Supported ionic liquid phase catalysis with supercritical flow

Ulrich Hintermair,[a] Guoying Zhao,[a] Catherine C. Santini,[b] Mark J. Muldoon[a] and David J. Cole-Hamilton*[a]

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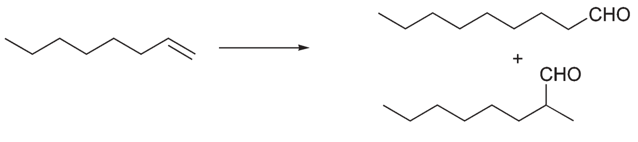
Rapid hydroformylation of 1-octene (rates up to 800 h^{-1}) with the catalyst remaining stable for at least 40 h and with very low rhodium leaching levels (0.5 ppm) is demonstrated when using a system involving flowing the substrate, reacting gases and products dissolved in supercritical CO_2 ($scCO_2$) over a fixed bed supported ionic liquid phase catalyst.

One of the main problems with homogeneous catalysis is that it can be difficult to separate the reaction product from the dissolved catalyst and any solvent. Conventional distillation often leads to decomposition of the expensive catalyst and this may also be the case for low pressure distillation if the product is of low volatility. Many alternative approaches have been attempted using catalysts on insoluble or soluble supports or using biphasic systems.[1–3] One very attractive new concept combines these approaches by supporting the catalyst in a thin film of either water[4] or an ionic liquid[5–10] absorbed within the pores of a microporous solid. When an ionic liquid is the supported solvent, long term reactions have shown that good results, albeit at rather low catalyst turnover frequencies (TOF), can be obtained when all the substrates are in the gas phase. However, in the example of hydroformylation, the activity falls with time because aldol condensation products start to fill the pores of the catalyst, reducing access by the substrates.[9] The catalytic reactivity can be restored by removing the aldol condensation products *in vacuo*. Reactions using liquid phase substrates are less successful because of problems with depletion of gaseous reagents. Only the gas initially dissolved in the liquid substrate is available for reaction and, once it is depleted, diffusion of further gas into the liquid filled pores is very slow. In addition, the ionic liquid can have significant solubility in the liquid substrate so is gradually removed along with some of the catalyst. However, we reasoned that combining $scCO_2$ with supported ionic liquids could circumvent these types of problems. $scCO_2$ can dissolve many organic compounds, is totally miscible with permanent gases and although it is soluble in ionic liquids it does not dissolve ionic compounds. We now report our preliminary studies on the hydroformylation of 1-octene (Scheme 1).

Two other reports on the use of supercritical fluids for transporting substrates across supported ionic liquid phase (SILP) catalysts have appeared.[11,12] One describes the synthesis of cyclic carbonates from CO_2 and epoxides,[11] whilst the other describes the oxidation of alcohols over a perrhenate catalyst.[12] Neither is carried out in continuous flow mode.



Scheme 1 The hydroformylation of 1-octene.

$scCO_2$, 1-octene, CO and H_2 were mixed and flowed upwards through a tubular reactor (length 17.5 cm, i.d. 6 mm. o.d. 10 mm) containing a catalyst composed of [PrMIM][$Ph_2P(3\text{-}C_6H_4SO_3)$] (PrMIM = 1-propyl-3-methylimidazolium), [Rh(acac)$(CO)_2$] (acacH = 2,4-pentanedione) and [OctMIM][Tf_2N] (1-octyl-3-methylimidazolium bis(trifluoromethylsulfonamide)) supported on silica gel.† The effluent from the reactor was depressurised and the liquid products collected for analysis by GC (organic products), NMR (ionic liquid) and ICPMS (Rh). A schematic diagram of the reactor is shown in Fig. 1, whilst results of selected reactions are shown in Fig. 2 and 3. The reaction parameters are collected in Table 1.

The conversions to aldehydes (typical linear/branched ratio = 3 ± 0.3 in all collected fractions) are based on assuming that any material lost (typical mass balances were 80% at low conversion and >95% at high conversion) was pure 1-octene, which was verified experimentally. The surface area of the silica was measured before and after loading of the catalyst to determine the layer

