ELSEVIER

Journal of Organometallic Chemistry 627 (2001) 37–43

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Modified silica-heterogenised catalysts for use in aqueous enantioselective hydrogenations

Jim Jamis, John R. Anderson, Ron S. Dickson *, Eva M. Campi, W. Roy Jackson

Department of Chemistry, PO Box 23, Monash University, Vic. 3800, Australia

Received 25 September 2000; received in revised form 26 November 2000; accepted 26 November 2000

Abstract

Modified mesoporous silicas have been prepared, homogeneous organometallic catalysts incorporated and the resulting heterogeneous systems used as catalysts in aqueous enantioselective hydrogenation reactions. A series of catalysts in which the organometallic species was incorporated during gel synthesis generally gave good conversions but low ee values which were usually less than 25%. Preformed silicas with a narrow range of pore size (26 and 37 Å) and an amorphous silica (average pore size 68 Å) were modified by external surface deactivation and/or derivatization of the internal surface for potential tethering of the catalytic species. In general, excellent conversions (80–100%) but modest enantioselectivities (40–50%) were obtained when using 37 and 68 Å silicas, similar to those values obtained using unmodified silicas. Only low conversions were obtained using the modified 26 Å silicas. Pore volume measurements suggest that this is due to very restricted access to the pores when the tether is present. The results indicate that for aqueous hydrogenation the van der Waals interactions of the catalyst with the porous matrix are sufficiently strong to retain the catalyst, thus allowing for its reuse. No major advantage then appears to be gained by the use of potential internal tethers.

Keywords: Rhodium; Ruthenium; Asymmetric hydrogenation; Aqueous solution; Heterogenised catalyst; Silica

1. Introduction

Incorporation of homogeneous organometallic catalysts into hexagonal mesoporous silicas (HMS) and their use for enantioselective hydrogenation reactions in aqueous media have been described by us [1]. Recently, other workers have incorporated similar organometallic catalysts into silicas by adding the catalyst to a sol–gel matrix based on tetramethyl orthosilicate prior to drying [2]. Use of these materials as heterogeneous catalysts for the enantioselective hydrogenation of, e.g. itaconic acid gave quantitative conversion to materials with enantioselectivities of up to 78%. The catalysts were recoverable and reusable. Catalyst activity was enhanced by a hot aqueous bicarbonate wash which was reported to open blocked pores and create new ones [2].

Other workers have modified preformed mesoporous silicas by attaching potential tethers, e.g. by reaction with $(MeO)_3SiCH_2CH_2CH_2NH_2$ (3AMPS) [3]. Restriction of reaction to within the pores of the silicas has been achieved by blocking the surface hydroxyl groups by reaction with Ph_2SiCl_2 followed by attachment of potential tethers to internal surfaces, e.g. by reactions with 3AMPS [4] or $(MeO)_3SiCH_2CH_2CH_2CN$ (CETS) (subsquently hydrolysed to the carboxylic acid) [5].

In this paper we report experiments designed to compare the efficiency of our previous methodology (in which the catalysts were simply incorporated into silicas of appropriate pore sizes) with that using modified silicas containing tethers with potential ligands for binding the metal atoms.

2. Experimental

2.1. Instrumentation

^{1}H-NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz). The ^{1}H-NMR spectra

---

* Corresponding author. Tel.: +61-3-99054560; fax: +61-3-99059129.

E-mail address: dickson@smtp.monash.edu.au (R.S. Dickson).

0022-328X/01/$ - see front matter
PII: S0022-328X(00)00925-6

were run in D_2O solution with TMSP as the internal standard or in CD_3OD with TMS as the internal standard with chemical shifts measured in ppm. Solid state ^{31}P-NMR spectra were recorded on an INOVA-300 spectrometer using magic-angle spinning at 121.5 MHz and were referenced to P_2O_5. The optical yields were determined by polarimetry using a Perkin Elmer 1600 polarimeter by comparison with the literature values for the optically pure compounds: *N*-acetyl-(*R*)-phenylalanine, $[\alpha]_D^{26}$ $-51.8°$ ($C = 1$, EtOH) [6]; (*R*)-2-methylsuccinic acid, $[\alpha]_D^{20}$ $+16.88°$ ($C = 22.2$, EtOH) [7]. Ru and Rh analyses were carried out using a Varian Liberty 200 inductively coupled plasma emission spectrometer (ICP-AES) with diisobutylketone or water as solvent.

