Catalyst Development

Very Stable and Highly Regioselective Supported Ionic-Liquid-Phase (SILP) Catalysis: Continuous-Flow Fixed-Bed Hydroformylation of Propene**

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In the last decade the application of ionic liquids in catalysis^[1] has been the subject of intensive research in academia and industry.^[2] A major reason for the growing interest is the use of ionic liquids as alternative solvents^[3] for many transition-metal-catalyzed reactions. In particular, liquid–liquid biphasic processes having an organic product phase have been examined since the ionic catalyst phase often induces excellent catalyst immobilization and also has low miscibility with the organic reaction products. However, implementation of these strategies in industrial processes is still hampered by the fact that the biphasic methodologies rely on relatively large amounts of ionic liquids. Even though ionic liquids have become commercially available^[4] they are still relatively expensive compared to traditional solvents.

In many cases, liquid–liquid biphasic catalysis makes use of only a fraction of the ionic-liquid solvent and of the catalyst dissolved therein. In the case of a fast chemical reaction and relatively slow mass transfer (caused by the relatively high viscosity of the ionic liquid) the concentration of the reactant in the bulk ionic-liquid phase is reduced significantly, and the reaction occurs primarily at the interphase or in the diffusion layer of the ionic-liquid catalyst phase rather than in the bulk solvent. An ideal catalyst system would thus consist of a bulk catalyst phase the same size as the diffusion layer. In this way the solubilized catalyst complex and the ionic liquid are all available. In addition, application of solid catalysts is pre-

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ferred from a technical standpoint due to easy product separation and the potential for developing a continuous-flow fixed-bed process.

Recently we and others introduced "heterogenized" versions of homogeneous ionic-liquid catalyst systems, described as supported ionic-liquid-phase (SILP) catalyst systems, for olefin hydroformylation^[5-7] (Rh-catalyzed), hydrogenation^[8] (Rh-catalyzed), Heck reactions^[9] (Pd-catalyzed), and hydroamination^[10] (Rh-, Pd-, and Zn-catalyzed). In these systems the catalysts are composed of a transition-metal complex dissolved in a thin film of the ionic liquid, which is held on a porous solid with high surface area by physisorption, tethering, or covalent anchoring. The SILP catalyst concept results in a very efficient use of the ionic liquid and relatively short diffusion distances for the reactants compared to those in conventional two-phase systems with an ionic-liquid catalyst phase. In addition, the negligible vapor pressure, large liquid range, and thermal stability of ionic liquids ensure that the solvent is retained on the support in its fluid state even at elevated temperatures; this makes SILP catalysts highly suitable for continuous processes. Moreover, the solvent properties of the ionic liquid are tuneable by the choice of the cation/anion combination. Further advantages of the SILP concept are, for example, compatibility with hydrolytically labile catalyst complexes and possible catalyst activation by interaction with the ionic liquid.^[11]

In rhodium-catalyzed olefin hydroformylation, Mehnert et al.^[7] examined the liquid-phase reaction of 1-hexene in a batch reactor using unselective (*n*/iso ratios of 0.4-2.4) SILP catalyst systems. The catalysts were composed of monophosphines (PPh₃ and TPPTS) dissolved in [bmim]X (bmim = 1-*n*-butyl-3-methylimidazolium, $X = PF_6$ or BF_4) on a 1-*n*butyl-3-[3-(triethoxysilanyl)propyl]imidazolium-modified silica gel support (average of 0.4 imidazolium fragments per nm², corresponding to the involvement of approximately 35% of the silanol groups of the support). The SILP catalysts were found to have higher activity than analogous biphasic systems; however, a significant amount of the metal catalyst leached into the product phase at high conversions (rhodium loss of up to 2.1 mol%), due to depletion of the ionic-liquid phase from the support. Importantly, even at lower conversion pronounced catalyst deactivation was observed during recycling, which was independent of the presilylation of the support.^[12] This deactiviation shortened the lifetime and limited the applicability of the catalysts significantly.

