DOI: 10.1002/ejic.200500872

# Supported Ionic Liquid Phase (SILP) Catalysis: An Innovative Concept for Homogeneous Catalysis in Continuous Fixed-Bed Reactors

Anders Riisager,*[a] Rasmus Fehrmann,[a] Marco Haumann,*[b] and Peter Wasserscheid[b]

**Keywords:** Ionic liquids / Supported catalysts / Immobilisation / Homogeneous catalysis / Hydroformylation

Applications of ionic liquids to replace conventional solvents in homogeneous transition-metal catalysis have increased significantly during the last decade. Biphasic ionic liquid/organic liquid systems offer advantages with regard to product separation, catalyst stability, and recycling but utilise in the case of fast chemical reactions only a small amount of expensive ionic liquid and catalyst. The novel Supported Ionic Liquid Phase (SILP) catalysis concept overcomes these drawbacks and allows the use of fixed-bed reactors for continuous reactions. In this Microreview the SILP catalysis concept is surveyed by presenting results for the continuous gas-phase hydroformylation of propene, as a reaction example.

## Introduction

In the last decade, ionic liquids have been studied extensively as alternative solvents for homogeneous catalysis.[1] Their ionic nature, nonvolatility, and thermal stability make them highly suitable for biphasic ionic liquid/organic liquid transition-metal catalysis.[2] The almost unlimited combinations of cation and anion allow the synthesis of tailor-made ionic liquids that can stabilise the catalytic species.[3] Moreover, appropriate ionic liquids can enhance substrate solubility while possessing low product solubility, and thus facilitate simple product separation and complete catalyst recovery.[4]

Biphasic ionic liquid/organic liquid systems generally require a large amount of ionic liquid. On the basis of economic considerations this is unattractive since ionic liquids remain relatively expensive even though they are now commercially available.[5] In addition, the high viscosity of ionic liquids can induce mass transfer limitations if the chemical reaction is fast, causing only a minor part of the ionic liquid and precious transition metal catalyst dissolved therein to take part in the catalysed reaction. This problem can, however, to some extent be circumvented by intense stirring to create smaller droplets with a larger reaction surface. This, on the other hand, necessitates a high energy input due to the viscosity of the ionic liquid and makes continuous processes economically unviable. Thus, in contrast to the conventional ionic liquid/organic liquid biphasic systems, an ideal catalyst system would consist of a bulk catalyst phase having the size of the diffusion layer, which allows all the available metal complexes and ionic liquid to be involved in the catalytic reaction. Additionally, solid catalyst systems would allow application of continuous-flow-operated fixed-bed processing.

A "heterogenised" type of homogeneous ionic liquid catalyst system, described as Supported Ionic Liquid Phase (SILP) catalysts, has recently been introduced and examined by us and other research groups for hydroformylation[6,7] (Rh-catalysed), carbonylation[8] (Rh-catalysed), hydrogenation[9] (Rh-catalysed), Heck reactions[10] (Pd-catalysed), hydroaminations[11] (Rh-, Pd-, and Zn-catalysed) and epoxidation[12] (W-catalysed). In these SILP systems, a thin film of ionic liquid containing the homogeneous catalyst is immobilised on the surface of a high-area, porous support material, as depicted in Figure 1.

In SILP catalysts the combination of high solvent polarity combined with nonvolatility [in contrast to water in Supported Aqueous Phase (SAP) catalysis], ensures that the catalytic species remain dissolved also in continuously operated reactions. Furthermore, the combination facilitates separation of the catalyst phase from the organic product

---

[a] Department of Chemistry and Center for Sustainable and Green Chemistry, Technical University of Denmark, Building 207,
2800 Kgs. Lyngby, Denmark
Fax: +45-4525-2235
E-mail: ar@kemi.dtu.dk
[b] Lehrstuhl für Chemische Reaktionstechnik (CRT), Universität Erlangen-Nürnberg,
Egerlandstrasse 3, 91058 Erlangen, Germany
Fax: +49-9131-8527421
E-mail: haumann@crt.cbi.uni-erlangen.de

**MICROREVIEWS:** This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

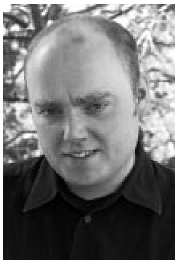
phase in contrast to many traditional organic liquid Supported Liquid Phase (SLP) catalysts. In addition, the high dispersion of the ionic liquid/catalyst solution on the support surface results in a very efficient use of ionic liquid, reducing the necessary amount of the precious catalyst and the ionic liquid required. Consequently, SILP catalyst systems offer significant advantages compared to biphasic catalysis in organic liquid/ionic liquid mixtures and to current SLP and SAP catalyst systems.

