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Supported Fluorous Phase Catalysis on PTFE, Fluoroalkylated Micro- and Meso-porous Silica

Eric G. Hope,[a,*] James Sherrington,[a] and Alison M. Stuart[a]

[a] Department of Chemistry, University of Leicester, Leicester, LE1 7RH, UK
Fax: (+44)-116-252-3789; e-mail: egh1@le.ac.uk

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Abstract: New perfluoroalkylated micro- and meso-porous silica, along with powdered Teflon, have been evaluated as solid supports for supported fluorous phase catalysis in a model reaction; the hydrogenation of styrene using a fluorous analogue of Wilkinson's catalyst. Each support material showed catalytic activity and catalyst-leaching behaviour related to its surface area and was consistent with supported liquid phase catalysis. However, catalyst decomposition on the silica supports resulted in substantial reductions in activity on catalyst recycle. In contrast, although activity and leaching levels on PTFE were poorer, the supported catalyst was recycled successfully.

Keywords: fluorous; hydrogenation; rhodium; supported catalysis

Introduction

In 1989 Davis et al. first introduced *supported aqueous phase catalysis (SAPC)* as a hybrid approach between existing supported liquid phase catalysis and aqueous biphase technologies. A homogeneous catalyst is dissolved in an immobilised layer of water on a high surface-area, hydrophilic material, that can be readily separated, recovered and reused by simple filtration following catalysis of substrates dissolved in an immiscible bulk organic phase.[1] The high catalyst mobility, low leaching levels and good reactivities offered by the SAPC approach have been exploited in a wide variety of catalytic reactions.[2–6] The concept has been extended to other combinations of immiscible solvents including *supported organic phase catalysis*, a mirror image of SAPC employing a supported hydrophobic solvent layer on reverse-phase silica and an immiscible polar bulk phase,[7] and *supported ionic phase catalysis*, where a silica surface, modified with imidazolium ions, supports [bmim][BF_4]-containing rhodium catalysts for the hydroformylation of 1-hexene.[8] Fluorous chemistry,[9] exploiting the immiscibility of perfluorinated and organic solvents, offers alternative solvent combinations for supported catalysis that do not require water or highly polar ionic liquids. Although perfluoroalkylated solid supports have found wide application in high throughput synthesis as a solid support for solid phase extraction,[10,11] and have received considerable interest recently as insoluble supports for supported[12–16] and thermomorphic[17–20] catalysis, their extension to *supported fluorous phase catalysis (SFPC)* has not been reported. Here, we describe the application of SFPC to a model reaction, the rhodium-catalysed hydrogenation of styrene.[21]

Results and Discussion

Three different types of fluorinated material were evaluated for SFPC; powdered Teflon, perfluoroalkylated micro- and meso-porous silicas. Fluoroalkyl surface modification of silicas with 1*H*,1*H*,2*H*,2*H*-tridecafluoro-*n*-octyldimethylchlorosilane has been described previously,[22,23] and we have adopted a similar route for the synthesis of both micro- and meso-porous support materials (**1, 2**). Following condensation of the silyl chloride with the dry, commercially available silica in dry toluene in the presence of base, the crude derivatised silicas were purified by sequential washing with organic solvents of differing polarities until no fluorine-containing species could be detected in the filtrate by NMR spectroscopy, affording the products as free-flowing white powders. Direct weighing of the products **1** and **2** indicated 0.050 and 0.99 $mmol\,g^{-1}$ of organic material bound to the micro- and meso-porous supports, respectively, in line with the much larger surface area ($550\,m^2g^{-1}$ *vs.* $11.5\,m^2g^{-1}$) of the meso-porous silica, whilst elemental analysis indicated slightly higher loadings (0.06 and 1.12 $mmol\,g^{-1}$, respectively). Simultaneous thermal analysis of the products revealed large endotherms around 100 °C, corresponding to the evaporation of water and, whilst that for **2** revealed no further mass loss up to *ca.* 500 °C, that for **1** did reveal an endotherm at *ca.* 190 °C, which is most reasonably ascribed to loss of the perfluoroalkylated silyl unit since the chlorosilane has a boiling point of 197 °C. In spite of the increasing number of applications of FRP silica gel in synthesis,[10–19] there have been few reports on the characterisation of these materials. Here, solid-state CPMAS $^{19}F\{^1H\}$ (Figure 1) and $^{13}C\{^1H\}$ NMR spectra of the products revealed five and eight broad singlet resonances, respectively (i.e., without spin-spin couplings), analogous to solution phase spectra for arylphosphines containing the same perfluoroalkylsilyl unit.[24] DRIFT IR spectra of **1** and **2** were dominated by vibrations arising from the silica matrix. Extremely broad peaks from 3740–3150 cm^{-1} correspond to silanol OH stretches, whilst bands around 1630 cm^{-1} revealed the presence of absorbed water. Very weak C–H stretching vibrations at 2958 and 2843 cm^{-1} are present in the spectrum of **2**, although the corresponding C–F absorptions are obscured by intense absorptions due to Si–O–Si stretches, but no comparable C–H stretching absorptions could be observed in the spectrum for **1**, perhaps reflecting the much lower surface loading of organic material for this support.

