Reactions in aqueous media using VPI-5 micropore impregnated with rhodium complexes

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Abstract

Two rhodium catalysts $ClRh(PPh_3)_3$ (1) and $HRh(CO)(PPh_3)_3$ (2) have been sorbed with the aluminophosphate molecular sieve VPI-5 and the resulting materials evaluated as catalysts for attempted hydrogenation and hydroformylation reactions of the water-soluble alkene, sodium 4-styrenesulfonate in aqueous media. Hydrogenation reactions at 50°C proceeded smoothly, giving good yields of sodium 4-ethylbenzenesulfonate using catalyst (1)/VPI-5. Attempted hydroformylations at 70–90°C using catalysts (1)/VPI-5 and (2)/VPI-5 gave low yields of the expected aldehydes together with substantial amounts of poly(sodium 4-styrenesulfonate). The catalysts were readily separable after reaction and could be re-used with relatively low loss of rhodium and reactivity. Characterisation of impregnated catalysts (before use) by spectroscopic methods proved to be difficult but no evidence for significant decomposition was obtained other than the release of a small amount of triphenylphosphine ligand from either (1) or (2). The evidence is also consistent with the rhodium complexes being retained in the micropores of VPI-5.

Keywords: Hydroformylation; Hydrogenation; VPI-5; Rhodium; Aqueous media

1. Introduction

In general, chemical conversions, particularly those in industry, are more conveniently carried out using heterogeneous catalysts since these are readily recovered at the end of the reaction. On the other hand, homogeneous catalysts are known to be advantageous, since with their use many reactions exhibit high reactivity and chemoselectivity under mild conditions [1]. Immobilisation of the catalytically active organometallic species is an attractive strategy

which preserves the best features of homogeneous systems whilst enhancing the economic viability of the process by facilitating catalyst recovery and minimising the risk of product contamination with toxic transition metals [1–3].

Most reactions involving homogeneous metal catalysts have utilised non-aqueous systems. Modified catalyst systems with enhanced water solubility have involved the purpose directed synthesis of ligands bearing hydrophilic substituents [4]. There is a need for methods which utilise established organometallic catalysts in aqueous media without the need for extensive ligand modifications. One method is to impregnate organometallic catalysts into the pores of

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aluminosilicates and aluminophosphates [5]. The aluminophosphate VPI-5 is a particularly attractive example as its large pore structure (ca. 12 Å pore diameter) allows for the incorporation of many organometallic compounds commonly used as homogeneous catalysts. It should be noted that in contrast to the polymer immobilisation technique [2,3] or the use of specially designed water soluble ligands, the impregnation technique allows for the use of off-the-shelf, commercially available catalysts with excellent potential for facile recovery and re-use.

In this paper we describe the impregnation of VPI-5 with two commonly used rhodium catalysts, $ClRh(PPh_3)_3$ (1) and $HRh(CO)(PPh_3)_3$ (2) and the use, recovery, and re-use of the resulting materials in hydrogenation and hydroformylation reactions of sodium 4-styrenesulfonate.

2. Experimental

2.1. General methods

The rhodium complexes $ClRh(PPh_3)_3$ (1) and $HRh(CO)(PPh_3)_3$ (2) were purchased from Aldrich. VPI-5 was prepared according to an optimised method [6]. Manipulations of rhodium complexes were carried out under an atmosphere of nitrogen. Solvents were distilled and deoxygenated before use. Rhodium analysis was carried out on a Varian Liberty 200 inductively coupled plasma emission spectrometer. IR spectra (KBr pellets) were recorded on a Perkin-Elmer 1600 FTIR spectrometer. ^1H, ^{13}C and ^{31}P NMR solution spectra were recorded on a Bruker AC-200 spectrometer. Solid state ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker MSL 400 spectrometer using magic-angle spinning at frequencies in the range 4–10 kHz. Solid state ^{31}P spectra were referenced to ADHP.

Negative ion electrospray mass spectrometry was performed on a VG Bio-Q triple quadrupole mass spectrometer in the electrospray mode. Gas chromatography (GLC) analysis was carried out using a 3700 Varian gas chromatograph

(capillary column 12QC5/BP5 1.0 μm) using a temperature program 100°C, 1 min, → 200°C at 10°C/min.