Despite the important advantages mentioned above it should be realised, however, that the use of SILP catalysts in most cases is limited to gas-phase applications. For liquid-phase reactions even a minor ionic liquid solubility in a liquid feedstock/product mixture can be sufficient to remove the catalyst from the carrier over time in both continuously operated or batch processes upon catalyst recycling (due to the very small amount of ionic liquid on the support). Even worse, the thin immobilised catalyst layer can physically be removed from the support by mechanical forces, for example, by a convective liquid flow.

One of the first examples of liquid SILP catalysis, where the problems of leaching became evident, was reported by Mehnert and co-workers on the hydroformylation of 1-hexene in batch autoclave mode.[6] They immobilised the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][$PF_6$]) by covalent bonding (through pendant silyl groups) to the chemically modified surface of a silica gel. Two monodentate phosphane ligands, tris(*m*-sulfonylphenyl)phosphane trisodium salt (TPPTS) and tris(*m*-sulfonylphenyl)phosphane tris(1-butyl-3-methylimidazolium) salt (TPPTI) were used for ligand modification of the rhodium precursor Rh(acac)$(CO)_2$. The activity of the obtained Rh/SILP catalysts was almost three times higher than for comparable biphasic systems and was attributed to a higher rhodium concentration at the large reaction interface. However, at higher conversions significant rhodium leaching occurred accompanied by significant depletion of the supported ionic liquid layer. Recently, Rh–TPPTS/SILP catalysts have also been prepared by immobilising the complexes in the ionic liquids [BMIM][$PF_6$], [BMIM][$BF_4$], and

*Anders Riisager was born in Glostrup, Denmark in 1973. He finished his Master studies in chemistry at the University of Copenhagen in 1999 with a thesis on metal-templated amino acid synthesis. In the same year he started his Ph.D. on immobilisation of biphasic hydroformylation catalyst systems by use of SAP and SILP methodologies at the Interdisciplinary Research Center for Catalysis (ICAT) and Department of Chemistry at the Technical University of Denmark with Prof. Rasmus Fehrmann. In the period 2002–2005 he continued the work on SILP catalysis and examined other phase-separable ionic liquid systems in a postdoctoral research project with the group of Prof. Peter Wasserscheid at RWTH Aachen (later University of Erlangen-Nürnberg), Germany. Currently he is employed as Assistant Professor at the Department of Chemistry, Technical University of Denmark, where his main research interests are focused on further developments of the concept of supported ionic liquid phase catalysis.*

*Rasmus Fehrmann was born in Denmark in 1948. He studied Chemical Engineering at the Technical University of Denmark (DTU), where he received his master degree (M.Sc. Eng.) in 1973 and his Ph.D. degree in 1976 at the Department of Chemistry. In 1977 and 1979 he was awarded candidate and senior scholarships, respectively, from DTU and during the years 1981–1985 he held postdoctoral positions at the Institute of Catalysis, Novosibirsk (Russia), Université de Provence, Marseille (France), and University of Patras (Greece) in addition to periods at the Department of Chemistry, DTU, where he has been Associate Professor since 1986. In 1997 he was visiting professor at Georgia Institute of Technology (USA), and since 2000 he has been a member of the Danish National Committee for Chemistry. Administratively, he has been a member of the board and assistant head of the Department of Chemistry, DTU, since 1987. His main research interests have been in the field of inorganic molten salt chemistry, complex formation in ionic media and, with increasing importance, also within the areas of molten salt catalysis, environmental catalysis, and catalysis in ionic liquids with emphasis on performance and mechanistic understanding of industrial catalysts and model systems.*



*Marco Haumann was born 1969 in Dortmund, Germany. After preliminary studies in mechanical engineering in Dortmund he moved to TU Berlin where he studied chemistry until 1998. He finished his Ph.D. thesis in the group of Prof. Schomäcker on hydroformylation in microemulsions in 2001. In 2002 he started a postdoctoral research project funded by Sasol Technology, Pty, Ltd. at the University of Cape Town (Prof. John R. Moss) aiming at the synthesis of novel cobalt-based catalysts. At the end of 2002 he moved to Rand Afrikaans University in Johannesburg (Prof. Andre Roodt) to study the mechanism of cobalt phosphite catalysed hydroformylation. Since 12/2003 he has been employed as a research assistant in the group of Prof. Peter Wasserscheid. His main research interests are in the field of homogeneous catalyst immobilisation using the Supported Ionic Liquid Phase (SILP) concept and reaction engineering aspects of this innovative technology.*

