Continuous fixed-bed gas-phase hydroformylation using supported ionic liquid-phase (SILP) Rh catalysts

Anders Riisager,[a,b] Peter Wasserscheid,[b] Roy van Hal,[b] and Rasmus Fehrmann [a,*]

[a] Interdisciplinary Research Center for Catalysis (ICAT) and Department of Chemistry, Technical University of Denmark, Building 207,
DK-2800 Lyngby, Denmark

[b] Institut für Technische Chemie und Makromolekulare Chemie, RWTH, Worringer Weg 1, D-52074 Aachen, Germany

Abstract

Continuous flow gas-phase hydroformylation of propene was performed using novel supported ionic liquid-phase (SILP) catalysts containing immobilized Rh complexes of the biphosphine ligand sulfoxantphos in the ionic liquids 1-*n*-butyl-3-methylimidazolium hexafluorophosphate and halogen-free 1-*n*-butyl-3-methylimidazolium *n*-octylsulfate on silica support. The Rh–sulfoxantphos SILP catalysts proved to be more regioselective than catalysts without ligand and the analogous ionic liquid-free catalysts, giving up to 96% linear product. Furthermore, the performance of the catalysts was generally strongly influenced by the catalyst composition. This is the first report on the use of SILP catalysts for fixed-bed gas-phase hydroformylation.
© 2003 Elsevier Inc. All rights reserved.

Keywords: Supported ionic liquid phase (SILP) catalysis; Hydroformylation; Gas-phase fixed-bed system; Propene; Rhodium; Sulfoxantphos

1. Introduction

In recent years, room-temperature ionic liquids (ILs) have received significant interest due to their potential applications for catalytic processes [1]. So far, work has mainly involved improvement of current two-phase liquid aqueous-organic catalytic systems by substituting water with IL as the solvent for immobilization of organometallic catalysts. This approach has been particularly successful for Rh-catalyzed, biphasic hydroformylation where several research groups have reported good to excellent results for conversion of pent-1-ene [2], hex-1-ene [3], oct-1-ene, and longer-chained olefins [4–9] to the corresponding aldehydes.

In essentially all of the present hydroformylation applications halogen-containing ionic liquids (usually hexafluorophosphate salts, e.g., [BMIM][PF$_6$]) were used generating an effective medium for catalyst separation and recycling, provided the Rh catalysts were modified with phos-phine ligands containing ionic groups. However, general concern about environmental impact, toxicology, and other undesired reactions potentially associated with ILs involving halogen-containing anions, e.g., formation of highly reactive and corrosive HF gas by hydrolysis, has recently lead to introduction of the halogen-free low-melting IL [BMIM][*n*-C$_8$H$_{17}$OSO$_3$] as a new "greener" solvent for hydroformylation [4]. During reaction the use of charged ligands ensured good catalyst immobilization in the IL phase due to a high relative affinity for the ionic phase compared to the organic product phase, but only in few cases high selectivities for the preferred linear products were obtained (usually *n*/*iso* ratios ⩽ 3). Hence, only in systems using xantphos-type biphosphines as the sulfonated ligand **1** [5] (sulfoxantphos, Fig. 1) or as cationic guanidinium [6] or phenoxaphosphino-modified ligands [7], sulfonated arylphosphites [3], or a specially designed cobaltocenium [8] ligand system have
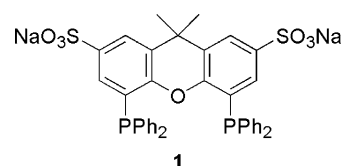

Fig. 1. Sulfonated xantphos ligand, sulfoxantphos.

n/iso ratios of 10 or higher currently been achieved. The high *n/iso* ratios observed with the derived xantphos ligands in ILs are consistent with prior results obtained for homogeneous as well as immobilized systems [10]. Here analogous ligands with the xanthene backbone structure resulted in highly selective catalysts due to their natural large P–metal–P bite angles.

The concept of "heterogenization" of aqueous Rh–phosphine complexes on solid supports generating supported aqueous-phase (SAP) [11] catalysts, is well known for both gas- and liquid-phase hydroformylation reactions [12]. It is unclear, though, whether the supported catalyst remains liquid under reaction conditions [13,14], which seems to be important for achieving good hydroformylation catalyst selectivity. In contrast, only minor attention has been given to analogous catalysts made by immobilization of ionic liquids on solids, despite their obvious potential for fixed-bed reactions leading to advantageous process design; e.g., the IL-phase remains liquid during reaction and is easy to maintain on the support due to the negligible volatility of ILs. Only very recently reports have appeared on liquid–liquid biphasic hex-1-ene hydroformylation [15] and C_6-olefin hydrogenations [16] using supported ionic liquid Rh-catalyst systems containing monoarylphosphines and ionic liquids [BMIM][PF$_6$] and [BMIM][BF$_4$]. In the hydroformylation reactions the ionic liquid was confined on a premodified silica support having a monolayer of covalent anchored fragments from 1-*n*-butyl-3-[3-(triethoxysilanyl)propyl]-imidazolium. Noteworthy, in all cases the processes were carried out as batch reactions and not as the technically more attractive continuous flow fixed-bed processes.