2.2. Impregnation of $ClRh(PPh_3)_3$ (1) and $HRh(CO)(PPh_3)_3$ (2) into VPI-5

Dehydration of freshly prepared VPI-5 was carried out under optimal conditions as described previously [6]. A sample (200 mg) of the dried VPI-5 was added to a solution of $HRh(CO)(PPh_3)_3$ (2) (8 mg, 0.0087 mmol) in dry degassed benzene (10 ml) and the suspension was stirred for 24 h at ambient temperature under nitrogen. The solid was collected by filtration, washed with degassed benzene (10 ml) and dried under vacuum to give the impregnated catalyst (2)/VPI-5. The combined washings and filtrate were evaporated and shown to contain less than 1 mg of material. A similar method was used to prepare catalysts with different loadings of (2).

In a similar manner, $ClRh(PPh_3)_3$ (1) (8 mg, 0.0087 mmol) was incorporated into VPI-5 (200 mg) to give the impregnated catalyst (1)/VPI-5.

2.3. Catalytic reactions

Reactions with H_2 and H_2/CO were carried out in a Parr 100 ml stainless steel autoclave with a glass liner. The temperature was measured using a thermocouple inserted between the autoclave and the heating block.

Sodium 4-styrenesulfonate (3) (300 mg, 1.45 mmol) and a sample of either (1)/VPI-5 (208 mg) or (2)/VPI-5 (208 mg) were placed in the autoclave under N_2, degassed water (10 ml) was added and, after closure, the autoclave was pressurized with H_2 or H_2/CO (1:1) to 400 psi (2.76 MPa). The autoclave was heated and stirred at a range of temperatures from ambient to 90°C for 20 h. The autoclave was cooled and the catalyst separated by filtration and washed with water (3 × 5 ml). The filtrate was evaporated to dryness under vacuum (ca. 1 mm) at ambient temperature and a portion of the residue

analyzed by ^{1}H NMR spectroscopy (D_2O solution).

A typical hydrogenation reaction at 50°C with (1)/VPI-5 gave sodium 4-ethylbenzene-sulfonate (4) (307 mg, 100%); ^{1}H NMR (D_2O): δ(ppm) 1.21 (t, J 7.6 Hz, 3H, CH_3), 2.70 (q, J 7.6 Hz, 2H, CH_2), 7.40 (d, J 8.2 Hz, 2H, ArH), 7.73 (d, J 8.2 Hz, 2H, ArH). The p-toluidinium salt had a mp and mixed mp of 207–208°C, identical to the value of an authentic sample. Elemental analysis (%), found: C, 61.7; H, 6.9; N, 4.5. $C_{15}H_{19}NO_3S$ requires C, 61.4; H, 6.5; N, 4.8.

A typical hydroformylation reaction at 70°C with (2)/VPI-5 gave a product (316 mg) which was shown by ^{1}H NMR (D_2O) to consist of starting material (30%), the branched-chain aldehyde (5) and its hydrate (6), (total 30%), and polymer (7) (40%). ^{1}H NMR (D_2O): for (5): 1.42 (d, J 7.2 Hz, 3H, CH_3), 3.85 (m, 1H, CH), 7.38 (d, J 8.1 Hz, 2H, ArH), 7.83 (d, J 8.1 Hz, 2H, ArH), 9.61 (bs, 1H, CHO); for (6): 1.30 (d, J 7.0 Hz, CH_3), 2.99 (m, 1H, CH), 5.17 (d, J 6.7 Hz, 2H, CH(OH)$_2$), 7.45 (d, J 8.1 Hz, 2H, ArH), 7.83 (d, J 8.1 Hz, 2H, ArH); for polymer (7): 1.0–2.0 (m, aliphatic), 6.1–7.0 (m, ArH), 7.3–7.8 (m, ArH).

The product mixture was reduced with sodium borohydride (400 mg) in water (5 ml) for 30 min at ambient temperature. The ^{1}H NMR spectrum of the resulting material showed no absorptions for (5) or (6) but peaks for the alcohol (8). ^{1}H NMR (D_2O): 1.25 (d, J 7.0 Hz, 3H,

CH_3), 3.05 (m, 1H, CH), 3.75 (d, J 6.9 Hz, 2H, CH_2O), 7.46 (d, J 8.2 Hz, 2H, ArH), 7.77 (d, J 8.2 Hz, 2H, ArH).

