Propene and 1-octene hydroformylation with silica-supported, ionic liquid-phase (SILP) Rh-phosphine catalysts in continuous fixed-bed mode

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Supported ionic liquid-phase (SILP) catalysts were made by immobilizing Rh-monophosphine complexes of bis(*m*-phenylguanidinium)phenylphosphine **1** and NORBOS **2** ligands in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF_6], on a silica support. The catalysts were active in continuous gas- and liquid-phase hydroformylation of propene and 1-octene, exhibiting TOFs up to 88 h^{-1} for SILP Rh-**2** catalysts, while only low selectivities up to 74% *n*-aldehyde (*n*/*iso* ratio of 2.8) were obtained. This is the first example of continuous fixed-bed liquid-phase hydroformylation using SILP catalysts.

KEY WORDS: hydroformylation; supported ionic liquid-phase (SILP) catalysis; continuous fixed-bed gas- and liquid-flow systems; rhodium; monophosphine.

1. Introduction

Immobilization of homogeneous organometallic catalysts in two-phase catalytic systems constitutes a well-established method for effective catalyst separation and recycling [1]. For Rh-catalyzed hydroformylation, this is demonstrated by the commercial aqueous two-phase Ruhr-chemie/Rhône-Poulenc (RCH/RP) process of C_3–C_5 olefins [2] applying water-soluble Rh-tris(*m*-sulfonatophenyl)phosphine (TPPTS) complexes as well as for hydroformylations [3] using related "heterogenized" supported aqueous-phase (SAP) catalysts with aqueous Rh-phosphine complexes immobilized on solid supports [4].

Recently, two-phase hydroformylation catalyst systems composed of Rh-phosphine complexes in room temperature ionic liquids (ILs) like, e.g., [BMIM][PF_6], have proved to be very attractive alternatives to current aqueous systems. Particularly, in reactions of higher olefins, where low reaction rates are usually obtained in aqueous systems because of phase-transfer limitations caused by low substrate solubility in the catalyst phase, several good results for the conversion of C_5–C_6 [5,6] and C_8 and longer-chained olefins [7–13] have been reported. In general, the ionic liquid catalyst phases generated effective media for catalyst separation and recycling, provided the Rh catalysts were modified with charged phosphine ligands, e.g., cationic phenylguanidinium phosphine **1** [8] (scheme 1), ensuring a high relative catalyst affinity for the polar IL phase compared to the lipophilic product phase.

In contrast to SAP Rh-phosphine hydroformylation catalyst systems, only minor attention has been given to analogous heterogenized supported ionic liquid-phase (SILP) Rh-phosphine catalysts. This is despite the obvious advantages of using ILs instead of water as a catalyst phase, e.g., low vapor pressures ensure that the IL remains liquid on the support at reaction conditions and is easy to retain in continuous processes. Hence, Mehnert *et al.* [14] has introduced supported ionic liquid Rh-catalyst systems containing monoarylphosphines like, e.g., PPh_3 and TPPTS, and [BMIM][X] ($X = PF_6$ and BF_4) ionic liquids for batch two-phase liquid 1-hexene hydroformylation using a modified silylimidazolium silica support. Furthermore, we recently demonstrated [15] the use of selective unmodified silica SILP Rh catalysts containing the xanthene-based biphosphine ligand sulfoxantphos and [BMIM][X] ($X = PF_6$ and $C_8H_{17}OSO_3$) for gas-phase propene hydroformylation in a technically more attractive continuous-flow process.