In this paper we report for the first time supported ionic liquid-phase (SILP) catalyst systems comprising a dissolved Rh–biphosphine catalyst in both halogen-containing and halogen-free ionic liquids immobilized on a silica support and their use for fixed-bed gas-phase hydroformylation in a continuous process design. In detail, we describe our preliminary kinetic results and examinations obtained from continuous gas-phase hydroformylation of propene using novel [BMIM][PF$_6$]/silica and [BMIM][*n*-C$_8$H$_{17}$OSO$_3$]/silica supported ionic liquid phase catalysts containing Rh complexes of the xanthene-based biphosphine ligand sulfoxantphos **1**.

2. Experimental

The supported ionic liquid phase catalyst systems were prepared by impregnation of silica gel by Rh(acac)(CO)$_2$ and ligand **1** [17] in a methanol/ionic liquid mixture under argon atmosphere according to the procedure below. The microcatalytic plug-flow system used for continuous gas-phase propene hydroformylation has previously been described in detail [14,18]. Methanol was dried with 3 Å molecular sieves and distilled prior to use. Ionic liquids [BMIM][PF$_6$]

and [BMIM][*n*-C$_8$H$_{17}$OSO$_3$] (> 98%, Solvent Innovation GmbH, Cologne, Germany) and silica gel 100 (Merck; BET surface area, 297.5 m^2/g; pore volume, 1.015 cm^3/g; mean pore diameter, 137 Å) were dried in vacuum before used (0.1 mbar, 24 h, ILs, 60 °C, and silica, 110 °C).

Rh(acac)(CO)$_2$ (5.0 mg, 0.0194 mmol) and **1** were dissolved in 10 mL degassed dry methanol with accurate amounts of ionic liquid [BMIM][PF$_6$] or [BMIM][*n*-C$_8$H$_{17}$OSO$_3$], thus generating catalysts with varying L/Rh ratios and ionic liquid loading. After stirring for 2 h, 1.0 g of silica gel (resulting in 0.2 wt% Rh metal loading) was added to the solution followed by an additional 2 h of stirring. Finally, the light-red dry catalysts were obtained by initial removal of the volatile solvent (10 mbar, 35 °C) followed by drying (0.1 mbar, 80 °C, 24 h). Catalysts were stored in vacuo over P$_4$O$_{10}$ prior to use.

3. Results and discussion

In continuous, gas-phase hydroformylation of propene the new Rh-**1**/silica supported ionic liquid-phase catalysts were found to be active, exhibiting TOFs of up to 37 mol propene converted per mole Rh per hour and with selectivity for the linear product up to 96% during typically 3–4 h (Table 1). It should be noted that both the L/Rh ratios and the pore filling degree of the ionic liquid, α, had a strong influence on the performance of the catalysts.

For the catalysts with low L/Rh ratios of 2.4–2.5 containing IL (entries 2–4) only low activities and—unusual for Rh-**1** catalysts [10]—low *n/iso* ratios of 1.7–2 (63–66% linearity) were obtained. Contrary, much higher activity was measured for the IL-free catalyst (entry 1). This suggests that most parts of the catalytically active complexes under these circumstances are surface-immobilized ligand-free complexes, where the presence of the IL solvent induces severe mass-transfer limitations due to poor gas solubilities in the ILs [19]. The presence of ligand-free complexes is further strongly supported by the low selectivity obtained using the ligand-free SILP catalyst system (entry 11). Additionally, formation of inactive dimers in the IL could also lead to the observed decrease in activity as found previously for sulfoxantphos in other solvents [20].

