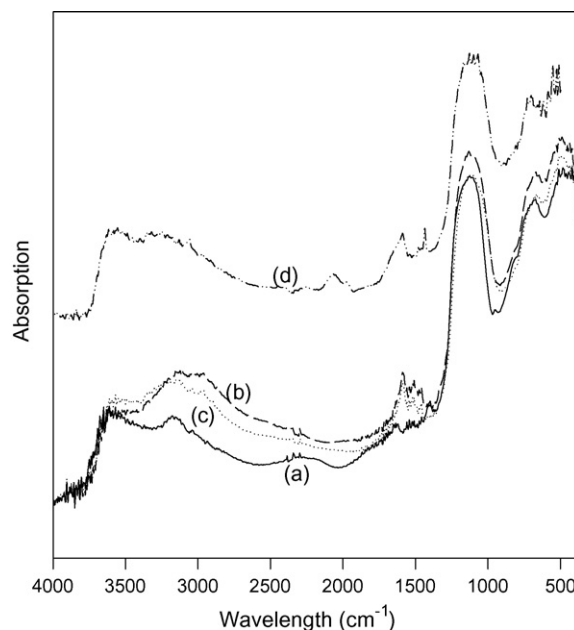

Fig. 1. FTIR spectra of different samples obtained in the different steps of preparation of the Ru catalyst: (a) AlPO$_4$ support (b) AlPO$_4$-ethylenediamine, (c) AlPO$_4$-bpea ligand, (d) [Ru^{II}(bpea)(PPh$_3$)Cl$_2$] complex.
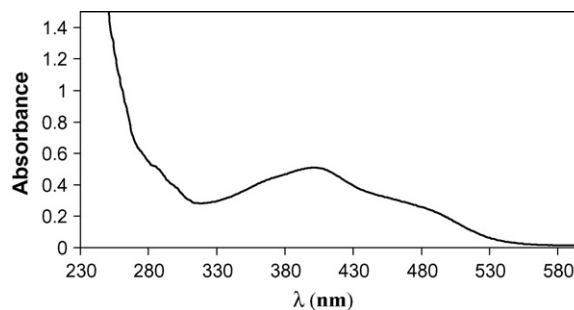
Fig. 2. UV–vis/Diffuse Reflectance spectra of the homogeneous Ru^{II}Cl$_2$(bpea)(PPh$_3$) complex.
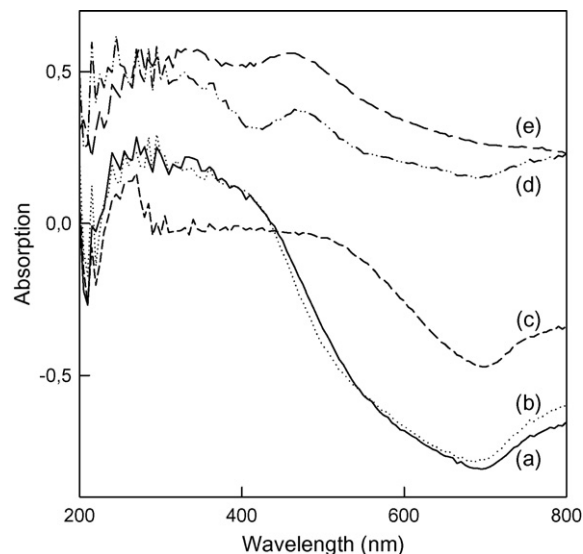

Fig. 3. UV–vis/Diffuse Reflectance spectra of different materials obtained in the different steps showed in Scheme 2; (a) amorphous AlPO$_4$ support; (b) ethylenediamine on support after microwave heating (Step 1); (c) bpea ligand obtained by reaction with 2-picholyl chloride (Step 2); (d) Ru^{II}Cl$_2$(bpea)(PPh$_3$), obtained by reaction with triphenylphosphine and RuCl$_3$ in ethanol (Step 3) and (e) Ru complex after 25 catalytic runs.
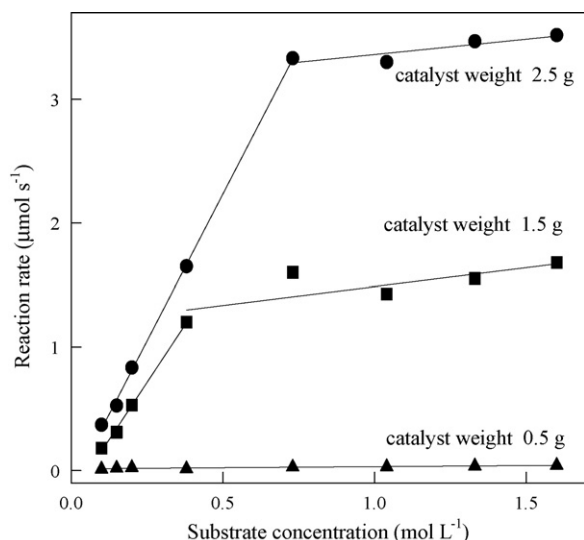
Fig. 4. Influence of substrate concentration and catalyst weight in the hydrogenation reaction rates of 1-hexene using immobilised $Ru^{II}Cl_2(bpea)(PPh_3)$ on $AlPO_4$. *Reaction conditions*: 20 mL of methanol, 50 °C, 5 bar of hydrogen pressure.