*Peter Wasserscheid was born 1970 in Würzburg, Germany. He studied chemistry at the RWTH Aachen from 4/1991 till 3/1995. After his Ph.D. thesis with Prof. Willi Keim (10/1995–5/1998) he worked as an industrial post-doc for four months at BP/Sunbury, GB. Returning to RWTH Aachen, he carried out his Habilitation (08/1998–10/2002) at the Institute of Technical and Macromolecular Chemistry (ITMC) entitled "Ionic liquids – a new Solvent Concept for Catalysis". Since 10/2003 Peter Wasserscheid has been full professor for Chemical Reaction Engineering at the University of Erlangen-Nürnberg, Germany. He has been awarded several research prizes including the Carl-Zerbe award of DGMK (2000), the DECHEMA award of the Max-Buchner Forschungsstiftung (2001), and the "Innovation award of the German Industry" (with Solvent Innovation GmbH, Cologne) (2003). Together with Tom Welton he edited the monograph "Ionic Liquids in Synthesis" (Wiley-VCH, 2003). His main research interests are in the field of ionic liquid chemistry and in the application of advanced materials in continuous catalytic processes.*

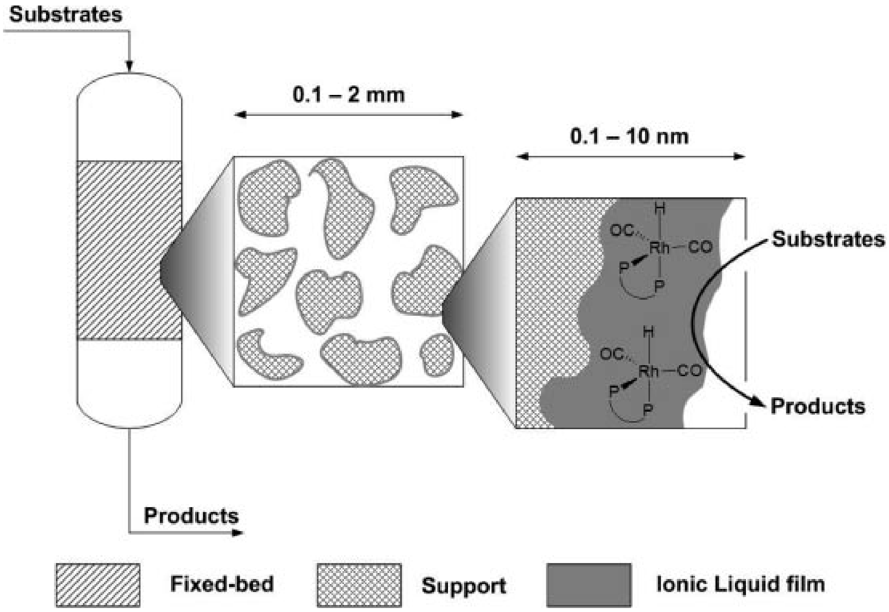
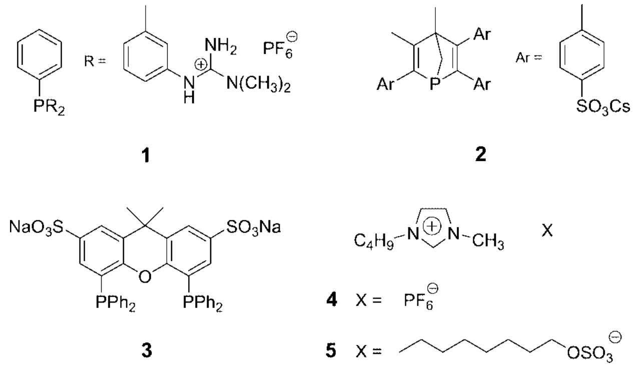