2.4. Catalyst recovery and reuse

Two series of reactions were carried out using (1)/VPI-5 and (2)/VPI-5 in which the catalysts were recovered by centrifugation, washed (3 × 5 ml H_2O) and immediately reused with rigorous exclusion of air. A sample of the supernatant reaction solution (15 ml) plus the aqueous washings was acidified with nitric acid such that the solution was 0.1 M in HNO_3 when made up to 50 ml. The Rh was determined by emission spectroscopy against a standard solution (50 ppm by weight of Rh).

3. Results and discussion

3.1. Catalyst preparation and characterisation

Catalysts prepared as described above were shown to readily adsorb or occlude the rhodium compound (2) (8 mg) in VPI-5 (200 mg) from benzene solution (10 ml) such that the resulting material contained ca. 4 wt% of complex. A small amount of triphenylphosphine (0.4 mg) was recovered in the solution together with ca. 0.2 mg of other unidentified material. If this triphenylphosphine resulted from the loss of not more than one triphenylphosphine per rhodium

Table 1
Sorption of HRh(CO)(PPh$_3$)$_3$ (2) with VPI-5 at ambient temperature

Amount of complex presented [a] (mg)	Residue recovered (mg)	PPh$_3$ in residue (mg)	[Rh] sorbed (%)	Fraction of pore volume occupied [b] (%)
8	0.6	0.4	98	ca. 25
20	2.8	1.3	93	ca. 60
60	28	na	ca. 50	ca. 100
100	68	2.8	32	ca. 100

[a] With 200 mg VPI-5 slurried in benzene (10 ml).

[b] Assuming all of sorbed complex present in pores of VPI-5; uncertainty in estimation of the Van der Waal's size of the complex leads to an uncertainty of about ± 10% of the recorded figures.

atom then this represents loss of 18% of (2). It can be estimated that this quantity of rhodium complex (7.8 mg) would occupy ca. 25% of the pore volume of VPI-5. This estimate is based on the N_2-accessible pore volume of 0.20 cm^3 g^{-1} [6]. Greater uptake of the rhodium complex (2) occurred when the same amount of VPI-5 (200 mg) was presented with greater amounts of complex. The results are summarised in Table 1.It can be seen that the VPI-5 easily sorbed a high percentage of a 20 mg sample of (2) which results in a material with a 60% occupancy of available pore volume. In contrast, only ca. 50% of a large 60 mg sample of (2) was sorbed, resulting in a calculated 100% occupancy of available pore volume. This suggests that most of the rhodium complex is occluded within the pores of VPI-5 rather than adsorbed on the external surface. In confirmation, treating VPI-5 with an even larger quantity of complex (2) (100 mg) resulted in no further increase in the quantity of sorbed (2). Nevertheless, we cannot exclude the possibility that some of the rhodium complex is sorbed onto the external surface of the VPI-5.

In order to assess the location of the sorbed complex (2), pore volume measurements were made on a VPI-5 sample (200 mg) containing sorbed complex (2). Nitrogen sorption at 77 K was used on samples outgassed for 24 h at ambient temperature to obviate decomposition of the complex. A sample containing 7.54 mg of complex (2) gave a measured pore volume which was 75% of the pore volume of a complex-free sample. This result is in good agreement with the data in Table 1 showing the fraction of pore-volume occupied for a similar sample as ca. 25% and indicates that the complex is largely included in the pores of the VPI-5 rather than adsorbed on the external surface.

Evidence in support of the proposal that most of (2) is occluded within the pores came from a study of the IR spectra of the resulting materials. The strong ν_{CO} stretch at 1922 cm^{-1} observed for HRh(CO)(PPh$_3$)$_3$ (2) was still evident in a sample obtained by thorough grinding

together the complex and VPI-5 in KBr. In contrast, the spectrum of an impregnated sample showed a very weak, broad absorption in the 2000 cm^{-1} region. It has been previously demonstrated that the carbonyl absorption of (2) can still be clearly observed as a sharp intense peak for samples of (2) adsorbed onto alumina [7].

^{31}P and ^{1}H solid state NMR spectra of (2) and of (2)/VPI-5 were recorded. None of the absorptions of the pure complex could be distinguished in the sorbed material though a solid state ^{13}C NMR spectrum of (2)/VPI-5 showed a broad absorption with a maximum at ca. 127 ppm, similar to that shown for the pure solid (2). In contrast, sorbed triphenylphosphine showed a sharp peak at −6.6 ppm in the solid state ^{31}P NMR spectrum similar to that observed in pure solid triphenylphosphine (−10.3 ppm). It thus appears that solid state NMR spectroscopy is of limited value in the characterisation of these rhodium complexes sorbed into VPI-5. However, the spectra suggest that breakdown of the complex with the release of triphenylphosphine has not occurred to any significant degree, in that none would be detected in the matrix and only relatively small amounts were detected in the supernatant liquid phase as described above.