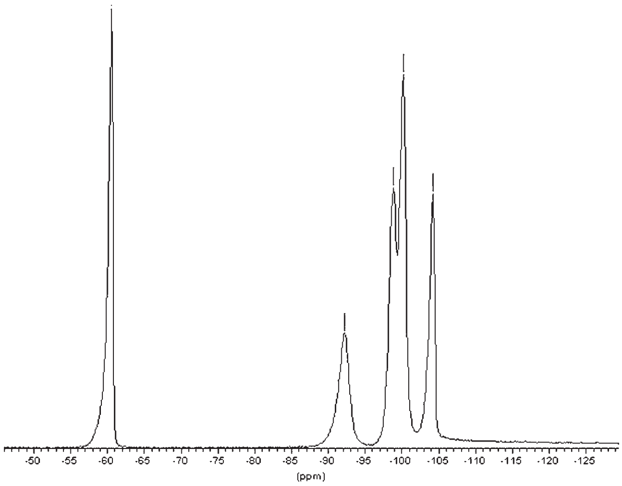

Figure 1. Solid-state CPMAS $^{19}F\{^1H\}$ NMR spectrum of perfluoroalkylated mesoporous silica (**2**).

We evaluated these supports for SFPC using the hydrogenation of styrene with a derivative of Wilkinson's catalyst as a model reaction, since it has been extensively studied under homogeneous and heterogeneous conditions and, most recently, under fluorous biphase conditions.[25,26] A reproducible and reliable route was identified for preparing the supported catalyst (Figure 2); reaction of $[RhCl(C_2H_4)_2]_2$ and the ligand in a toluene:perfluoro-1,3-dimethylcyclohexane (PP3) biphase, removal of the organic layer *prior* to addition of the dried support, and removal of the PP3 under vacuum. The catalytic experiments were then performed on a weighed amount of the supported catalyst together with styrene in toluene with or without aliquots of PP3 as the supporting solvent under 1 atm H_2 at 63.5 °C for 1 hour. Crucially, in order to obtain a uniform distribution of the fluorous solvent over the support material, it was necessary to add the PP3 slowly to a rapidly stirred suspension of the supported catalyst in toluene. At the end of the reaction, the mixtures were quenched in an ice/salt bath and the organic layer was removed for GC and ICP MS analysis (Table 1); for comparative purposes a set of identical experiments in the absence of a support was also undertaken.

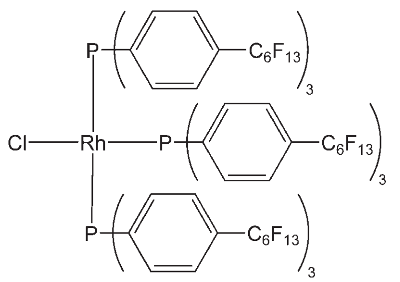

Figure 2. Perfluoroalkylated Wilkinson's catalyst.