2.2. Materials and reagents

Benzene was dried over phosphorus pentoxide, decanted, distilled from fresh phosphorus pentoxide and stored over sodium wire. Tetrahydrofuran (THF) was stirred over KOH pellets, decanted and distilled under N_2 from sodium and benzophenone prior to use. Distilled water was used for all aqueous manipulations. Methanol was freshly distilled before use. All manipulations were carried out under N_2 and solvents degassed before use.

Itaconic acid (**3**); α-acetamidocinnamic acid (**1b**); bis(cycloocta-1,5-diene)dichlorodirhodium (I), [Rh-(COD)Cl]$_2$; (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, (+)-(BINAP); (2S,4S)-*N*-(*tert*-butoxycarbonyl) - 4 - (diphenylphosphino) - 2 - [(diphenylphosphino)methyl]pyrrolidine, (BPPM); [(*R*)-(+)-2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl]chloro(*p*-cymene)-ruthenium chloride, [Ru-BINAP(cymene)] and the dimer, dichloro[(*R*)-(+)-2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl]ruthenium(III) dimer triethylamine adduct, [(Ru–BINAP)$_2$] were obtained from commercial sources. Sodium α-acetamidocinnamate (**1a**) was prepared by stirring α-acetamidocinnamic acid (**1b**) (2.03 g, 9.9 mmol) in an aqueous solution of sodium hydroxide (10 ml) containing 9.8 mmol of NaOH. Excess acid was removed by filtration and the sodium salt isolated by the removal of water under vacuum at ambient temperature.

2.3. Silicas and modified silicas

Ordered mesoporous silica (HMS) of 26 Å average pore size was synthesised in the presence of dodecylamine in water with ethanol as a co-solvent by following procedures similar to those reported previously [8]. Before impregnation, the hexagonal mesoporous silica (HMS) was calcined in air at 550°C for 4 h to remove the structurally incorporated template and fully hydrated by saturation with water vapour at ambient temperature in a desiccator over saturated aqueous NH_4Cl for 48 h. The water content determined by TGA was 21%. The average pore size was confirmed as 26 Å by nitrogen adsorption at −196°C using a standard procedure [9]. An HMS of 37 Å average pore size was prepared following the published procedure [10] and the average pore size confirmed using the standard procedure [9] (see Fig. 1).

An amorphous mesoporous silica was obtained by first preparing a solution of triethanolamine (3 ml), *N*,*N*-dimethylformamide (2 ml) and phosphoric acid (10 ml, 85% w/w) in water (125 ml). A portion of this solution (10 ml) was added with rapid stirring to a

