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The preparation of silica entrapped homogeneous hydrogenation catalysts by conventional and ionic liquid mediated sol–gel routes

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Abstract

$[RhCl(PPh_3)_3]$ has been entrapped inside silica matrices by two methods: a conventional sol–gel synthesis in ethanol/water and a new route performed in an ionic liquid. The activity of these heterogenised catalysts has been tested for the hydrogenation of styrene. The catalyst prepared in an ionic liquid was found to be more active and have low Rh leaching.
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1. Background

The perfect catalyst would combine the selectivity of homogeneous catalysts with the ease of separation of their heterogeneous counterparts. One solution to the synthesis of such catalysts is the entrapment of a homogeneous catalyst within a porous matrix by the sol–gel method [1].

Ionic liquids have been show to act as excellent templates for porous amorphous oxides [2]. The application of ionic liquids to the preparation of highly active heterogeneous hydrogenation and Heck catalysts has been demonstrated by Marr and co-workers [3]. In this communication, we report the use of an ionic liquid in the synthesis of a heterogenised homogeneous catalyst.

Hydrogenation is of interest to chemists involved in heterogenising homogeneous catalysts as it is an example of a reaction for which heterogeneous and homogeneous catalysts are very widely applied in industry. $[RhCl(PPh_3)_3]$ (**1**), often referred to as Wilkinson's catalyst, is certainly one of the most famous homogeneous hydrogenation catalysts [4]. **1** will hydrogenate alkenes under a wide variety of conditions; in this study, we use it under conditions that emphasise the difference in selectivity between $[RhCl(PPh_3)_3]$ and a heterogeneous catalyst Rh on carbon.

Styrene is an interesting substrate for initial catalyst testing as it provides two potential sites for hydrogenation: the terminal alkene and the aromatic ring. In general **1** shows complete selectivity towards alkene hydrogenation to yield ethyl benzene as the sole product. In contrast, the heterogenous catalyst Rhodium on carbon is capable of hydrogenating the ring and selectivity is not absolute. The entrapment of catalysts for the hydrogenation of styrene to ethyl benzene [5],

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and the hydrogenation of an arene ring [6] have been reported previously. Here, we record the facile preparation of a heterogenised homogeneous catalysts based on [RhCl(PPh$_3$)$_3$] (**1**) in air by two methods, including the first preparation of such a catalyst in an ionic liquid, and contrast the stability and activity of the two solid catalysts.

2. Materials preparation

Two methods of entrapment were used in this study. The entrapment of a homogeneous catalyst in a conventional sol–gel derived glass and the entrapment in an aerogel prepared by an ionic liquid route.

In the case of the traditional sol–gel derived glass, alcohol and water are the common solvents used to elicit glass formation. Catalysts to be entrapped are usually required to be soluble in the alcohol, water or the silica precursor. The method described here adds the catalyst in a minimum amount of a volatile solvent, followed by fast gelation facilitated by the addition of benzylamine, (a basic catalyst for the sol–gel reactions). Preparation of the aerogel entrapped catalyst is performed in a similar manner. The catalyst is solubilised in a minimum amount of a volatile solvent and then added to the ionic liquid. The silica precursor is then added and gelation is catalysed by the addition of an acid; again gelation is fast. Both sol–gel derived materials are washed with dichloromethane and dried. The resulting silica entrapped catalysts were obtained as pale yellow powders. Any catalyst decomposition is typically accompanied by a darkening of the solid. Using other methods of catalyst synthesis we have observed extensive decolouration, when these solids were applied as catalysts in the hydrogenation of styrene some hydrogenation of the aromatic ring was observed.

3. Catalyst testing

Four catalysts were tested for their activity in the hydrogenation of styrene: homogeneous [RhCl(PPh$_3$)$_3$] (**1**), 5% Rh on carbon (Aldrich) (**2**), silica-entrapped **1** prepared in ethanol/water (**3**) and silica-entrapped **1** prepared in an ionic liquid (**4**). The results are given in Table 1. In each catalytic experiment conditions were identical. The solid catalysts (**2**–**4**), were reused by removing the product solution and injecting a fresh substrate solution.