In this paper, we report the catalytic results obtained from continuous gas- and liquid-phase hydroformylation of propene and 1-octene, respectively, using [BMIM][PF_6]/silica-supported ionic liquid-phase catalysts containing charged Rh-monophosphine complexes of the ligands **1** and **2** (scheme 1). Previously, use of cationic ligand **1** in liquid two-phase [BMIM][PF_6]/1-octene hydroformylation [8] showed that a good Rh-**1** catalyst solubility allowed a combination of high catalytic activity and complete retention of the catalyst

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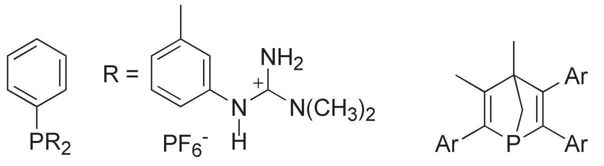


1 **2:** Ar = p-PhSO$_3^-$Cs$^+$

Scheme 1. Charged monophosphine ligands. **1**: bis(m-phenylguanidinium)phenylphosphine hexafluoro-phosphate, **2**: tri-cesium 3,4-dimethyl-2,5,6-tris(p-sulfonatophenyl)-1-phosphanorbornadiene(NORBOS-Cs$_3$).

in the IL phase. The sulfonated phosphanorbornadiene ligand **2** has previously induced high activity in propene hydroformylation in both two-phase aqueous systems [16] and in derived SAP systems [17] using Rh-**2** catalysts. Hence, the work reported here continues our study on gas-phase propene hydroformylation with SILP Rh-phosphine catalysts in continuous-flow processes, and introduces for the first time, as far as we are aware of, continuous liquid-phase SILP catalysis exemplified by 1-octene hydroformylation.

2. Experimental

2.1. General comments

Catalyst preparations were carried out with degassed solvents under an argon atmosphere using standard Schlenk techniques. Methylenchloride was dried with 4 Å molecular sieves and distilled prior to use. Ionic liquid [BMIM][PF$_6$] (>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 vacuo* before use (0.1 mbar, 24 h, IL: 80 °C and silica: 110 °C). The phenylguanidinium phosphine ligand **1** [8] and the NORBOS-Cs$_3$ ligand **2** (prepared by a modified procedure [17] to the one described by Herrmann *et al.* [16]) were prepared according to literature procedures.

For hydroformylation reactions, propene (99.4%), CO (99.997%), H$_2$ (99.9997%), and (50 : 50) vol% CO/H$_2$ (>99.8%) gases were used as received from Hede Nielsen A/S, Denmark. 1-octene (98%, Aldrich) was distilled prior to use. Analyses of reaction products were performed by gas chromatography using FID detection by comparison with samples of aldehyde products. For propene reactions, analyses were conducted by on-line detection on outlet gas mixtures using a Shimadzu GC-9A (Nukol$^{\text{TM}}$ capillary column, 15 m × 0.50 mm × 0.53 μm, Supelco Inc.). For the 1-octene reaction product, analyses were performed off-line using a Perkin Elmer Autosystem XL (PE-WAX capillary column, 15 m × 0.323 mm × 0.50 μm). *n*-butanal (99%), *iso*-butanal (>98%) and *n*-nonanal (97%) (Aldrich) used for GC calibrations were distilled prior to use, while 2-methyloctanal was prepared in accordance with literature procedure [18]. All other reagents and solvents were purchased from commercial sources in high-purity grades and used without further treatment.

2.2. Preparation of Rh-monophosphine SILP catalysts

The supported ionic liquid-phase catalysts systems were prepared by impregnation of silica using Rh(acac)(CO$_2$) precursor and ligands in two-phase water/methylenchloride/[BMIM][PF$_6$] mixtures. Rh (acac)(CO)$_2$ (5.0 mg, 0.0194 mmol) and ligand **1** or **2** were dissolved in (50 : 50) vol% H$_2$O/CH$_2$Cl$_2$ (10 ml) and reacted for 2–4 h under vigorous stirring until complete decoloring of the organic phase had occurred, indicating the transfer of all Rh complexes to the aqueous phase. Afterward, ionic liquid [BMIM][PF$_6$] and 1.0 g of silica gel (giving 0.2 wt% Rh metal loading) were added to the mixture, followed by stirring for an additional 2 h. Finally, catalysts were obtained by removal of volatile solvents (10 mbar, 35 °C), followed by drying (0.1 mbar, 80 °C, 24 h) to prevent hydrolysis of PF$_6^-$ ions. The catalysts were stored *in vacuo* over P$_4$O$_{10}$ prior to use.