For all systems, at low fluorous solvent levels (0–0.2 cm^3), the catalyst showed thermomorphic behaviour. At elevated temperatures, the rhodium catalyst desorbed from the support material, as evidenced by colouration of the bulk organic phase, and was readsorbed on quenching. The reaction rates for the four sets of catalytic experiments under these conditions are very similar, indicating that the support materials do not impede or accelerate the reaction and, whilst the catalyst leaching levels are high throughout, the fluorous mesoporous support offers the best material for reabsorption of the thermomorphic catalyst. At higher levels of PP3, sufficient fluorous solvent is present to completely solubilise the catalyst and thermomorphic behaviour is not observed.

In the absence of a support, the biphasic hydrogenation of styrene does show marginal initial improvements in rate as the amount of PP3 increases, perhaps reflecting an increase in the concentration of catalyst in the organic phase since PP3 is sparingly soluble in toluene, but this decreases markedly after a genuine biphasic system is reached. The affinity of the catalyst is clearly visible in the rhodium leaching levels, which drop markedly as the volume of PP3 increases. Surprisingly, the data from the experiments using PTFE as a solid support are virtually identical to those with no support, indicating that PTFE is not sufficiently fluorophilic to act as a support for SFPC in this catalyst system, which should be compared to the recently

Table 1. Supported fluorous phase hydrogenation of styrene

Volume of PP3 added[a]	No Support		FRP Monospher		FRP Meso-porous Silica		PTFE powder	
	Rate[b]	Rh leaching[c]	Rate[b]	Rh leaching[c]	Rate[b]	Rh leaching[c]	Rate[b]	Rh leaching[c]
0	67.2	29.20 (17.9)	68.2	25.63 (15.7)	67.6	12.61 (7.7)	66.2	18.51 (11.3)
0.2	68.7	6.22 (3.8)	70.5	7.72 (4.7)	71.6	2.66 (1.6)	67.6	13.38 (8.2)
0.4	71.2	5.49 (3.4)	74.2	4.25 (2.6)	73.8	1.16 (0.7)	75.4	5.91 (3.6)
0.6	69.5	4.08 (2.5)	78.0	1.69 (1.0)	76.2	0.49 (0.3)	64.1	5.18 (3.2)
0.8	67.4	2.41 (1.5)	70.3	0.89 (0.5)	81.7	0.47 (0.3)	57.1	4.52 (2.8)
1.0	65.1	1.88 (1.1)	68.9	1.71 (1.0)	83.9	0.32 (0.2)	55.4	4.11 (2.5)
1.2	63.3	0.63 (0.4)	67.0	0.83 (0.5)	75.2	0.30 (0.2)	51.3	2.69 (1.6)
1.4	61.8	0.42 (0.3)	63.2	0.69 (0.4)	72.1	0.21 (0.15)		
1.6	60.8	0.35 (0.2)	61.0	0.48 (0.3)	64.3	0.21 (0.15)		
1.8	58.1	0.31 (0.2)	58.6	0.29 (0.2)	61.7	0.24 (0.15)		

[a] cm^3.
[b] mmol dm^{-3} h^{-1}.
[c] ppm; % in parentheses.

reported highly effective recovery and recycle of a fluorous catalyst using Teflon tape.[20]