Table 1 illustrates the differences in selectivity for the molecular and entrapped catalysts (**1**, **3** and **4**) and the metallic catalyst (**2**). All catalytic systems derived from [RhCl(PPh$_3$)$_3$] (**1**, **3** and **4**) gave 100% selectivity, producing ethyl benzene as the sole product. 5% Rh on carbon (**2**) yielded a mixture of ethyl benzene, 1-ethyl

Table 1
Catalyst activity and selectivity

Catalyst	Conv (%)	Ethyl benzene (%)	Ethyl-cyclo-hexane (%)	Ethyl-cyclo-hexene (%)
(**1**)	100	100	0	0
(**2**) 1st run	100	88*	6*	6*
(**2**) 2nd run	100	92*	3*	5*
(**3**) 1st run	62	100	0	0
(**3**) 2nd run	77	100	0	0
(**4**) 1st run	99	100	0	0
(**4**) 2nd run	98	100	0	0

* The calculation of the listed percentages is based on the relative areas.

cyclohexene and ethyl cyclohexane. A direct comparison of the homogeneous and the commercial heterogeneous systems (**1** and **2**) is possible as the quantity of rhodium added was kept the same in each experiment (7.6×10^{-6} mol). The complete selectivity observed for the entrapped catalysts suggests that the entrapment of the molecular hydrogenation catalyst in **3** and **4** has been completely successful, this is further supported by the continuance of selectivity for the second catalytic run. Longer reaction times (2 h) led to full conversion and total selectivity. Further catalyst recycle is detailed in supplementary data.

Table 1 allows a comparison of the percentage conversion for the entrapped catalysts **3** and **4**. The catalyst entrapped in silica prepared by conventional sol–gel synthesis yields a catalyst that converts styrene to ethyl benzene 62% and 77% in the first and second runs, respectively. This change in conversion may suggest a change in catalyst character during activity. The performance of the aerogel catalyst prepared in an ionic liquid is more promising; styrene is close to full conversion after 30 min (99% and 98% converted) and activity is almost identical for the two consecutive catalytic runs. These trends are continued when the number of runs is extended to 10 (see Supplementary data).

Table 2 summarises ICP results on the metal loading of the entrapped catalysts and rhodium analysis of the product solutions resulting from catalyst testing. First we should note that the concentration of rhodium is 4 times higher in catalyst **3**, this is reflected in the turnover frequency for the catalytic runs. We conclude that the [RhCl(PPh$_3$)$_3$] entrapped in an ionic-liquid derived aerogel (**4**) is 5 times more active than the [RhCl(PPh$_3$)$_3$] entrapped in silica prepared by a more conventional sol–gel route (**3**). Catalyst leaching rates are also much lower for the aerogel system. Whilst 2.8% of the rhodium leached from catalyst **3** in the first catalyst run and 0.3% in the second; less than 0.3% of the rhodium leached from **4** in the first run and no leaching was detected from the second run.

Table 2
Summary of ICP OES results and turnover numbers for entrapped catalysts

Catalyst	Rh conc. in entrapped catalyst/(wt%)	Wt. entrapped catalyst added/(g)	Rh leaching/ $(mol \times 10^{-8})^*$	Moles of Rh in catalytic run/(10^{-7})	Moles of styrene converted/(10^{-3})	Turnover frequency/s^{-1}
(**3**) 1st run	0.668	0.0150	2.76	9.74	5.41	3
(**3**) 2nd run			0.31	9.46	6.72	4
(**4**) 1st run	0.161	0.0158	0.08	2.47	8.64	19
(**4**) 2nd run			<0.05	2.46	8.55	19

*By ICP/OES.