Recently we have described a selective (*n*/*iso* ratios up to 23.7, that is, 96.0% linearity) SILP catalyst for the Rhcatalyzed gas-phase hydroformylation of propene in a fixedbed reactor.^[6] The rhodium catalyst contains the bisphosphine ligand sulfoxantphos **1** and is dissolved in either a halogencontaining or halogen-free ionic liquid ([bmim]X (X = PF₆ or



 $n-C_8H_{17}OSO_3$)). These ionic catalyst solutions were physisorbed on the unmodified silica support. However, these systems were also deactivated after prolonged use (reaction time > 24 h) regardless of the type of ionic liquid, the loading α (defined as the volume of the ionic liquid divided by the pore volume,) and the ligand/rhodium ratio.

Very recently, Han et al.^[13] demonstrated an interesting variation of the SILP concept. They immobilized Pd nanoparticles with a lactate-based ionic liquid on molecular sieves and used the resulting systems for the liquid-phase hydrogenation of cyclohexene and 1-hexene.

In this communication we demonstrate the first use of a SILP catalyst system in which the catalyst remains active, highly selective, and stable over extended periods in a continuous gas-phase process. The catalysts are composed of Rh-1 in [bmim][n-C₈H₁₇OSO₃] on a partly dehydroxylated silica support (hereafter referred to as Rh-1/IL/SiO₂). Moreover, we propose an explanation for the deactivation phenomena previously observed with analogous nondehydroxylated SILP silica catalysts. Our proposal is based on FTIR studies of the catalyst conducted in situ (syngas atmosphere at elevated temperature), as well as characterization of the support by MAS ³¹P NMR spectroscopy and temperature-programmed desorption of ammonia (NH₃-TPD).

In our previous studies of silica-based Rh-1 SILP catalysts on nondehydroxylated supports in the continuous-flow hydroformylation of propene (reaction times of 4–5 h),^[6] we found that the catalyst performance was strongly influenced by the ligand/rhodium ratio and the loading of the ionic liquid, but less affected by the choice of ionic liquid (except for the catalyst preformation, which appears to depend on the solubility of the ligand and precursor). High selectivities (n/iso > 20) were obtained only for Rh-1/IL/SiO₂ catalyst systems with an L/Rh ratio of more than 10; this is in contrast to analogous reactions performed with an ionic-liquid catalyst solution without a support where high selectivities were observed even at 1/Rh ratios of 2.^[14] The results clearly indicate a significant effect of the inorganic support. Accordingly, we devised a suitable preparation for the support (catalysts with an untreated support were not stable beyond 12–24 h).

In our continuous-flow gas-phase hydroformylation of propene with a reaction time of 60 h, we applied a partially dehydroxylated silica support (heating at 500 °C in air for 15 h). In the earlier work^[6] support pretreatment implied only drying the support in vacuo (110 °C, 24 h). The thermal pretreatment proved to be a crucial parameter for obtaining Rh-**1** silica-based catalysts with high stability during prolonged reactions (Figure 1).

The catalytic performance and catalyst stability, however, still proved to be significantly influenced by the catalyst composition, (loading α and 1/Rh ratio; Figures 2 and 3). In reactions with catalysts having various 1/Rh ratios we found that catalysts with low ligand contents (1/Rh = 3 and 5) were initially very active compared to the catalyst with 1/Rh = 10 but less selective (Figure 2). In addition, the catalysts with low ligand content were deactivated relatively quickly within the first 24 h; the turnover frequency (TOF) dropped to 4–5 h⁻¹, and the selectivity fell to n/iso = 1-1.3). In contrast, the



Figure 1. Hydroformylation of propene on untreated (\triangle , **A**) and partly dehydroxylated supports (\bigcirc , **e**). Plots of activity (mol butanal (mol Rh)⁻¹ h⁻¹, closed symbols) and selectivity (*n*/isobutanal, open symbols) of Rh-1/[bmim][*n*-C₈H₁₇OSO₃] on silica (α = 0.1, 1/Rh = 10) as function of reaction time.