For the other fluorinated supports, as predicted by the SAPC model,[1–3] a gradual rise and subsequent fall in catalytic activity is observed with increasing solvation of the catalyst (Figure 3). The peak in activity, which corresponds to the optimum surface area:volume ratio for the supported perfluorocarbon layer on the support, increases from the fluoroalkylated microporous to the meso-porous support, in line with the variation in surface areas for these supports. The maximum reaction rates are comparable to, but slightly lower than, that observed in a toluene/PP3 biphase at 63.5 °C; 86 mmol dm^{-3} h^{-1}.[25] Beyond these maxima in reaction rates, the addition of more PP3 results in a reduction in the availability of the catalyst, which is preferentially soluble in PP3 over toluene, to the immiscible organic phase and reductions in rates, eventually leading to two phase systems that contain an insoluble support material. Indeed, the similarity in activities for all three systems at high PP3 volumes indicates that the presence of the support has little impact upon the reactivity of the catalyst in the biphase. In line with the trend observed in rhodium leaching levels in the absence of a support, rhodium leaching levels drop consistently as the volume of PP3 increases.

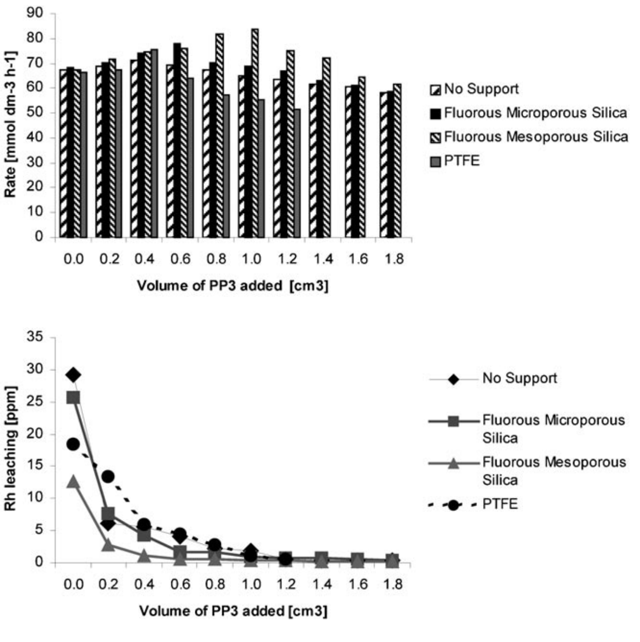

Figure 3. Hydrogenation of styrene under supported fluorous phase conditions.

Having established the optimum fluorous solvent volumes necessary for SFPC on each support, catalyst recycle and reuse experiments were carried out. In each case, following a catalytic run/cooling sequence, the organic phase was removed for analysis, further aliquots of fresh toluene, styrene and PP3 were added to the supported catalyst and the catalytic runs repeated. Unfortunately, all of the supported catalysts exhibited a decrease in activity with each cycle {microporous support at 0.6 cm^3 PP3 76.2, 60.6, 44.4; mesoporous support at 1.0 cm^3 PP3 84.9, 51.8, 38.1; PTFE at 0.4 cm^3 PP3 71.8, 62.7, 59.4 mmol dm^{-3} h^{-1}}. The PTFE supported catalyst proved to be more effective in these recycle experiments than the fluoroalkylated silica supported catalysts, which showed substantial reductions in catalytic activity. At the same time, the rhodium leaching levels of the PTFE supported catalyst were an order of magnitude greater over the three recycles than those of the mesoporous silica supported catalyst (14.22 *vs.* 1.36 ppm), clearly indicating that the loss of activity is not associated with rhodium leaching from the support. During the course of these reactions, both of the silica-supported catalysts changed from orange to dark brown suggesting that, although these materials do act as supports for SFPC, they both promote catalyst decomposition, possibly as a result of reaction of the metal catalyst with the free hydroxy functionalities identified in the DRIFT infrared spectra for these materials. This is consistent with other observations of metal catalyst decomposition on FRP silica gel.[13,16,27] In marked contrast, the PTFE supported catalyst, where free hydroxy groups are not present, remained orange throughout the three catalyst recycles.

Conclusions

SFPC can be undertaken effectively on fluorinated inorganic supports in the presence of minimal quantities of the expensive perfluorocarbon solvents. However, at present, catalyst decomposition and/or catalyst leaching levels preclude a widespread investigation of this approach until alternative fluorinated supports become available; work in this area is currently in progress.