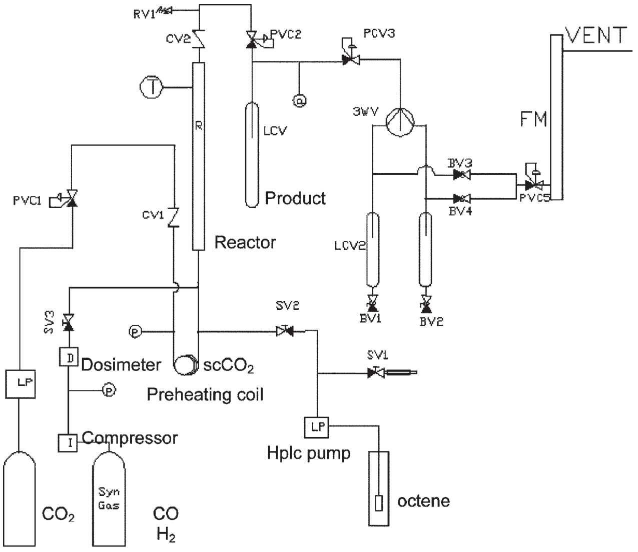


Fig. 1 Schematic diagram of reactor used for SILP-SCF experiments.

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[a] *EaStCHEM, School of Chemistry, University of St. Andrews, St. Andrews, Fife, Scotland, UK KY16 9ST. E-mail: djc@st-and.ac.uk; Fax: 44 1334 463808; Tel: 44 1334 463805*
[b] *Laboratoire de Chimie Organometallique de Surface, UMR 9986 CNRS, CPE Lyon, 43 Bd du 11 Novembre 1918, 69616, Villeurbanne Cedex, France*

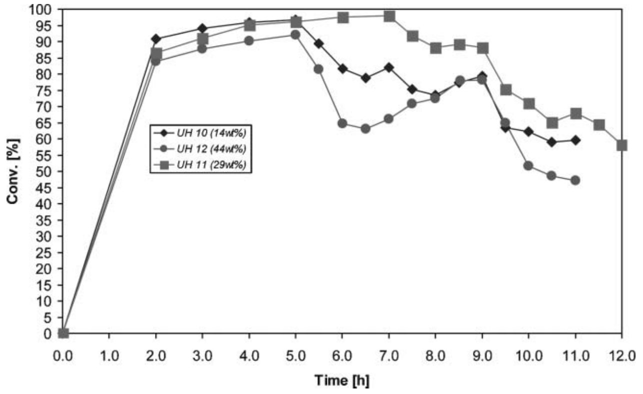

Fig. 2 1-Octene conversion to aldehydes using SILP based catalysts with different loadings of ionic liquid. (●) 44%, (■) 29%, (◆) 14% w/w. Percentages are of IL relative to silica. For conditions, which were changed after 5, 7, 9 and 11 h, see Table 1.

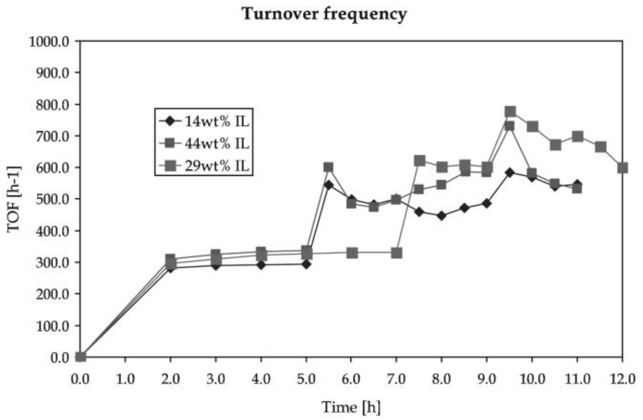

Fig. 3 Data from Fig. 1 expressed as turnover frequency. Details as Fig. 2.

Table 1 Conditions for the continuous flow hydroformylation of 1-octene catalysed by a rhodium complex in a supported ionic liquid[a]

Time/h	0–4	4–5	5–7	7–9	9–11	11–12.5	12.5–13
Substrate flow/cm^3 min^{-1}							
44% w/w	0.12	0.12	0.24	0.24	0.36		
29% w/w	0.12	0.12	0.12	0.24	0.36	0.36	0.36
14% w/w	0.12	0.12	0.24	0.24	0.36		
CO/H$_2$: substrate							
44% w/w	15	15	10	20	15		
29% w/w	15	20	20	15	10	20	20
14% w/w	15	15	10	20	15		
Total flow/cm^3 min^{-1} (STP)							
44% w/w	247	247	513	539	778		
29% w/w	247	380	380	513	778	804	1043
14% w/w	247	247	513	539	778		