The results pointed out the immobilisation of the ruthenium complex on the $AlPO_4$ material rendered a less active catalyst (TOF values, Table 1), but the stability of the immobilised solid was improved. We believe the decrease in activity may be due to the steric effects related to the presence of the complex on the $AlPO_4$ surface that could affect the formation of the transition state between the ruthenium compound, the alkene and hydrogen as well as diffusional effects that may be present. The conversion of starting material was also significantly increased in the heterogeneous systems compared to that of the homogeneous complex. Of note was also the stability of the immobilised complex. The heterogenized material could be reused over 25 times without a significant decrease in activity (less than 25% of the initial activity, Table 1) and with an accumulative conversion capacity (TON) almost 10 times higher than the homogeneous $[Ru^{II}Cl_2(bpea)(PPh_3)]$ complex, demonstrating its high stability.

To further extend the scope of the methodology, a range of alkenes were then investigated in the hydrogenation reaction as well as a compound with carbonyl groups (methyl acetoacetate). Results have been included in Table 2. In general, the immobilised complex provided very good to excellent activities in the hydrogenation of alkenes under the mild hydrogenation conditions, preserving almost its initial activity after several uses. Complete selectivity to the hydrogenated product was obtained for all substrates with the exception of metal acetoacetate for which a very low selectivity to methyl hydroxybutyrate was found, with mainly hemiketals and ketals of methanol obtained as by-products (Table 2,

Table 1

Activity comparison between the homogeneous and heterogenized $[Ru^{II}Cl_2(bpea)(PPh_3)]$ complex in the hydrogenation of 1-hexene[a].

Reaction	Homogeneous complex	Heterogenized complex	
	1-hexene	1-hexene (First use)	1-hexene (25 uses)
Substrate (mmol)	16	16	16
Catalyst (mmol/g)	0.0484	0.374/2.5	0.374/2.5
Reaction rate (μmol s^{-1})	0.898	3.330	2.500
TOF (h^{-1})	67	32	29
Reaction time (h)	35	3	5
Conversion (mol%)	48	>99	>99
TON [subs]/[cat]	160	43	1423

[a] *Reaction conditions*: 50 °C, 5 bar hydrogen, 20 mL methanol.

Table 2

Rates of reaction for the hydrogenation of a range of alkenes using $[Ru^{II}Cl_2(bpea)(PPh_3)]$ supported on $AlPO_4$[a].

Substrate	Conversion (mol%)	Reaction rate (μmol s^{-1})	TOF (h^{-1})	Time of reaction (h)
1-hexene	>99	3.330	32	3
Ethyl vinyl ether	>99	0.222	2.1	22
Styrene	>99	0.196	1.9	83
Ethyl acrylate	56	0.037	0.4	168
2-methyl-1-pentene	>99	0.065	0.6	100
Cyclohexene	>99	0.130	1.3	18
N-Benzyl methyl cinnamate[b]	>99	0.080	0.8	48
Methyl acetoacetate[c]	31	0.110	1.1	48

[a] *Reaction conditions*: 14.6 mmol substrate, 5 bar H_2, 20 mL methanol, 2.5 g catalyst (0.374 mmol complex, 0.057 mg Ru), 50 °C.
[b] 4 mmol substrate, 6.6 bar H_2.
[c] 7.6 mmol substrate, 5.9 bar H_2. Only 10% selectivity to methyl hydroxybutyrate. Many hemiketals and ketals of methanol were obtained as by-products.

footnote). The leaching of the catalyst was also assessed by ICP-AES. No significant leaching (<4 ppm Ru) was determined in the reaction mixture after the hydrogenation, indicating the stability of the supported Ru complex under the reaction conditions.

4. Conclusions

$AlPO_4$ materials featuring high surface areas and high density of Brönsted acid sites have been found to be excellent inorganic supports for the covalent attachment of organic moieties through the formation of hybrid phosphamide bonds. The preparation of a heterogenized ruthenium complex on $AlPO_4$ was successfully accomplished and the materials exhibited lower activities but greater stability and recyclability properties in the liquid-phase hydrogenation of alkenes compared to the homogeneous complex. We envisage our methodology can be extended to the heterogenization of different organic compounds and/or inorganic complexes on $AlPO_4$ to prepare heterogenized catalysts with improved stabilities and reusabilities.

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