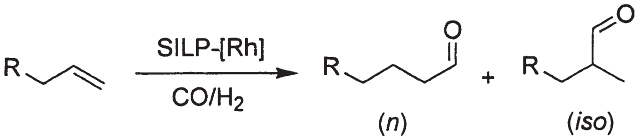
2.3. Continuous-flow hydroformylation

The continuous gas-phase propene hydroformylation reactions were studied using a microcatalytic flow system with the SILP catalysts forming a fixed bed in a stainless-steel tubular reactor, as previously described [17,19]. The reactor setup used for continuous-flow liquid-phase 1-octene reaction was essentially applied as previously described for Rh-catalyzed methanol carbonylation [20]. Both reaction systems were operated differentially with negligible reactor gradients using isobaric and isothermal reaction conditions, thus allowing for determination of intrinsic kinetics. The observed rates corresponded to the hydroformylation activities since no byproducts were observed from, e.g., hydrogenation or isomerization.

During the 1-octene reaction, the substrate phase containing (80 : 20) vol% 1-octene : decane ratio (decane added as internal reference) was saturated with CO/H$_2$ gas prior to reaction. This was done in a reservoir by bubbling gas through the liquid for 1 h at ambient pressure, followed by storage at the reaction pressure for 24 h. The reaction pressure was regulated and maintained by a back-pressure valve positioned at the substrate reservoir. From the bottom of the reservoir, the gas-saturated liquid was pressed into a heating foil before entering a vertically positioned tubular reactor containing 600 mg of catalyst. The flow rate was adjusted to 0.40 mL min^{-1} (LHSV = 16 h^{-1} and $\tau = 225$ s) by a two-step regulation composed of a second back-pressure regulator followed by a fine meter valve. Lowering of the reactor/foil unit into a preheated oil bath followed by the opening of a liquid feed valve started the reaction. Samples were periodically taken from the outlet of the system and analyzed.

3. Results and discussion

Continuous gas- and liquid-phase hydroformylation of propene and 1-octene were performed with new SILP catalysts composed of the ionic liquid $[BMIM][PF_6]$ containing monophosphine Rh-**1** or Rh-**2** complexes immobilized on a silica support (equation 1, R = H and C_6H_{13}).



(1)

The described one-pot, two-phase catalyst preparation procedure was applied instead of preparation by consecutive addition of precursor complex and ligand, since only this procedure gave reproducible kinetic results with the obtained catalysts in subsequent reactions. Probably, the consecutive addition only partly gave coordination of ligand to the precursor complex.

The catalytic results obtained from propene hydroformylation with the SILP catalysts modified with the two ligands at different L/Rh ratios and ionic liquid loadings (α) are shown in table 1.

The SILP catalyst systems were found to exhibit steady state TOFs of up to 88 mol propene converted per mol rhodium per hour with *n*/*iso* ratios of up to 2.8 during typically 4–5 h after initial catalyst preformation reaction (duration typically 0.5–1 h). However, it cannot be excluded that long-time deactivation of the catalysts takes place, as previously seen for SILP Rh-sulfoxantphos catalysts using unmodified silica supports [15]. This issue will be the subject of a future investigation. Further, the data (table 1) indicates the presence of an optimum L/Rh ratio with respect to catalyst activity as previously found for the analogous SAP Rh-**2** catalysts [17].

In general, an increased degree of pore filling with ionic liquid of the catalysts induced an overall tendency of decreasing activity. However, for catalysts having ionic liquid loading around 0.3 (entry 2 and 10), surprisingly low activities were obtained. The reason for this behavior is at present not clear to us. The highest activities for the investigated catalyst systems were obtained with the ionic liquid solvent-free catalysts (entry 1, 7, and 9). Most likely, this is due to the catalysts being heterogeneous and free of mass-transfer limitations caused by poor solubilities of the gaseous reactants in the ionic liquid solvent [21]. In addition, catalytic tests of pure supported $[BMIM][PF_6]$ catalyst, i.e., catalyst containing ionic liquid only (entry 13), established the IL solvent to be catalytically inactive.