In contrast to the catalysts with low L/Rh ratios, the catalysts with L/Rh ratios of 10 and 20 (entries 5–10) were all highly selective giving a *n/iso* ratio of 16.9 for the solvent-free catalyst (entry 5) and in presence of IL up to 23.7 (96% linearity, entry 10). This strongly indicates that active ligand containing Rh complexes are formed under these circumstances. However, as for the reactions with the catalysts having a low L/Rh ratio, increased liquid loading (α) also here leads to decreasing activity though much more moderate. This supports the conclusion that the catalysts are operating as mass-transfer limited. The intermediate selectivity obtained from the catalysts with no ionic liquid present could here be attributed to an increased amount of

Table 1
Propene hydroformylation[a] with SILP Rh-**1**/silica catalysts

Entry	L/Rh ratio[b]	Ionic liquid [BMIM]X	Ionic liquid loading		TOF[d]	n/iso ratio[e]	Linear prod.
			wt%	α[c]	(1/h)		(%)
1	2.5	–	–	0.00	37.4	1.7	63.0
2	2.4	[PF$_6$]	23.6	0.17	1.5	1.8	64.0
3	2.5	[PF$_6$]	68.1	0.49	5.1	2.0	66.4
4	2.5	[n-C$_8$H$_{17}$OSO$_3$]	56.0	0.52	6.4	1.9	65.4
5	10.2	–	–	0.00	40.8	16.9	94.4
6	10.0	[PF$_6$]	11.1	0.08	37.0	23.3	95.9
7	10.0	[PF$_6$]	25.0	0.18	34.9	22.6	95.8
8	10.0	[PF$_6$]	72.2	0.52	25.4	22.0	95.6
9	10.0	[n-C$_8$H$_{17}$OSO$_3$]	53.8	0.50	17.9	18.6	94.9
10	20.0	[PF$_6$]	27.8	0.20	16.7	23.7	96.0
11[f]	–	[n-C$_8$H$_{17}$OSO$_3$]	54.9	0.51	0.2	1.0	50.0
12[g]	–	[PF$_6$]	105.6	0.76	0.0	–	–

[a] General conditions: C$_3$H$_6$:CO:H$_2$ = 1:1:1; p(C$_3$H$_6$/CO/H$_2$) = 10 bar; T = 100 °C; conversion ≈ 1%; GHSV = 7000 h^{-1}; 0.2 wt% Rh metal loading; Rh-precursor, Rh(acac)(CO)$_2$; support, silica gel 100.
[b] Molar ligand-to-Rh ratio.
[c] Pore filling degree of support as the ratio IL volume/support pore volume.
[d] Turnover frequency at steady state (4 h) in moles aldehyde per mole of Rh per hour. Selectivity toward aldehydes was 100%.
[e] Linear to branched aldehyde ratio.
[f] Ligand-free catalyst.
[g] Support with [BMIM][PF$_6$] only.

ligand being coordinated. Based on these observations and on prior results [10,17] the active components in the catalysts with high L/Rh ratios are therefore most likely dissolved [HRh(**1**)(CO)$_2$] complexes, possibly immobilized via ionic ligand–surface interactions.

The effect on the catalytic performance of the catalysts by varying the [BMIM] ionic liquid anions from [PF$_6$] to [n-C$_8$H$_{17}$OSO$_3$] is not significant, and exhibits same effects of both L/Rh ratios and α. It is also evident from the pure supported [BMIM][PF$_6$]/silica catalyst (entry 12), that the IL functions as solvent only.

As expected from the applied experimental conditions an initial rate increase during the reactions (see examples in Fig. 2) indicated an in situ formation of the catalytically active complex. This was supported by the fact that the solid catalysts changed color from light red to yellow during reaction in accordance with [HRh(**1**)(CO)$_2$] complex formation [10], and from FT-IR spectra of the catalyst after 4–5 h on stream. Here the appearance of CO stretching bands at ν(CO) = 1998 and 1940 cm^{-1} could be observed, which was not the case for the catalysts prior to reaction or after storage of the catalysts for 48 h in air after reaction. No additional bands in the 1700–2100 cm^{-1} region were observed in either of the catalysts excluding, e.g., complexes with bridging CO. It can be noted that a similar catalyst complex preformation was also reported for liquid biphasic oct-1-ene/[BMIM][PF$_6$] hydroformylation using in situ formed Rh–guanidinium–xantphos catalysts [6], thus suggesting that neither the ionic liquid nor the heterogenization itself affected the prereaction.

Finally, it should be noted that despite the fact that steady-state performance of the catalysts was obtained within the reported 4- to 5-h reaction period, prolonged use resulted in
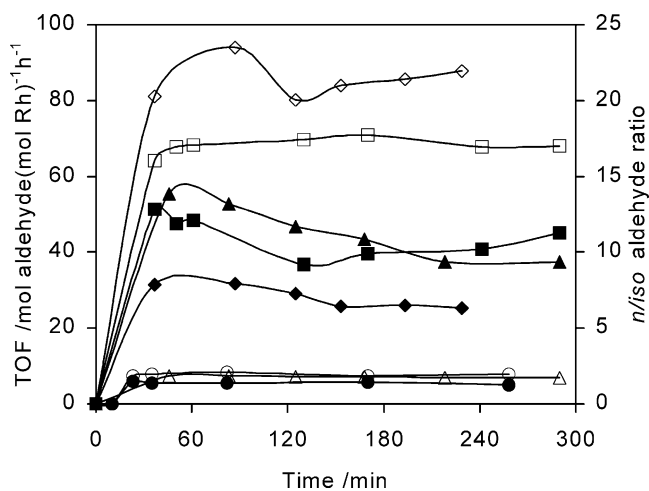