4. Conclusions

We have reported the successful entrapment of the hydrogenation catalyst [RhCl(PPh$_3$)$_3$] by conventional and ionic liquid-mediated sol–gel syntheses. The synthetic procedures for catalyst synthesis are simple and conducted in air; and the catalysts are active, selective and reusable. Initial results suggest that that the ionic liquid route provides a catalyst of higher activity and stability.

Further research is ongoing into the structure of the catalysts, the kinetics of reactions, the hydrogenation of alternative substrates, the entrapment of other catalysts and the assessment of other ionic liquids as solvents for aerogel synthesis.

5. Experimental procedures

5.1. Catalyst preparations

5.1.1. Preparation of glass entrapped catalyst (3)

Tetraethoxysilane (TEOS) 2.42 g (0.0107 mol) was added to Ethanol 1.73 g (0.03604 mol) and stirred for 20 min. Four drops of distilled water was added under continuous stirring. [RhCl(PPh$_3$)$_3$] 0.0189 g (2.04×10^{-5} mol) was dissolved in the minimum quantity of dichloromethane (4 drops). This catalyst solution was added to the mixture and stirred for 60 s. Four drops of benzylamine were added and stirring was continued until the gel point was reached. The sample was left to age for one week. After which time the sample was ground into a powder and extracted by soxhlet extraction with dichloromethane. The resultant pale yellow powder was recovered and left to dry before catalyst testing.

5.1.2. Preparation of aerogel entrapped catalyst (4)

[RhCl(PPh$_3$)$_3$] 0.0037 g (4.00×10^{-6} mol) was dissolved in the minimum quantity of dichloromethane (4 drops), this catalyst solution was added to 3-methyl imidazolium bistrifluoromethanesulfonimide [Bmim][NTF$_2$] 1 cm^3 (0.00525 mol). TEOS, 0.919 g (0.00441 mol) was added and the mixture was stirred for 20 min. To this was added methanoic acid 2 cm^3, 2.44 g, (0.0530 mol) whilst stirring. The gelation time was less than 30 min.

The gel was covered and left to age for one week. After one week the monolith was removed and the ionic liquid was extracted by heating under reflux in dichloromethane. The product was a pale yellow monolith of frozen smoke. The sample was ground into a powder and left to dry before catalyst testing.

5.2. Catalyst testing

5.2.1. [RhCl(PPh$_3$)$_3$] (1), was prepared by a literature procedure [7]

The catalyst (0.0070 g **1**, 0.0156 g **2**, 0.0150 g **3**, 0.0158 g **4**) was weighed out and flushed with N$_2$, CH$_2$Cl$_2$ (10 cm^3) and styrene (1 cm^3, 8.73 mmol) were added. The autoclave was pressurised to 20 bar with H$_2$, stirred (1200 rpm) and heated to 100 °C for 30 min. Liquid products were analysed by GC/MS (Perkin–Elmer Turbo Mass fitted with a Restek RTX5MX column). Conversion was calculated by peak area relative to internal standard tetrahydropyran.

5.2.2. Digesting the entrapped catalysts for ICP/OES analysis

A mixture of conc. HCl (11.5 M, 2.5 cm^3) and conc. HNO$_3$ (16 M, 2.5 cm^3) was heated and added to the sample to be digested (0.01 g). The solution was stirred for 5 min then water was added to make the volume up to 100 cm^3. Once cooled a 10 cm^3 aliquot was submitted for analysis on a ThermoElemental IRIS Duo.

5.2.3. Preparing product solution for ICP/OES analysis

The sample was dried under reduced pressure to leave the solid residues. A preheated mixture of conc. HCl (11.5 M, 0.25 cm^3) and conc. HNO$_3$ (16 M, 0.25 cm^3) was added and the solution stirred to dissolve the residue. Water was added to make the volume up to 10 cm^3. Once cooled the solution was submitted for analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/ j.jorganchem.2005.03.038.

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