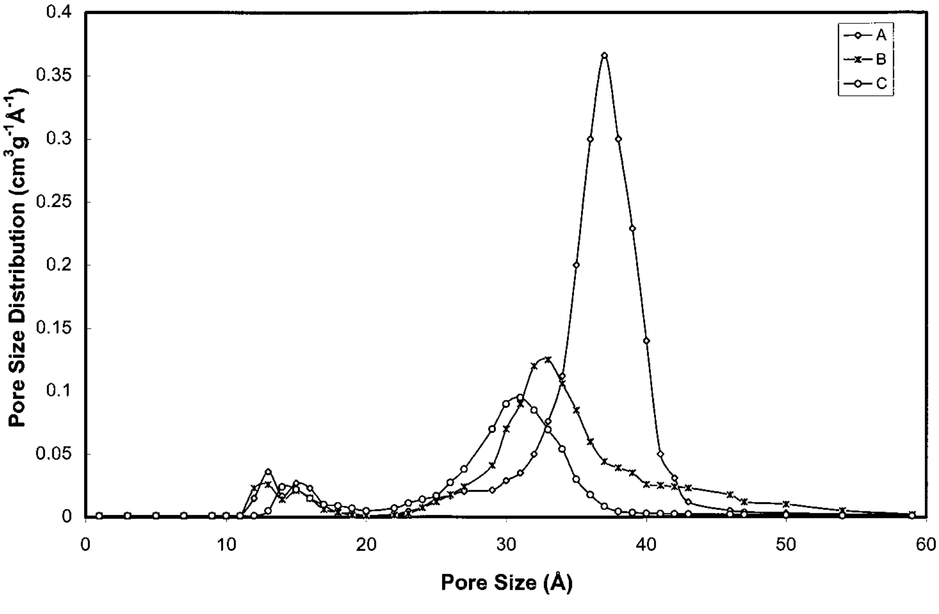


Fig. 1. Pore size distributions for unmodified silicas, [A, Si (37); B, CO_2HSi (37); C, NH_2Si (37)].

solution (40 ml) made up by adding a solution of sodium silicate (density 1.37 g ml^{-1}) (5 ml) and tetramethylammonium bromide (3 g) in water (125 ml). The resulting gel was left to stand overnight, washed with water, filtered and dried overnight at ambient temperature. Calcination at 550°C for 72 h gave a white powder shown to be amorphous by XRD and characterised as above as having an average pore size of 68 Å.

Selected silicas were modified using standard literature procedures [4b] to prepare:

The silica with average pore size 26 Å and the amorphous silica (68 Å) were treated with Ph_2SiCl_2 to give PhSi (26) and PhSi (68), respectively.

Silicas (26 and 37 Å) treated with 3AMPS gave NH_2Si (26) and NH_2Si (37).

Silicas (26 and 37 Å) treated with Ph_2SiCl_2 followed by 3AMPS gave Ph/NH_2Si (26) and Ph/NH_2Si (37).

The silica (37 Å) was reacted with CETS [4b] and hydrolysed using H_2SO_4 50% v/v to the acidic form to give CO_2HSi (37) [5b,c].

2.4. Incorporation of a ruthenium complex into prepared silicas

Commercial Ru–BINAP(cymene) (4.64 mg, 0.005 mmol) was dissolved in dry, deoxygenated benzene (5 ml) by stirring for 30 min and the resulting solution added, using a syringe, to a Schlenk flask containing the pretreated HMS (100 mg). The mixture was stirred for 16 h at ambient temperature, filtered under dry N_2 and washed three times with degassed benzene (3 × 5 ml). The filtrate and washings were collected and evaporated in vacuo in order to determine the amount of catalyst absorbed. The impregnated support was dried under vacuum at ambient temperature for 4 h and then used immediately. In this manner the following incorporated Ru catalysts were prepared:- Ru/PhSi (26 and 68); Ru/NH_2Si (26 and 37); $Ru/Ph/NH_2Si$ (26 and 37); and Ru/CO_2HSi (37).

2.5. Preparation of sol–gel entrapped catalyst species

A modification of a two step procedure described previously [2] was used. A rhodium catalyst solution was prepared by stirring $[Rh(COD)Cl]_2$ (10.85 mg, 0.022 mmol) with the ligand BPPM (24.92 mg, 0.044 mmol) in dry, deoxygenated THF (2.5 ml) for 30 min. Aqueous NH_4OH (0.44 ml of 0.1 M) and the prepared catalyst solution were added simultaneously but separately to a Schlenk flask containing a pre-stirred mixture (15 min) of HCl (1.2 ml of a HCl solution, pH 1.96), $(EtO)_4Si$ (3.8 ml) and MeOH (3.5 ml). The mixture was stirred for 5 min at ambient temperature. Addition of Et_3N (0.5 ml) resulted in gel formation in a few minutes. The gel was dried, crushed, washed thoroughly with boiling CH_2Cl_2, sonicated for 30 min in CH_2Cl_2 and dried under vacuum to constant weight. The rhodium content of the washings was ca. 5% of the Rh used (as estimated by ICP-AES analysis).

A commercial Ru–BINAP(cymene) catalyst (20.41 mg, 0.022 mmol) was also incorporated using the above procedure. The washings contained ca. 6% of the Ru used.