Figure 2. Hydroformylation of propene with catalysts having different amounts of ligand. Plots of activity (mol butanal (mol Rh)⁻¹ h⁻¹, closed symbols) and selectivity (*n*/isobutanal, open symbols) of Rh-1/[bmim][*n*-C₈H₁₇OSO₃] on silica (α =0.1). Results for catalysts with 1/Rh=3 (\diamond , \blacklozenge), 1/Rh=5 (\triangle , \blacktriangle), and 1/Rh=10 (\bigcirc , \bullet) are shown.



Figure 3. Hydroformylation of propene with catalysts having different loadings α . Plots of activity (mol butanal (mol Rh)⁻¹ h⁻¹, closed symbols) and selectivity (*n*/isobutanal, open symbols) of Rh-1/[bmim][*n*-C₈H₁₇OSO₃] on silica (1/Rh=10). Results for catalysts with $\alpha = 0$ (\diamond , \blacklozenge) and $\alpha = 0.1$ (\bigcirc , \blacklozenge) are shown.

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catalyst with 1/Rh = 10 retained the initial catalytic performance over at least 60 h (TOF = 44 h⁻¹, TON \approx 2600, *n/iso* > 20).

These results clearly indicate that a large excess of ligand is required for a stable SILP catalytic system. Even when the support is pretreated, reactions presumably occur between the ligand and the support, rendering some of the ligand inaccessible for complex formation. Evidence for the interaction of the ligand and the support was provided by solid-state MAS ³¹P NMR spectra of Rh-1/IL/SiO₂ (1/Rh = 10) recorded prior to reaction (see the Supporting Information). Here, the signals measured could be assigned to free ligand ($\delta = -13$ ppm, 27%), surface-bonded ligand ($\delta = -21$ ppm, 54%), and complexed ligand ($\delta = 31$ ppm, 19%).

Moreover, in studies with catalysts having different loadings of the ionic liquid ($\alpha = 0-0.5$), the catalyst systems containing no ionic liquid were deactivated rapidly; after a reaction time of 60 h only 30% of the initial activity and selectivity remained (Figure 3). The slow deactivation of the other catalysts can be explained by the slow surface diffusion of the ligand from the initial Rh-coordinated active state to the surface-bonded state, in which the metal atom is less coordinated to the ligand but possibly more strongly coordinated to the support and thus less active and selective. Evidently the SILP catalysts require a certain amount of ionic-liquid solvent—not only for high selectivities (n/iso >20) as previously seen-but also for stability over longer periods during continuous processes. Further, since the n/iso selectivity in hydroformylation reactions is known to depend on the amount of ligand available for coordination,^[15] the simultaneous decrease in selectivity along with activity lends additional support to the hypothesis that deactivation is closely related to a gradual degradation and removal of ligand from the catalyst complex system.

To further explain the observed results, we studied the catalyst in situ under conditions closely related to the reaction conditions by FTIR spectroscopy (Figure 4). The FTIR spectra of the system Rh-1/IL/SiO₂ (1/Rh = 10; 100 °C) show the relatively fast transformation of the red dimeric catalyst precursor [{Rh(μ -CO)(1)(CO)}₂] (2)^[16]—characterized by a broad band for the terminal CO stretch at $\tilde{\nu}$ (CO) = 1990 cm⁻¹—to the light-yellow monomeric compound



Figure 4. Part of an FTIR spectra of Rh-1/IL/SiO₂ catalysts (1/Rh = 10, α = 0.5) at 100 °C after: a) 15 min in nitrogen, b) 15 min in syngas, and c) 30 min in syngas.

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[HRh(CO)₂(1)] (Scheme 1), which has two isomeric forms, 3ea ($\tilde{\nu}$ (CO) = 1994, 1948 cm⁻¹) and 3-ee ($\tilde{\nu}$ (CO) = 2035 (w), 1964 cm⁻¹) coexisting in dynamic equilibrium. Reexposure of the 3-ea/3-ee mixture to nitrogen slowly regenerates the dimer 2 reversibly, while air treatment leads to irreversible degradation of the complex and presumably to the oxidation of excess ligand. This is supported by a significant change in the color of the sample along with the appearance of a new broad CO band at $\tilde{\nu}$ (CO) = 1972 cm⁻¹.