Fig. 2. Hydroformylation of propene using Rh-**1**/[BMIM][PF$_6$]/silica catalysts (C$_3$H$_6$:CO:H$_2$ = 1:1:1; p(C$_3$H$_6$/CO/H$_2$) = 10 bar; T = 100 °C. Filled symbols: TOFs; open symbols: n/iso ratios. Catalytic data from Table 1 as (L/Rh ratio, α): triangles (2.5, 0.00) (entry 1); circles (2.5, 0.49) (entry 3); squares (10.2, 0.00) (entry 5); diamonds (10.0, 0.52) (entry 8).

a decrease in catalytic activity and selectivity independent of the type of ionic liquid, α, and the L/Rh ratio. However, ongoing attempts to stabilize the catalysts by pretreatment of the support indicate no long time deactivation. Therefore, examination of supported ionic liquid-phase Rh-**1** catalysts with respect to support effects and catalyst stability is in progress and will be the subject of a subsequent paper.

In perspective, we believe that other applications using ILs as solvents for organometallic catalysts could be considered in the form of supported ionic liquid-phase catalysts well-suited for continuous fixed-bed processing. In this context, ILs composed of halogen-free ions, e.g.,

[BMIM][n-C$_8$H$_{17}$OSO$_3$], could serve as attractive alternatives to halogen-containing ILs.

References

[1] P. Wasserscheid, W. Keim, Angew. Chem., Int. Ed. Engl. 39 (2000) 3772;
R. Sheldon, Chem. Commun. 2399 (2001);
C.M. Gordon, Appl. Catal. A 222 (2001) 101;
D. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 74 (2002) 157;
H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A 182–183 (2002) 419;
J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667.

[2] Y. Chauvin, L. Mussmann, H. Olivier, Angew. Chem., Int. Ed. Engl. 34 (1995) 2698;
Y. Chauvin, H. Olivier, L. Mussmann, Eur. patent 776880A1, 1997, IFP.

[3] F. Favre, H. Olivier-Bourbigou, D. Commereuc, L. Saussine, Chem. Commun. 1360 (2001).

[4] P. Wasserscheid, R. van Hal, A. Bösmann, Green Chem. 4 (2002) 400.

[5] J. Dupont, S.M. Silva, R.F. de Souza, Catal. Lett. 77 (2001) 131.

[6] P. Wasserscheid, H. Waffenschmidt, P. Machnitzki, K.W. Kottsieper, O. Stelzer, Chem. Commun. 451 (2001).

[7] R.P.J. Bronger, S.M. Silva, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. 3044 (2002).

[8] C.C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, Organometallics 19 (2000) 3818.

[9] D.J. Brauer, K.W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt, P. Wasserscheid, J. Organomet. Chem. 630 (2001) 177;
K.W. Kottsieper, O. Stelzer, P. Wasserscheid, J. Mol. Catal. A 175 (2001) 285.

[10] P.W.N.M. van Leeuwen, A.J. Sandee, J.N.H. Reek, P.C.J. Kamer, J. Mol. Catal. A 182–183 (2002) 107.

[11] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, Nature 339 (1989) 454.

[12] M.S. Anson, M.P. Leese, L. Tonks, J.M.J. Williams, J. Chem. Soc., Dalton Trans. 3529 (1998), and references cited therein.

[13] B.B. Bunn, T. Bartik, B. Bartik, W.R. Bebout, T.E. Glass, B.E. Hanson, J. Mol. Catal. 94 (1994) 157.

[14] A. Riisager, K.M. Eriksen, J. Hjortkjær, R. Fehrmann, J. Mol. Catal. A 193 (2003) 259.

[15] C.P. Mehnert, R.A. Cook, N.C. Dispenziere, M. Afeworki, J. Am. Chem. Soc. 124 (2002) 12932.

[16] C.P. Mehnert, E.J. Mozeleski, R.A. Cook, Chem. Commun. 3010 (2002).

[17] M.S. Goedheijt, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Mol. Catal. A 134 (1998) 243.

[18] B. Heinrich, Y. Chen, J. Hjortkjær, J. Mol. Catal. 80 (1993) 365.

[19] J.L. Anthony, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 106 (2002) 7315.

[20] A.J. Sandee, V.F. Slagt, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. 1633 (1999).