Only very low *n*/*iso* selectivities of 0.9–1 were obtained for the catalysts with L/Rh ratios of 2.9 and ionic liquid (entry 2–4 and 10–12). This strongly indicates that the catalytically active complexes at these conditions are ligand-free complexes interacting

Table 1
Catalytic performance of SILP Rh-monophosphine/$[BMIM][PF_6]$/silica catalysts in continuous gas-phase hydroformylation of propene[a]

Entry	Ligand	L/Rh ratio	$[BMIM][PF_6]$ loading		TOF[c] (h^{-1})	*n*/*iso* ratio	Linear prod. (%)
			wt%	α[b]			
1	**2**	2.9	–	0.00	114.8	1.0	50.0
2	**2**	2.9	41.7	0.30	6.9	0.9	47.4
3	**2**	2.9	108.4	0.78	38.0	0.9	47.4
4	**2**	2.9	138.9	1.00	30.5	0.9	47.4
5	**2**	11.3	6.9	0.05	88.4	2.0	66.7
6	**2**	11.3	20.8	0.15	79.4	1.3	56.5
7	**2**	21.4	–	0.00	45.8	2.8	73.8
8	**2**	21.3	6.9	0.05	28.2	2.6	72.2
9	**1**	2.9	–	0.00	55.5	0.9	47.4
10	**1**	2.9	45.8	0.33	3.7	1.0	50.0
11	**1**	2.9	108.4	0.78	20.6	0.9	47.4
12	**1**	2.9	138.9	1.00	16.8	1.0	50.0
13[d]	–	–	105.6	0.76	0.0	–	–

[a] *Hydroformylation conditions*: $C_3H_6 : CO : H_2 = 1:1:1$; $p(C_3H_6/CO/H_2) = 5$ bar; $T = 120\,°C$; conversion ≈1 %; GHSV = 12,000 h^{-1}; 0.2 wt% Rh metal loading; Rh precursor: $Rh(acac)(CO)_2$; support: silica gel 100.

[b] Pore filling degrees of ionic liquid in the silica support as volume IL/pore volume support.

[c] Turn-over frequencies are reported in mol aldehyde formed per mol of Rh per h at steady state rates after 4 h reaction. Selectivity to aldehyde was 100 % in all reactions.

[d] Catalyst was made by immobilizing ionic liquid without dissolved Rh precursor complex or ligand on silica support.

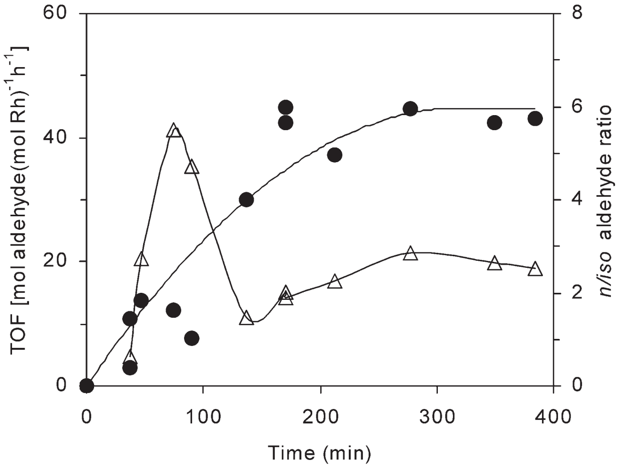


Figure 1. Catalytic performance of SILP Rh-**2**/[BMIM][PF_6]/silica catalyst in continuous liquid-phase hydroformylation of 1-octene (L/Rh = 11.3; $\alpha = 0.05$; CO : H_2 = 1; $p(CO/H_2) = 14$bar; $T = 115\,^{\circ}C$; LHSV = 16 h^{-1}; ● : TOF; Δ: *n*/*iso* ratio).

with the support, e.g., $[Rh(CO)_2]^+$, in accordance with the conclusion made for the analogous SILP Rh-sulfoxantphos biphosphine systems [15].