Two other ruthenium containing gels were prepared in which solutions of either $(Ru–BINAP)_2$ (16.92 mg, 0.01 mmol) or Ru–BINAP(cymene) (12.06 mg, 0.013 mmol) in THF (2.5 ml) were added simultaneously but separately with the NH_4OH (0.44 ml) to a pre-stirred mixture of HCl (1.2 ml of a HCl solution, pH 1.96), $(EtO)_4Si$ (3.8 ml), Ph_2SiCl_2 (0.84 ml) and MeOH (3.5 ml). The mixture was stirred for 5 min at ambient temperature. Addition of 3AMPS (1 ml) gave a gel. The gel was dried, crushed, washed thoroughly with boiling CH_2Cl_2, sonicated for 30 min in the same solvent and dried under vacuum until constant weight was achieved. The ruthenium content of the washings was negligible (ICP-AES).

2.6. Hydrogenation procedure

The procedure was essentially identical to that described previously [1]. A solution of the substrate (200 mg) in degassed distilled water or $MeOH.H_2O$ (1:1, v/v) (10 ml) and the impregnated silica (100 mg) were hydrogenated under the reported hydrogen pressure with stirring.

Product isolation from reactions of itaconic acid (**3**) involved washing the silica with distilled water (3 × 5 ml) and evaporating combined filtrate and washings. ^{1}H-NMR spectroscopy was used to determine the extent of reaction by integration of the CH_2 signals at δ 2.6 and 2.7 (D_2O) in the product and δ 3.4 (D_2O) in itaconic acid (**3**).

In the case of sodium α-acetamidocinnamate (**1a**), the silica was washed with distilled water (3 × 15 ml). The combined filtrate and washing were evaporated to ca. 10 ml residue and acidified with 1 M HCl. The free acid was extracted with ethyl acetate (3 × 15 ml) and the extract was dried and evaporated. The conversion was determined by integration of the CH_3CON peaks at δ 1.92 (CD_3OD) for *N*-acetylphenylalanine (**2**) and δ 2.1 (CD_3OD) for α-acetamidocinnamic acid (**1b**).

The product from reactions of the free acid (**1b**) was isolated by washing the silica with $MeOH–H_2O$ (1:1, v/v) (3 × 15 ml). The combined washing and filtrate were evaporated and the residue quickly dissolved in 0.5 M NaOH (5 ml) and filtered through a Celite pad. The flask and Celite pad were washed with water (2 × 20 ml). The combined filtrate and washings were reduced to ca. 10 ml under vacuum and extracted with ethyl acetate (2 × 20 ml). The aqueous layer was acidified and the product isolated as above.

Table 1
Heterogeneous hydrogenation of sodium α-acetamidocinnamate (**1a**) in water [a,b]

Entry	Catalyst	Run [c]	Temp. (°C)	Time (h)	Conv. (%)	Ee (%), (*R*)
1	Ru/NH_2Si (26)	0	70	72	21	
2	Ru/NH_2Si (37)	0	70	72	100	49
3	Ru/PhSi (26)	0	70	72	99	44
4	Ru/PhSi (26)	1	70	72	99	41
5	Ru/PhSi (26)	2	70	72	99	40
6	Ru/PhSi (68)	0	70	72	99	43
7	Ru/PhSi (68)	1	70	72	99	42
8	Ru/PhSi (68)	2	70	72	99	39
9	Ru/PhSi (68)	0	70	22	97	42
10	Ru/PhSi (68)	1	70	22	95	42
11	Ru/PhSi (68)	2	70	22	87	40
12	Ru/Ph/NH_2Si (26)	0	70	72	17	
13	Ru/Ph/NH_2Si (37)	0	70	72	100	51
14	Ru/Ph/NH_2Si (37)	1	70	72	97	48
15	Ru/Ph/NH_2Si (37)	2	70	72	97	44
16	Ru/Ph/NH_2Si (37)	0	70	22	89	50
17	Ru/Ph/NH_2Si (37)	1	70	22	80	47
18	Ru/Ph/NH_2Si (37)	2	70	22	67	45
19	Ru/CO_2HSi (37)	0	60	72	91	41
20	Ru/CO_2HSi (37)	1	60	72	85	37
21	Ru/CO_2HSi (37)	2	60	72	80	37
22	Ru/CO_2NaSi (37) [d]	0	60	72	100	46
23	Ru/CO_2NaSi (37) [d]	1	60	72	100	45
24	Ru/CO_2NaSi (37) [d]	2	60	72	98	45

[a] Hydrogenation using 2.76 Mpa H_2.