Importantly, the complex formation in the SILP Rh-1/IL/ SiO₂ catalysts with 1/Rh = 10 (Scheme 1) is very similar to that previously reported for Rh-1 and analogous rhodium– xanthene-based systems^[16] in organic and ionic-liquid solvents (Table 1). Thus, it seems reasonable to conclude that complex formation in the SILP catalyst systems takes place in the



Scheme 1. Formation of Rh complexes in the Rh-1/IL/SiO₂ catalyst systems (1/Rh = 10) at 100 °C during various gas treatments.

Table 1: Comparison of $\tilde{v}(CO)$ bands of $[HRh(CO)_2(L)]$ complexes in different systems.

	Solvent	ea isomer $ ilde{v}$ (CO) [cm ⁻¹]	ee isomer $ ilde{ u}(CO) [cm^{-1}]$
SILP (Rh-1/IL/SiO ₂)	[bmim][<i>n</i> - C ₈ H ₁₇ OSO ₃]	1994, 1948	2035, 1964
[RhH(CO) ₂ (1)] ^[16b]	[bmim][PF ₆]	1985, 1935	2032, 1967
[RhH(CO) ₂ (xantphos)] ^[16b]	benzene	1991, 1941	2036, 1969
[RhH(CO) ₂ (thixantphos)] ^[16b]	cyclohexane	1999, 1953	2040, 1977

ionic-liquid solvent, and consequently that the examined SILP hydroformylation reactions are indeed homogeneously catalyzed.

The FTIR spectra of the analogous catalysts with 1/Rh = 3and 5 show that degraded catalysts formed irreversibly regardless of the gas treatment. The decrease in the intensity of the two characteristic absorption bands was more pronounced for catalysts with 1/Rh = 3 than for catalysts having 1/Rh = 5 (Figure 5). For catalysts with 1/Rh = 10 no loss in intensity was observed. This clearly suggests that catalysts with 1/Rh = 10 contain a sufficient amount of ligand to stabilize the monomeric, catalytically active monomers. Since this is in excellent accordance with the relative catalyst stabilities measured, the stability of the SILP catalyst is directly related to the degradation of the catalytically active complex, which in turn is correlated to the amount of ligand available for complex formation.

The proportion of acidic OH groups (mostly Brønsted sites) on the partly dehydroxylated silica support used was evaluated by NH_3 -TPD to be 69 µmol OH g⁻¹, which corre-



Figure 5. Part of an FTIR spectra of Rh-1/IL/SiO₂ catalysts ($\alpha = 0.1$, 100°C, after 15 min in syngas) containing different ligand/Rh ratios: a) 1/Rh = 10, b) 1/Rh = 5, and c) 1/Rh = 3.

sponds to 26% of the original content present in the untreated support (see the Supporting Information for details). This is in relatively good agreement with the remaining fraction of 35% Si-OH groups (Q3, $\delta \approx -100$ ppm) relative to Si-O-Si groups (Q4, $\delta \approx -111$ ppm) determined by solid-state MAS ²⁹Si NMR spectroscopy for analogous samples (see the Supporting Information). Therefore, it seems reasonable to assume that the pretreatment decreases the amount of acidic OH groups on the support only by dehydroxylation of surface silanol groups and not by, for example, inducing structural changes in the support. This is further affirmed by the identical T_{max} values obtained for ammonia desorption and by the practically unchanged BET surface area and pore volume after dehydroxylation.