This was further confirmed by an exhaustive extraction using heated benzene (40 or 60°C) with sonication. Only very small amounts of triphenylphosphine oxide were recovered. No rhodium–phosphine complexes were detected in the sample by ^{31}P NMR. Thus, it appears that the rhodium complex is relatively strongly bound to the VPI-5.

Similar preparation of catalysts from VPI-5 (200 mg) and the rhodium complex (1) (8 mg) from benzene solution (10 ml) led to almost total incorporation of the complex. The residual solution again only contained a small amount of triphenylphosphine (ca. 0.4 mg). No attempts were made to characterise these materials in view of the limited success of our attempts to characterise the catalysts prepared from VPI-

Table 2
Hydrogenation of (3) using ClRh(PPh$_3$)$_3$ (1) as catalyst [a]

Run	Catalyst	Temperature (°C)	Conversion (%)
1	(1)/VPI-5	50	100
2	(1)/VPI-5	20	5
3	(1)+VPI-5 [b]	50	38
4	VPI-5	50	0
5	(1)	50	17 [c]

[a] Reaction conditions: sodium 4-styrenesulfonate (3), 300 mg, 1.45 mmol; complex (1), 8 mg, 0.0087 mmol, or (1)/VPI-5, 208 mg; water, 10 ml; H$_2$, 400 psi; 20 h. Ratio of substrate: [Rh] ca. 170:1.
[b] VPI-5 (200 mg) and (1) (8 mg) added separately.
[c] Trace of polymer obtained.

Table 3
Re-use of (1)/VPI-5 in hydrogenation of (3) at 50°C

Run	Conversion (%)	Rh loss (wt%) [a]
6	100	5.7
7	100	3.3
8	41	2.3

[a] Determined as described in Section 2.4.

5/(2) by ^{31}P NMR and IR. The ^{31}P spectra of (1) and (2) are very similar and the absence of a clearly visible carbonyl band made IR measurements unattractive.

The lack of recovery of significant amounts of triphenylphosphine suggests that rhodium cluster formation has not occurred to any significant extent.
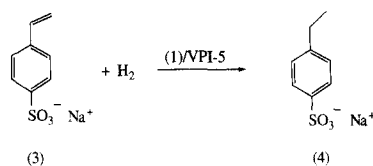
3.2. Hydrogenation reactions

Samples of (1)/VPI-5 were used as catalysts for the hydrogenation of sodium 4-styrenesulfonate (3) in water. Clean conversions to

sodium 4-ethylbenzenesulfonate (4) were obtained as summarised in Table 2.

Complete conversion occurred at 50°C when (1)/VPI-5 was used (run 1) but only a low conversion (17%) was obtained when (1) was used alone at this temperature (run 5). VPI-5 alone had no catalytic activity (run 4) and a mixture of (1) and VPI-5 gave a significantly lower conversion (38%) (run 3) than when the sorbed material was used. A low conversion (5%) was obtained using (1)/VPI-5 at ambient temperature (run 2).

Table 4
Hydroformylation of (3) using various catalysts [a]

Run	Catalyst	Temperature (°C)	Conversion [b] (%)	Ratio of products [b]	
				Aldehyde plus hydrate	Polymer
9	(2)/VPI-5	70	70	43	57
10	(2)/VPI-5	90	100	20	80
11	(2)+VPI-5	90	< 5	95	5
12	VPI-5	90	0	0	0
13	(2)	90	0	0	0
14	(1)/VPI-5	70	50	44	56
15	(1)/VPI-5	90	60	18	82

[a] Reaction conditions: sodium 4-styrenesulfonate (3), 300 mg, 1.45 mmol; complex (1) or (2), 8 mg, 0.0087 mmol, or (1)/VPI-5 or (2)/VPI-5, 208 mg; water, 10 ml; H$_2$/CO, 1:1, 400 psi; 20 h. Ratio of substrate: [Rh] ca. 170:1.
[b] Determined by ^{1}H NMR spectroscopy.
[c] VPI-5 (200 mg) and (2) (8 mg) added separately.