[b] All solutions were examined for metal content by ICP-AES and leaching was found to be negligible.

[c] Number of previous runs with the catalyst (reuse).

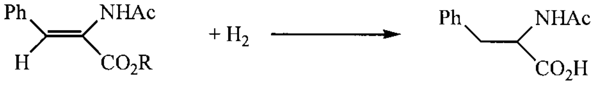
[d] CO_2HSi (37) treated with $NaHCO_3$ prior to incorporation of [Ru].

3. Results and discussion

3.1. Reactions involving catalysts prepared from modified silicas

The results of hydrogenations of sodium acetamidocinnamate (**1a**) in aqueous solutions using a ruthenium catalyst incorporated into modified silicas are summarised in Table 1 (Scheme 1).

The catalyst formed by incorporation of Ru–BINAP(cymene) into the silica with average pore size 26 Å which had been treated with 3AMPS (Ru/NH_2Si (26)) gave only a low conversion and no ee (entry 1). In contrast similar modification of a 37 Å silica, Ru/NH_2Si (37) led to complete conversion and a 49% ee (entry 2) comparable with values using the same catalyst and unmodified silica [1]. A reaction in water carried out using a mixture of the unmodified silica Si (37) together with the Ru–BINAP(cymene) catalyst gave only 1% conversion, confirming the lack of catalytic activity of non-incorporated ruthenium species. External surface deactivation of both the 26 Å, Ru/PhSi (26) and 68 Å, Ru/PhSi (68) silicas by treatment with Ph_2SiCl_2 [4] led to systems which again gave complete conversions, even after two recoveries and reuse with ee's all 39–44% (entries 3–8). Reactions for a shorter time (22 h) gave incomplete conversion. Recovery of the catalyst and reuse under the shorter reaction time conditions (entries 9–11) showed a small decrease in conversion but no significant change in enantioselectivity. External surface deactivation with Ph_2SiCl_2 followed by derivatisation of the internal surface with 3AMPS of the silicas 26 Å, Ru/Ph/NH_2Si (26), and 37 Å, Ru/Ph/NH_2Si (37) gave, as expected, results almost identical to those obtained where the treatment with Ph_2SiCl_2 had been omitted (compare entry 12 with entry 1 and entries 13–15 with entry 2). Reactions using the Ru/Ph/NH_2Si (37) catalyst system were repeated using the shorter reaction time (22 h). Again recovery and reuse led to some loss of conversion but little change in enantioselectivity. The possibility that the amino function may have been protonated and thus become unlikely to coordinate to a cationic



(**1a**); R = Na
(**1b**); R = H

(**2**)

Scheme 1.

Table 2
Pore size and pore volumes of modified silicas

Entry	Silica	Pore Size (Å) [a]	Pore volume (cm^3 g^{-1})
25	Si (37)	37	0.99
26	NH_2Si (37)	31	0.45
27	Ph/NH_2Si (37)	32	0.41
28	Si (26)	26	0.86
29	NH_2Si (26)	23	0.28
30	CO_2HSi (37)	32	0.79

[a] Indicates most frequent pore size in the distribution.

ruthenium species was considered. Thus alternative tethers containing either a carboxylic acid function or its carboxylate analogue were prepared, Ru/CO_2HSi (37) and Ru/CO_2NaSi (37). Reactions using these catalyst systems at a slightly lower temperature (60°C) all gave conversions between 80–100 and ee's 37–46% even after two recoveries and reuse (entries 19–24).

3.2. Pore volume measurements

The pore volumes of the 26 and 37 Å silicas were measured [9] and compared with similar measurements for some of the modified silicas and the results summarised in Table 2.