The amount of ligand 1 present in the Rh-1/IL/SiO2 system during catalysis was determined for L/Rh=3 to be 58 μ mol1g⁻¹; for L/Rh = 5, 97 μ mol1g⁻¹ support; and for L/ Rh = 10, 194 µmol1g⁻¹ support. These values can be correlated to the measured OH content of the support, by assuming that the ligand bonds irreversibly to one acidic OH group on the surface of the support. Hence, very little ligand should be available for complex formation in the case of a catalyst with L/Rh = 3, 30% of the ligand should still be available with L/Rh = 5 (i.e. effective 1/Rh ratio = 1.5), and 65 % of the ligand should still be available with L/Rh ratio = 10 (effective 1/Rh =6.5). Consequently, highly selective and stable catalyst systems can be obtained only when the amount of ligand is sufficient to compensate for the loss induced by the surface bonding, that is, when the effective 1/Rh ratio is greater than 1. This is in excellent agreement with the experimental data, thus underlining the importance of the acidic OH groups of the support for the long-term stability of SILP Rh-phosphine catalysts.

This paper describes important progress in the very promising field of SILP catalysis. We demonstrate for the first time the long-term stability of Rh-1/[bmim][n-C₈H₁₇OSO₃] catalysts supported on partly dehydroxylated silica in the selective, continuous, gas-phase hydroformylation of propene. Clear spectroscopic evidence also indicates that the catalysis in the supported ionic-liquid layer is homogeneous. Moreover, decreasing the number of surface silanol

groups on the support material by thermal treatment is a crucial parameter in the preparation of stable hydroformylation systems that are selective and active for at least 60 h on stream.

We have found that the effect of the support is directly related to the irreversible reaction of the ligand with the acidic silanol surface groups before and during catalysis. Therefore, the prerequisites for active, highly selective, and long-term stable SILP catalysts are not only the ionic-liquid solvent but also a relatively large excess of phosphine ligand to compensate for some detrimental surface reactions.

We hope that the knowledge gained in this work will lead to the development of new SILP catalysts for hydroformylations, hydrogenations, and C–C coupling reactions. The combination of well-defined catalyst complexes, nonvolatile ionic liquids, and porous solid supports offers many advantages over traditional catalysis with water (SAPC) or with organic solvents with low vapor pressure (SLPC) on supports,^[17] which are clearly limited by solvent volatility.^[18] We therefore consider the SILP catalysis concept to be a significant contribution to the development of highly selective, heterogenized homogeneous catalysts.

Experimental Section

The SILP catalysts were prepared according to our previously reported method^[6] by impregnation of the partly dehydroxylated silica support with an anhydrous methanolic solution of the ionic liquid [bmim][n-C₈H₁₇OSO₃]^[19] containing the catalyst precursor [Rh(acac)(CO)₂] (Aldrich, 98%) and bisphosphine ligand $\mathbf{1}^{[20]}$ under argon atmosphere using standard Schlenk techniques. The partial dehydroxylation of the support (silica gel 100, Merck) was performed by heating at 500 °C in air for 15 h followed by storage in vacuo over P₄O₁₀ prior to use (BET surface area: 304 m²g⁻¹, pore volume: 1.01 cm³g⁻¹, mean pore diameter (monomodal): 132 Å).

The continuous-flow gas-phase hydroformylation of propene was performed at a total pressure of 10 bar (C_3H_6 :CO:H₂=1:1:1) and *T*= 100 °C with differential conversion (<10% conversion) using a microcatalytic flow system. The solid SILP catalyst was used as a fixed bed in a stainless-steel tubular reactor, as previously described.^[5,6] The activity (TOF) and selectivity (*niso*) of the catalysts were determined directly from online FID-GC measurements (Shimadzu GC-9A, Nukol capillary column, 15 m × 0.53 mm ID, Supelco Inc.) of the reaction products by comparison with authentic samples of aldehydes.

FTIR spectra of the catalysts were recorded on a Perkin Elmer Paragon 1000 FTIR spectrophotometer. Samples were prepared as KBr catalyst wafers by pressing catalyst onto the KBr and mounted for measurements in situ under various gas atmospheres at 100 °C in a stainless-steel variable-temperature transmittance IR cell (Infraspac LB-100, Infraspac Ltd, Novosibirsk, Russia; Si optical windows) having gas inlet and outlet ports and an adjustable sample holder. With this setup each recording could be corrected for background absorbance without changing the atmosphere.

Experimental details and data from MAS ^{31}P and ^{29}Si NMR spectroscopy and NH₃-TPD measurements are available in the Supporting Information.

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