The performance of catalysts modified with ligands **1** and **2** established Rh-**2** catalysts to be significantly more active than Rh-**1** catalysts at the same L/Rh ratios and α values. Interestingly, activities obtained using monophosphine Rh-**2** catalysts were equal to activities previously found [15] for biphosphine SILP Rh-sulfoxantphos catalysts having similar composition. Hence, compensating for pressure and temperature differences of the reactions (i.e., first-order dependence of olefin pressure and logarithmic Arrhenius temperature dependence), the Rh-**2** catalyst with an L/Rh ratio of 11.3 and an ionic liquid loading of 0.15 gave an activity (TOF) of 79.4 h^{-1} at $p = 5$ bar and $T = 120\,^{\circ}C$ (entry 6), while the activity for the analogous Rh-sulfoxantphos catalyst (L/Rh = 10.0, $\alpha = 0.18$) at $p = 10$ bar and $T = 100\,^{\circ}C$ was found to be 34.9 h^{-1} [15]. Furthermore, the selectivity obtained using the monophosphine Rh-**1** and Rh-**2** catalyst systems was at all L/Rh ratios similar and in the usual range obtained for Rh-monophosphine catalysts, i.e., *n*/*iso* ≤ 2.8 and independent of α. In contrast, selectivities corresponding to *n*/*iso* ratios >20 was found for analogous Rh-sulfoxantphos catalyst systems, thereby clearly indicating that multidentate ligands are required for obtaining high hydroformylation selectivity with SILP hydroformylation catalysts.

The concept of continuous-flow-supported ionic liquid-phase hydroformylation was extended from gas-phase reactions to include biphasic, liquid–liquid hydroformylation. The results obtained from continuous-flow two-phase hydroformylation of 1-octene using Rh-**2** catalyst are shown in figure 1.

A monotonic increase in catalytic activity was observed during preformation of the active catalyst, until steady state rate corresponding to a TOF of 44 h^{-1} was reached after 3–4 h (figure 1). At prolonged reaction time, the activity remained unchanged for at least an additional 3 h (end of the experiment), indicating no sign of deactivation. Presaturation of the 1-octene substrate with CO/H_2 gas confined the reactions to two phases instead of three. Probably this solved the problems that otherwise could be anticipated by operating tri-phasic reactions in continuous modes. However, the presaturation introduced a limitation to the reaction efficiency, since low solubility of H_2 and CO gas in 1-octene (about 45 mM [22]) are anticipated at reaction conditions. At steady state conditions, a *n*/*iso* ratio of 2.6 was obtained, although fluctuations were observed initially in the reaction period, most likely due to the prereaction. ICP-AES analysis of outlet samples taken at steady state conversion demonstrated rhodium metal leaching to be negligible ($\leq 0.7\%$, detection limit).

4. Conclusion

The concept of continuous SILP catalysis has been extended for continuous gas-phase hydroformylation reactions to include Rh-monophosphine complexes, Rh-**1** and Rh-**2**. Interestingly, the Rh-**2** catalysts proved to possess similar activity as analogous Rh-sulfoxantphos catalysts but lower selectivity, indicating the importance of the multidentate character of the phosphine ligand [15]. In addition, the continuous SILP catalysis concept has for the first time been demonstrated for the liquid-phase hydroformylation reaction of 1-octene using the SILP Rh-**2**/[BMIM][PF_6]/silica catalyst. Importantly, the liquid reaction proceeded without detectable catalyst leaching, but poor solubility of CO/H_2 gas in [BMIM][PF_6] suggests that the catalyst suffers from gas mass-transfer limitations using the described reaction design. Generally, the supported ionic liquid-phase catalyst systems, however, offer the significant advantage of very efficient ionic liquid use and relative short diffusion distances due to the highly dispersed ionic liquids catalyst solution in comparison to the conventional two-phase liquid-liquid catalysis in organic/IL mixtures. Consequently, other catalyzed processes applying organometallic catalysts are presently under consideration using the SILP catalysis concept.

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