Modification of Si (37) either by treatment with 3AMPS or by prior treatment with Ph_2SiCl_2 followed by 3AMPS gave materials NH_2Si (37) and Ph/NH_2Si (37) with pore volumes 0.45 and 0.41 cm^3 g^{-1} (entries 25–27). Fig. 1 shows the distribution of pore size for Si (37) and the modified materials NH_2Si (37) and CO_2HSi (37). The peaks have been broadened and shifted to a smaller pore size. Treatment of Si (26) with 3AMPS gave a material NH_2Si (26) with a pore volume of 0.28 cm^3 g^{-1} (entries 28 and 29). The lack of reactivity when NH_2Si (26) was used as the matrix for attempted hydrogenations involving Ru-BINAP (cymene) as the catalyst system (see Table 1, entries 1 and 12) could therefore be attributed to difficulties in incorporating a molecule of the catalyst and a molecule of the substrate in the same cavity.

Introduction of the tether containing a carboxylic function gave a material CO_2HSi (37) with a pore volume of 0.79 cm^3 g^{-1} (entry 24) smaller than that of Si (37) but significantly larger than that of both NH_2Si (37) and Ph/NH_2Si (37). This difference could be due to incorporation/retention of fewer tether groups. There was considerable tailing in the pore size distribution which could possibly be attributed to the hydrolysis process. However, using this material as Ru/CO_2HSi (37) gave an almost identical conversion and ee to reactions involving RuSi (37) and its amino-modified analogues (see Table 1, entries 2 and 13–15).

3.3. Solid state ^{31}P-NMR measurements

Solid state ^{31}P-NMR spectra of Ru–BINAP(cymene) and Ru/Si (37), where this catalyst had been incorporated into Si (37) gave spectra with identical major peaks at 31 and 44 ppm. A further spectrum of the Ru/Si (37) after it had been used and recovered from a hydrogenation was recorded and gave three major peaks at 31, 57 and 71 ppm. No peaks were observed in the region around 0 ppm where free phosphine would be expected to resonate. One of these peaks could be due to adventitious BINAP oxide but its chemical shift is almost coincident with the peak at 31 ppm assigned to metal coordinated phosphorus. In addition IR could not be used to establish the presence of phosphine oxides due to the overlap of P–O and Si–O absorption regions.

3.4. Hydrogenations using catalyst systems with Ru or Rh incorporated into silica gels

A series of catalysts was prepared in which a ruthenium or rhodium compound was added to tetraethoxysilane and the resulting mixture converted into a gel using the two step procedure described by Gelman et al. [2]. It was found necessary to add some triethylamine to induce gel formation in this system based on $(EtO)_4Si$ in contrast to the literature preparation based on $(MeO)_4Si$ [2]. The resulting catalysts were used for hydrogenations of aqueous solutions of sodium acetamidocinnamate (**1a**) and itaconic acid (**3**) and the results summarised in Table 3.

The amount added was such that the mol ratio of metal:substrate was the same as in the experiments described above. Similar reaction conditions were also used to facilitate comparisons. Use of the catalyst based on Ru–BINAP(cymene) initially gave a lower conversion (69%) but a comparable ee (41%) (entry 31) to those reported by us using preformed silicas as described above and previously [1]. In contrast to these results, recovery and reuse led to a decrease in conversion and ee (entries 32 and 33). Two gels were prepared in which 3AMPS was used in place of Et_3N and some Ph_2SiCl_2 was also added. It has been reported that use of Ph_2SiCl_2 leads to the formation of gels in which the external surfaces are capped [11]. Both catalysts however were virtually inactive (entries 34 and 35). Hydrogenation of an aqueous solution of itaconic acid (**3**) using the sol–gel system used in entries 31–33 gave conversion (100%) and ee (15%) virtually identical to that reported by us previously using a catalyst based on preformed mesoporous silica [1]. A gel containing Rh–BPPM was prepared as for the Ru–BINAP gel and used as a catalyst for the hydrogenation of aqueous solutions of sodium acetamidocinnamate (**1a**). The initial reaction of the cinnamate (**1a**) gave a low conver-

Table 3
Heterogeneous hydrogenation of sodium α-acetamidocinnamate (**1a**) and itaconic acid (**3**) in water using sol–gel systems [a]