Experimental Section

Gas chromatography was performed using a Philips PU4500 chromatograph fitted with an SGE SE30 capillary column. The gas chromatograph was interfaced with a Spectra Physics auto integrator for the determination of peak areas by electronic integration. Rhodium analysis was carried out on a JY Horiba Ultima 2 sequential ICP-OES, DRIFT IR spectral measurements were carried out on a Bruker Equinox 55 spectrometer, solid state NMR spectra were performed at 376.49 with 30 kHz spinning (^{19}F) and at 100.61 with 12 kHz spinning (^{13}C) on a Bruker 400 Avance NMR spectrometer, and STA was carried out on a Stanton Redcroft STA 625 machine from 25 °C to 625 °C at a heating rate of 20 °C per minute. Elemental analyses were performed by the Elemental Analysis Service at the University of North London.

Preparation of Fluorous Reverse Phase Monospher® 250N (1)

Imidazole (4 g, 60 mmol) and (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-*n*-octyl)dimethylchlorosilane (17 g, 33 mmol) in toluene (70 cm^3) were added to dry Monospher 250N® (10.00 g) and the mixture refluxed for 78 h. The product was filtered, washed sequentially with toluene, *n*-hexane, methanol, methanol/water (1:1), THF, diethyl ether and acetonitrile (50 cm^3 each) to give the product as a fine white powder; yield: 10.20 g (74.8 %); anal. found: C 1.78, H 0.92, F 1.35 %; ^{19}F{^{1}H} NMR: $\delta = -60.60$ (3F, s, CF_3), −92.18 (2F, s, α-CF_2), −98.92 (2F, s, CF_2), −100.18 (4F, s, 2 × CF_2), −104.21 (2F, s, CF_2); ^{13}C{^{1}H} NMR: $\delta = -3.2$ (s, CH_3), 6.4 (s, CH_2Si), 24.2 (s, CH_2CF_2), 108.2 (s, CF_2), 111.1 (s, CF_2), 114.8 (s, CF_2), 115.7 (s, CF_3), 119.0 (s, α-CF_2).

Fluorous Reverse Phase Mesoporous Silica (2)

Support **2** was prepared similarly using Merck 70–230 mesh silica to afford the product as a fine white powder; yield: 25.9 %; anal. found: C 8.98, H 0.76, F 19.49 %; ^{19}F{^{1}H} NMR: $\delta = -60.58$ (3F, s, CF_3), −92.22 (2F, s, α-CF_2), −98.90 (2F, s, CF_2), −100.18 (4F, s, 2 × CF_2), −104.21 (2F, s, CF_2); ^{13}C{^{1}H} NMR: $\delta = -3.2$ (s, CH_3), 6.7 (s, CH_2Si), 23.9 (s, CH_2CF_2), 108.2 (s, CF_2), 111.6 (s, CF_2), 114.8 (s, CF_2), 115.6 (s, CF_3), 119.2 (s, α-CF_2).

Preparation of Supported Catalyst

A 4 cm^3 aliquot of $[RhCl(C_2H_4)_2]_2$ in toluene (3.93×10^{-3} M) was added to a solution of tris(4-tridecafluoro-*n*-hexylphenyl)phosphine[28] (0.152 g, 0.125 mmol) in PP3 (2 cm^3) and the mixture stirred for 15 min. The PP3 layer was separated and added to the dry support (1.0 g). After stirring the mixture, the solvent was removed under vacuum to afford the supported catalyst.

Typical Catalytic Run

Toluene (18 cm^3) and PP3 (0–2.0 cm^3) were added to the dried supported catalyst (1.0 g) in a Schlenk flask. The reaction vessel was evacuated and back-filled three times with hydrogen (1 atm). The reaction mixture was heated at 63.5 °C before adding the styrene (2 cm^3). After 1 h, the reaction was quenched by immersion in an ice-salt bath for 5 min and a 10 cm^3 sample removed for analysis.

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