The possibility of re-using recovered catalysts was investigated by carrying out a series of successive hydrogenations. Table 3 summarises the amount of rhodium lost in each hydrogenation and the % conversion of (3) to (4).

The first reaction using freshly prepared catalyst (run 6) gave complete conversion and 5.7 wt% of rhodium was determined to be in the supernatant liquid. Re-use of the recovered catalyst (run 7) gave 100% conversion and a further loss (3.3%) of rhodium. Recovery of the catalyst from this reaction and reuse (run 8) gave a reduced but still significant conversion (41%) and a further rhodium loss. The rhodium lost into solution was shown not to be catalytically active as re-use of the supernatant liquor with fresh substrate gave no conversion. Some water-soluble rhodium compounds, e.g. $RhCl_3 \cdot 3H_2O$ can act as catalysts under these reaction conditions and complete conversion was obtained in a reaction using 2.5 mg of $RhCl_3 \cdot 3H_2O$. However, a reaction using 0.13 mg of $RhCl_3 \cdot 3H_2O$, equivalent to the 5.7% weight loss (run 6) gave only a low conversion (19%). It thus appears that the catalytic activity is restricted to the sorbed rhodium compounds.

3.3. Hydroformylation reactions

The use of the rhodium catalysts (1)/VPI-5 and (2)/VPI-5 as catalysts for the hydroformylation of (3) in water was investigated and the results are summarised in Table 4.

A reaction at 70°C using (2)/VPI-5 (run 9) gave a 70% conversion of (3) to a mixture of the aldehyde (5), its hydrate (6) and poly(sodium 4-styrenesulfonate) (7).
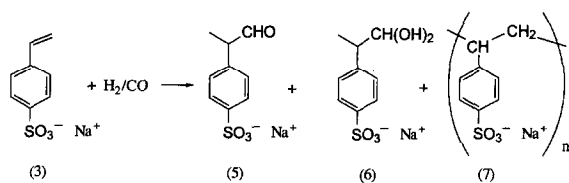
Confirmation of the structure of (5) and (6) was obtained by a reduction using aqueous sodium borohydride which converted both compounds into the related alcohol (8). The polymer (7) was characterised by comparison of spectral data with those of a commercial sample. Negative ion electrospray mass spectrometry showed that the polymer (7) had a more uniform MW distribution than the commercial sample.

A reaction at 90°C (run 10) gave complete conversion but a higher proportion of polymeric product. None of VPI-5 alone (run 12), complex (2) (run 13) or a mixture of the two (run 11) gave any significant conversion. Reactions using (1)/VPI-5 at 70°C or 90°C (runs 14 and 15) gave slightly lower conversions than for (2)/VPI-5 with similar product ratios.

Reactions using a catalyst with a loading of (2) increased to 20 mg, as compared to the 8 mg in (2)/VPI-5, gave a conversion increased to 94% with a higher proportion of polymer in the product.

The formation of polymers in rhodium-catalyzed hydroformylation reactions of alkenes is not common. We note however that aqueous solutions of rhodium species have led to oligomerisation of reactive alkenes, e.g. cyclobutene [8].

4. Note added in proof

Further evidence for the structure of catalysts obtained by incorporation of $HRh(CO)(PPh_3)_3$ (2) into VPI-5 was provided by ESCA examination, the ESCA technique being strongly surface composition specific. (The authors are grateful to Dr. Kingsley Cavell, Chemistry Department, University of Tasmania for carrying out the ESCA measurements). A catalyst containing 32 mg of (2) in 200 mg VPI-5 (ca. 100% fraction of occupied pore volume, cf. Table 1) gave by ESCA the atom number ratio

$$\frac{(Al + P)/2}{Rh} = \frac{8}{1},$$

while the corresponding ratio for the catalyst containing 8 mg of (2) in 200 mg VPI-5 was

27/1 (ca. 25% fraction occupied pore volume, cf. Table 1). These ratio values may be compared with the value of

$$\frac{(Al + P)/2}{Rh} = \frac{9}{1}$$

calculated form the known crystal structure of VPI-5, assuming every pore mouth to be occupied by a molecule of (2). It is clear that the calculated ratio agrees well with the value observed for the catalyst with ca. 100% fraction of occupied pore volume (i.e. with a molecule of (2) occupying every pore mouth), but in the case of the catalyst with ca. 25% fraction of occupied pore volume, only about 1/3 of the pore mouths contained a molecule of (2).

Acknowledgements

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