Entry	Substrate	Catalyst	Run [b]	Time (h)	Temp. (°C)	Pressure (MPa)	Conv. (%)	Ee (%)
31	**1a**	Ru–BINAP-(cymene) [c]	0	92	60	2.76	69	41
32	**1a**	Ru–BINAP–(cymene) [c]	1	92	60	2.76	50	15
33	**1a**	Ru–BINAP–(cymene) [c]	2	92	60	2.76	39	
34	**1a**	Ru–BINAP–(cymene) [d]	0	72	70	2.76	5	
35	**1a**	$(Ru–BINAP)_2$ [d]	0	72	70	2.76	4	
36	**3**	Ru–BINAP–(cymene) [c]	0	46	60	1	100	15
37	**1a**	Rh–BPPM [c]	0	46	50	0.2	37	21
38	**1a**	Rh–BPPM [c]	1	46	50	0.2	88	
39	**1a**	Rh–BPPM [c]	2	46	50	0.2	100	
40	**3**	Rh–BPPM [c]	0	46	50	0.3	100	24
41	**3**	Rh–BPPM [c]	1	46	50	0.3	75	15
42	**3**	Rh–BPPM [c]	2	46	50	0.3	100	

[a] All solutions were examined for metal content by ICP-AES and leaching was found to be negligible.

[b] Number of previous runs with the catalyst (reuse).

[c] Et_3N used to form gel.

[d] 3AMPS used to form gel in presence of Ph_2SiCl_2.

sion (37%) and ee (21%) (entry 37) compared to quantitative conversion and ee (49%) when preformed silicas were used [1]. Recovery and reuse led to increased conversions (88 and 100%) but gave a racemic product (entries 38 and 39), consistent with formation of highly active but non-enantioselective catalyst which could be small rhodium particles. Solid state ^{31}P-NMR spectra of recovered material (δ 21.8 ppm) indicated that not all of the Rh–P bonds had broken (δ 24.8 ppm before reaction). However it is not possible to establish whether these Rh–P containing species are the active species leading to racemic products. Hydrogenation of itaconic acid (**3**) using this catalyst system initially gave a quantitative conversion with 25% ee (entry 40), identical to the result obtained using a preformed silica. High conversions were obtained for recovered and reused catalyst but with an eventual total loss of enantioselectivity (entries 41 and 42). A closely related reaction has been reported to give a similar high conversion but improved ee (78%) [2].

Some hydrogenations of α-acetamidocinnamic acid (**1b**) in a methanol/water, 1/1 solvent system were carried out using the Rh–BPPM containing gel and the results summarised in Table 4. The initial reaction gave a quantitative conversion with a reasonable ee (59%) (entry 43), comparable with that obtained using a catalyst involving apreformed silica (100% conversion, 80% ee) [1]. However, use of the gel-based catalyst led to a major loss of Rh (41%) and the recovered catalysts showed decreasing reactivity and enantioselectivity (entries 44 and 45).

These results contrast with the reported use of a similar material for hydrogenations of itaconic acid (**3**) with methanol/benzene, 3/1 as solvent where the ee's were maintained at 67% but the conversions decreased with repeated use [2]. These authors also reported that catalyst activity could be improved by treatment with hot aqueous sodium bicarbonate solution but this treatment proved ineffective in our case (entry 46).

3.5. Pore volumes of gel-based catalysts

The pore volume of the Rh–BPPM gel recovered after use from the hydrogenation of sodium acetamidocinnamate (**1a**) (Table 3, entry 37) was found to have increased to a value of 0.37 $cm^3\ g^{-1}$ from an initial value of 0.21 $cm^3\ g^{-1}$ presumably by a hydrolytic process. These values are consistent with an increase in conversion (compare entries 37 and 38). This, coupled with the total loss of enantioselectivity, could be explained by the improved access of the substrate to internal pores containing active catalyst species or possibly finely divided rhodium. The pore volume of the gel incorporating Ru–BINAP(cymene) involving Et_3N was 0.45 $cm^3\ g^{-1}$. In contrast, the gels obtained when Et_3N was replaced by 3AMPS for preparations involving both Ru–BINAP(cymene) and $(Ru–BINAP)_2$ were

Table 4
Heterogeneous hydrogenation of α-acetamidocinnamic acid (**1b**) in $MeOH–H_2O$ (1:1 v/v) using a sol–gel system [a]

Entry	Run [b]	Conv. (%)	Ee (%)	Rh leached (%) [c]
43	0	100	59	41
44	1	79	47	Neg
45	2	57	26	Neg
46	3 [d]	8		Neg

[a] Hydrogenation at 50°C for 20 h using 0.2 MPa H_2 and sol–gel system containing Rh–BPPM, prepared using Et_3N to form gel.