[a] [Rh(acac)(CO)$_2$] (14%, 0.15 mmol; 29%, 0.133 mmol; 44%, 0.122 mmol); P : Rh = 10 : 1; catalyst volume = 7.5 cm^3; silica (after pre-treatment, but before loading) surface area = 321.7 m^2 g^{-1}; pore volume = 0.982 cm^2 g^{-1}, mean pore size = 10.7 nm, 100 °C, 100 bar total pressure

thickness and the extent of pore filling. Very active stable catalysis was observed over prolonged periods. An analysis of the effect of variables on the reaction, using a statistical experimental design approach showed that the film thickness (ionic liquid loading) had rather little effect on the reaction rate at constant catalyst loading despite the lower concentration of catalyst in the thicker films (see Fig. 2 and 3). In the early part of the reactions described in Fig. 2 and 3, the conversions are close to 100% so the similarity in conversion may not be significant, but for the catalysts with loadings of 14 and 44% in the time period 9–11 h, the other reaction parameters are identical and the TOFs are very similar even though the yields are of the order of 50–70% This limited dependence on ionic liquid loading is somewhat surprising, because in other SILP systems, the loading of the ionic liquid has a dramatic effect.[9] At very low film thicknesses, the rate is low because the support interferes with the catalyst. The rate then increases until an optimum loading is reached but decreases at higher loadings. This has been interpreted[9] as arising from poor substrate and/or gas diffusion rates into the ionic liquid reducing access to the catalyst. The optimum rate is obtained when all the catalyst molecules are confined within the diffusion layer, but are sufficiently distant from the surface not to suffer from surface interactions. The fact that such behaviour is not observed in the SILP process with supercritical fluid transport (SILP-SCF) suggests that diffusion is no longer rate limiting and that all the catalyst molecules can be accessed by the 1-octene and the CO/H$_2$. [OctMIM][Tf$_2$N] was selected as the ionic liquid because it had previously been shown to be the best of several ionic liquids for the hydroformylation of 1-octene using the same catalyst in a bulk biphasic system consisting of [OctMIM][Tf$_2$N] and scCO$_2$.[13] 1-Octene is highly soluble in [OctMIM][Tf$_2$N] and the presence of scCO$_2$ is known to improve the solubility and mass transport of the permanent gases into the ionic liquid.[14] Although scCO$_2$ is very soluble in [OctMIM][Tf$_2$N], the ionic liquid and the ionic catalyst are essentially insoluble in scCO$_2$,[13] so that they are not dissolved by the flowing supercritical CO$_2$ phase.

The main factor affecting the reaction rate appears to be the substrate flow rate, although we have not varied this independently of the total flow rate. It is probable, however, that these changes are amplified by the fact that the conversions at low flow rate are close to 100% so they underestimate the rate. After optimisation of the conditions, rates corresponding to 800 mol substrate (mol catalyst)$^{-1}$ h^{-1} were observed. This is higher than the rates observed in the bulk biphasic system (max. 527 h^{-1}) and higher than the rates observed during commercial propene hydroformylation reactions (550–700 h^{-1}),[15] although we note that we are working at lower phosphine : Rh ratio (10 : 1 for the SILP catalyst, compared with 15 : 1 for the bulk supercritical fluid – ionic liquid system[13] and >100 : 1 for the commercial systems[15]). The total pressure (100 bar) is also lower in the SILP system than in the bulk system (200 bar).[13] Conversions close to 100% were obtained even though the catalyst bed was very small (7.5 cm^3).

The catalyst is stable over at least 40 hours, as illustrated in Fig. 4 where the straight line indicates a constant turnover frequency of 500 h^{-1} throughout the reaction. The conversion throughout the reaction was 42 ± 2%. Here again, the presence of the supercritical fluid offers advantages because it is able to extract aldol condensation products (traces are observed in the product by GC analysis) and prevent the fouling of the catalyst, which bedevils the gas phase reaction when using propene as the substrate.[9]

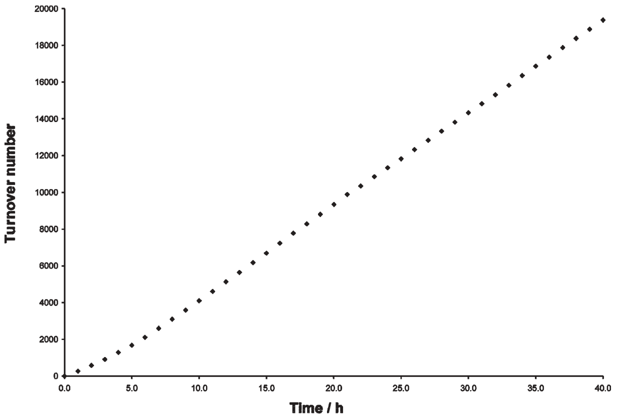

Fig. 4 Cumulative turnover number for the hydroformylation of 1-octene over 40 h. 14 w/w IL; Rh 0.146 mmol; P : Rh = 10, silica (7.5 cm^3) as Table 1; substrate flow 0.42 cm^3 min^{-1}, CO/H_2 : substrate = 10, total flow = 854 cm^3 min^{-1} (STP), 100 °C, 100 bar.