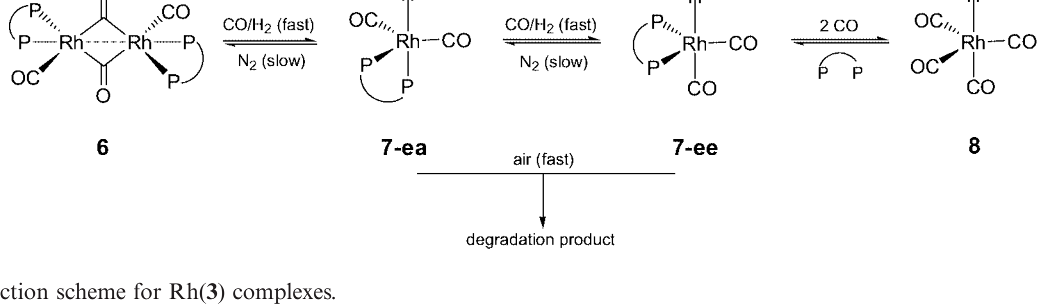
Figure 1. Schematic illustration of Supported Ionic Liquid Phase (SILP) catalysts for fixed-bed reactor technology.

tetramethylguanidinium lactate (TMGL) supported on mesoporous MCM-41.[13] The catalytic performance of these catalysts was investigated in hydroformylation of different alkenes ($C_6$ to $C_{12}$), and the SILP catalysts were further characterised by various methods. $^{31}P$ NMR spectroscopic data revealed that the Rh–TPPTS complex formation in the SILP system occurred in a similar way to that in an aqueous solution, clearly indicating the homogeneous nature of Rh/SILP catalyst systems. Using the specific combination of TMGL ionic liquid and MCM-41 support the leaching problem was here claimed to be negligible, most likely because of the slightly coordinating ability of the ionic liquid to the rhodium atom. Notable, however, in none of the above examples has a combination of good catalyst durability and high product selectivity towards linear aldehyde been demonstrated.

In this Microreview the advantages of SILP catalysis are exemplified for the Rh-phosphane catalysed, continuous gas-phase hydroformylation of propene. The Rh/SILP catalysts employed in the study contained 1-butyl-3-methylimidazolium-based ionic liquids and the phosphane ligands shown in Scheme 1. The involved ligands comprised both mono- and bisphosphanes modified with ionic groups. All the Rh(phosphane)/SILP systems, which can be stored under argon over several months, were prepared using impregnation by dissolving appropriate amounts of catalyst precursor, ligand, and ionic liquid in dried methanol, followed



Scheme 1. Phosphane ligands and ionic liquids applied in the study.



Scheme 2. Reaction scheme for Rh(**3**) complexes.

by addition of dried support material and removal of methanol in vacuo (details about materials and methods are described in previous reports[7,14,15]). The catalysts are characterised by the nature of the support, the ionic liquid loading *α* (ratio ionic liquid volume/support pore volume), the rhodium content (mass ratio rhodium/support) and the molar ligand/rhodium ratio (L/Rh).

The $[Rh(\mu\text{-}CO)(\mathbf{3})(CO)]_2$ precursor **6** (see Scheme 2), dissolved in ionic liquid $[BMIM][PF_6]$, has been investigated by van Leeuwen et al. in the hydroformylation of 1-octene.[16] In-situ high-pressure IR and NMR studies indicated that the formation of the active catalyst complex **7** occurred in a similar fashion to the formation in organic solvents.[17] Beside these studies, detailed mechanistic understanding of homogeneous catalysis in ionic liquids is still scarce.[18]

## Catalyst Composition Studies

### Variation of Support Material

As a first approach, different commercially available porous, high-area supports were used to prepare Rh(phosphane)/SILP catalyst systems containing the same type of ionic liquid and ligand content.[14] Table 1 compiles the support characteristics and Figure 2 shows the performance of the Rh(**3**)/SILP catalysts with regard to activity (turn-over frequency, TOF) and aldehyde selectivity (% *n*-butanal).

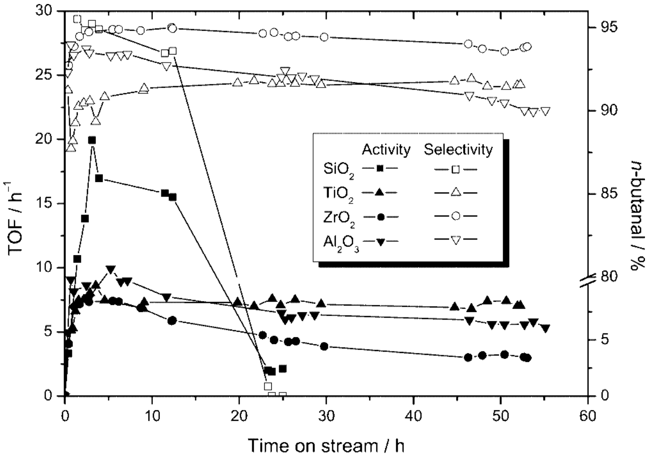


Figure 2. Propene hydroformylation activities and selectivities of Rh(**3**)/SILP catalyst systems.