[b] Number of previous runs with the catalyst (reuse).

[c] Measured by ICP-AES.

[d] The recovered and reused catalyst was treated with boiling 2% aqueous $NaHCO_3$ solution.

essentially non-porous. These results are consistent with the lack of catalytic reactivity of the latter systems (compare entires 34 and 35 with entry 31, Table 3).

4. Conclusion

The hydrogenation catalysts obtained by incorporating Ru or Rh species into mesoporous silicas which have been modified by external surface deactivation and/or internal derivatisation show no improvement over catalysts prepared using the non-modified mesoporous silicas when there is an effective match between pore size and catalyst dimension. The results vindicate the approach to developing recoverable and reusable heterogeneous catalysts by incorporating commercially available homogeneous catalysts in non-modified silicas.

Acknowledgements

This project has been supported by funds from the Australian Research Council and we thank Johnson Matthey Pty Ltd. for loan of precious metals. We also thank Dr F. Separovic, School of Chemistry, University of Melbourne (solid state NMR spectra), John Barnard, Department of Chemical Engineering, Monash University (pore size/pore volume measurements) and Dr R. Hodges, School of Applied Chemistry, Monash University (ICP-AES measurements).

References

[1] J. Jamis, J.R. Anderson, R.S. Dickson, E.M. Campi, W.R. Jackson, J. Organomet. Chem. 603 (2000) 80.

[2] F. Gelman, D. Avnir, H. Schumann, J. Blum, J. Mol. Catal. A: Chem. 146 (1999) 123.

[3] C.-J. Liu, S.-G. Li, W.-Q. Pang, Chi.-Ming Che, Chem. Commun. (1997) 65.

[4] (a) A. Bleloch, B.F.G. Johnson, S.V. Ley, A.J. Price, D.S. Shephard, A.W. Thomas, Chem. Commun. (1999) 1907. (b) D.S. Shephard, W. Zhou, T. Maschmeyer, J.M. Matters, C.L. Roper, S. Parsons, B.F. Johnson, M.J. Duer, Angew. Chem. Int. Ed. Engl. 37 (1998) 2719. (c) J. Liu, X. Feng. G.E. Fryzell, L.-Q. Wang, A.Y. Kim, M. Gong, Adv. Mater. 10 (1998) 161.

[5] (a) J. Macquarrie, D.B. Jackson, J.E.G. Mdoe, J.H. Clark, New J. Chem. 23 (1999) 539. (b) J.A. Elings, R. Ait-Meddour, J.H. Clark, D.J. Macquarrie, Chem. Commun. (1998) 2707. (c) J.H. Clark, A.J. Butterworth, S.J. Tavener, A.J. Teasdale, S.J. Barlow, T.W. Bastock, K. Martin, J. Chem. Tech. Biotechnol. 68 (1997) 367.

[6] F. Knoop, J.G. Blanco, Hoppe-Seyler's Z. Phys. Chem. 146 (1925) 272.

[7] (a) J.P. Genet, C. Pinel, V. Ratovelomana-Vidal, S. Mallart., X. Pfister, L. Bischoft, M.C. Cano De Andrade, S. Darses, C. Galopin, J. Laffittee, Tetrahedron: Asymmetry 5 (1994) 675. (b) E. Berner, R. Leonardsen, Liebigs Ann. Chem. 538 (1939) 1.

[8] P.T. Tanev, T.J. Pinnavaia, Science 267 (1995) 865.

[9] P.A. Webb, C. Orr, Analytical Methods in Fine Particle Technology, Micrometrics Instrument Corporation, Norcross, GA, USA, 1997, p. 53.

[10] R. Mokaya, W. Zhou, W. Jones, J. Mater. Chem. 10 (2000) 1139.

[11] D.J. Macquarrie, Green Chem. 1 (1999) 195.