Leaching levels measured by ICPMS tend to start high (2–4 ppm) in the first fractions collected during a run, but drop to 0.5 ppm later on. We are currently investigating whether this is genuine leaching or physical abrasion.

We conclude that continuous hydroformylation of 1-octene can be carried out at high rates when using a supported ionic liquid phase catalyst, provided that the substrate and gases are transported in $scCO_2$. Advantages of this process include excellent diffusion of the substrate and gases to the catalyst surface, excellent solubility of the substrates and gases within the supported ionic liquid and extraction of heavy products that might otherwise foul the catalyst by filling the pores. A stable, efficient catalyst system with very low catalyst losses is obtained.

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Notes and references

† A typical preparation of the SILP catalyst (0.14% loading; amounts for other loadings are shown in the footnote to Table 1) was performed by dissolving $[Rh(acac)(CO)_2]$ (0.04 g, 0.15 mmol), [PrMIM][TPPMS] (0.738 g, 1.5 mmol) and degassed $[OctMIM][Tf_2N]$ in purified methanol (40 cm^3, 10 cm^3 per gram of silica). After stirring for 1 h at room temperature, the silica gel (4 g, pretreated by heating at 500 °C for 16 h and stored over P_2O_5 under N_2) was added, and the mixture was stirred for a further 2 h. Then the methanol was very slowly removed at 35 °C under reduced pressure. The residual powder was dried for 6 h at 100 °C under vacuum. Every catalyst was synthesized just prior to use, and not stored for longer periods.

1 *Multiphase Homogeneous Catalysis*, ed. B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Borbigou and D. Vogt, Wiley-VCH, Stuttgart, 2005.

2 *Catalyst Separation, Recovery and Recycling, Chemistry and Process Design*, ed. D. J. Cole-Hamilton and R. P. Tooze, Springer, Dordrecht, 2006.

3 D. J. Cole-Hamilton, *Science*, 2003, **299**, 1702.

4 M. E. Davies, in *Aqueous-phase Organometallic Catalysis*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 1998, p. 241.

5 A. Riisager, P. Wasserscheid, R. van Hal and R. Fehrmann, *J. Catal.*, 2003, **219**, 452.

6 A. Riisager, K. M. Enksen, P. Wasserscheid and R. Fehrmann, *Catal. Lett.*, 2003, **90**, 149.

7 A. Riisager, R. Fehrmann, S. Flicker, R. van Hal, M. Haumann and P. Wasserscheid, *Angew. Chem., Int. Ed.*, 2005, **44**, 815.

8 A. Riisager, R. Fehmann, P. Wasserscheid and R. van Hal, in *Ionic Liquids IIIb: Fundamentals, Progress, Challenges and Opportunities: Transformations and Processes*, ACS Symp. Ser., Washington, DC, 2005, vol. 902, p. 334.

9 A. Riisager, R. Fehrmann, M. Haumann and P. Wasserscheid, *Eur. J. Inorg. Chem.*, 2006, 695.

10 C. P. Mehnert, R. A. Cook, N. C. Dispenziere and M. Afeworki, *J. Am. Chem. Soc.*, 2002, **124**, 12932.

11 J.-Q. Wang, D.-L. Kong, J.-Y. Chen, F. Cai and L.-N. He, *J. Mol. Catal. A: Chem.*, 2006, **249**, 143.

12 R. Ciriminna, P. Hesemann, J. J. E. Moreau, M. Carraro, S. Campestrini and M. Pagliaro, *Chem. Eur. J.*, 2006, **12**, 5220.

13 P. B. Webb, M. F. Sellin, T. E. Kunene, S. Williamson, A. M. Z. Slawin and D. J. Cole-Hamilton, *J. Am. Chem. Soc.*, 2003, **125**, 15577.

14 M. Solinas, A. Pfaltz, P. G. Cozzi and W. Leitner, *J. Am. Chem. Soc.*, 2004, **126**, 1614.

15 C. D. Frohning and C. W. Kohlpaintner, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, p. 27.