Among the examined catalysts, the Rh(phosphane)/$SiO_2$/SILP catalysts revealed the highest initial activity (TOF = 21 h$^{-1}$) and selectivity (95% *n*-butanal), but deactivated almost completely within 24 h on stream ending up with very low activity and only half the initial selectivity. The Rh(phosphane)/$Al_2O_3$/SILP and Rh(phosphane)/$ZrO_2$/SILP catalysts had both a lower initial activity and selectivity than the $SiO_2$-based system but deactivated only slightly at prolonged reaction (55 h). The most stable system examined was the Rh(phosphane)/$TiO_2$/SILP catalyst which maintained the initial (but rather poor) performance over 55 h, showing no sign of deactivation. It should be noted that the ionic liquid loading differed for the various systems which made the comparison of the absolute catalyst activities difficult. Though, a trend appeared to be that higher pore volume of the support had a more pronounced effect on the initial activity of the resultant catalyst than the BET surface area. The use of supports with both low pore volume and BET area (i.e. $Al_2O_3$ and $ZrO_2$) apparently resulted in the least active SILP catalysts.

The different SILP catalysts were analysed by FT-IR prior to and after reaction. After short-term reactions, all SILP catalysts revealed CO stretching bands at ν(CO) ≈ 1998 and 1940 cm$^{-1}$, corresponding to the presence of catalytically active $[HRh(\mathbf{3})(CO)_2]$ complexes (examples are shown in Figure 3 for $TiO_2$ catalysts). However, only the FT-IR spectra of the used Rh(phosphane)/$TiO_2$/SILP cata-

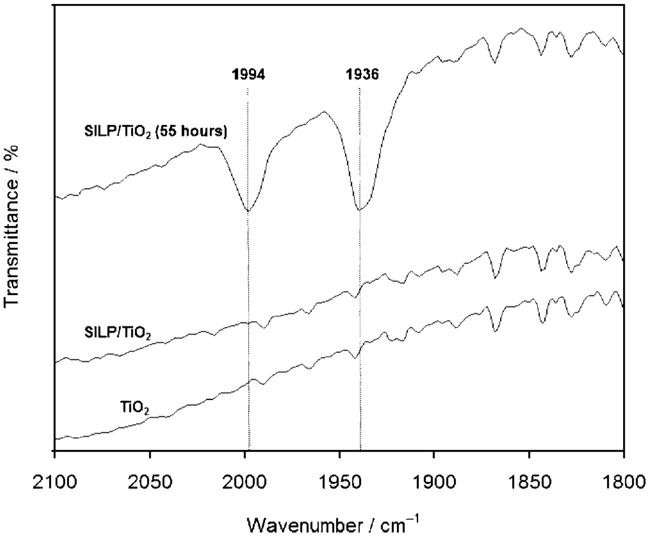


Figure 3. FT-IR spectra of $TiO_2$-based Rh(**3**)/SILP catalyst system.

Table 1. Support material used for SILP-catalysed hydroformylation of propene.[a]

| | $SiO_2$ | $Al_2O_3$ | $TiO_2$ | $ZrO_2$[b] |
|---|---|---|---|---|
| Supplier | Merck | Merck | Millennium Co. | MEL Chemicals |
| Trade name | Silica gel 100 | Alumina 90 neutral | TIONA-G5 anatase | MELCAT XZO-882 |
| BET area [m$^2$·g$^{-1}$] | 298 | 103 | 309 | 100 |
| Pore volume [cm$^3$·g$^{-1}$] | 1.02 | 0.25 | 0.37 | 0.13 |
| Mean pore diameter [Å] | 137 | 98 | 47 | 50 |
| Particle size [µm] | 63–200 | 63–200 | n/a | 15[c] |

[a] The BET surface areas, pore volumes, and pore diameters were determined by nitrogen adsorption/desorption experiments and are reproduced from ref.[14] [b] Obtained by calcination of $Zr(OH)_4 \cdot xH_2O$ (500 °C, 15 h). [c] Corresponds to the 50% fractile.

lyst exhibited bands at ν(CO) = 1994 and 1936 $cm^{-1}$ after 55 h on-stream. In contrast, the analogous CO bands for the Rh(phosphane)/$SiO_2$/SILP catalyst gradually disappeared after only 4 h in use and were not present after 55 h of reaction.

For all SILP catalysts additional bands in the 1700–2100 $cm^{-1}$ region corresponding to bridging CO ligands, indicative of formation of inactive dimer or cluster compounds, were not observed. Hence, it was concluded that the deactivation was caused by a support effect. Because of the highest initial catalyst activity and selectivity, $SiO_2$ was used as the support material in all further experiments.

## Variation of Ligand and Ionic Liquid

In homogeneous hydroformylation with rhodium–phosphane catalysts the nature of the involved ligands are known to have a large influence on the catalytic performance of the resultant catalyst.[19] Generally, this is attributed to a combination of electronic and steric factors induced by the ligands to the metal atom thereby altering its coordination chemistry.

The effect of the phosphane ligand and of the ligand content (i.e. L/Rh ratio) contained in the SILP catalysts were evaluated by determining the catalytic performance of SILP catalysts containing the different ligands **1**–**3** (see Scheme 1).[7] These ligands are based on triphenylphosphane, bridged phosphinane (both monodentate), and diphenyl-xantphos (bidentate) backbones, respectively. The obtained results are summarised in Table 2.

Table 2. Catalytic performance of Rh(L)/$SiO_2$/SILP systems with different types of ligand and L/Rh ratios.

| Entry | L | L/Rh | $\alpha$[a] | TOF [$h^{-1}$] | *n*/iso | *n*-Butanal [%] |
|---|---|---|---|---|---|---|
| 1 | – | – | 0.76 | 0.0 | – | – |
| 2 | **1** | 2.9 | 0.00 | 55.5 | 0.9 | 47.4 |
| 3 | **1** | 2.9 | 0.33 | 3.7 | 1.0 | 50.0 |
| 4 | **1** | 2.9 | 0.78 | 20.6 | 0.9 | 47.4 |
| 5 | **1** | 2.9 | 1.00 | 16.8 | 1.0 | 50.0 |
| 6 | **2** | 2.9 | 0.00 | 114.8 | 1.0 | 50.0 |
| 7 | **2** | 2.9 | 0.30 | 6.9 | 0.9 | 47.4 |
| 8 | **2** | 2.9 | 0.78 | 38.0 | 0.9 | 47.4 |
| 9 | **2** | 2.9 | 1.00 | 30.5 | 0.9 | 47.4 |
| 10 | **2** | 11.3 | 0.05 | 88.4 | 2.0 | 66.7 |
| 11 | **2** | 11.3 | 0.15 | 79.4 | 1.3 | 56.5 |
| 12 | **2** | 21.4 | 0.00 | 45.8 | 2.8 | 73.8 |
| 13 | **2** | 21.3 | 0.05 | 28.2 | 2.6 | 72.2 |
| 14 | **3** | 2.5 | 0.00 | 37.4 | 1.7 | 63.0 |
| 15 | **3** | 2.4 | 0.17 | 1.5 | 1.8 | 64.0 |
| 16 | **3** | 2.5 | 0.49 | 5.1 | 2.0 | 66.4 |
| 17 | **3** | 10.2 | 0.00 | 40.8 | 16.9 | 94.4 |
| 18 | **3** | 10.0 | 0.08 | 37.0 | 23.3 | 95.9 |
| 19 | **3** | 10.0 | 0.18 | 34.9 | 22.6 | 95.8 |
| 20 | **3** | 10.0 | 0.52 | 25.4 | 22.0 | 95.6 |
| 21 | **3** | 20.0 | 0.20 | 16.7 | 23.7 | 96.0 |
| 22[b] | – | – | 0.51 | 0.2 | 1.0 | 50.0 |
| 23[b] | **3** | 2.5 | 0.52 | 6.4 | 1.9 | 65.4 |
| 24[b] | **3** | 10.0 | 0.50 | 17.9 | 18.6 | 94.9 |

[a] Ionic liquid loading, $\alpha$ = ratio of ionic liquid volume to support pore volume. [b] Ionic liquid = [BMIM][$n$-$C_8H_{17}O$–$SO_3$]. All other catalysts were based on [BMIM][$PF_6$].

For the monophosphane catalysts the obtained selectivities were significantly lower than for analogous bis(phosphane) catalysts, as expected, with only 47–74% linear aldehyde being formed compared to typically 94–96% for the Rh(**3**) catalyst at identical catalyst composition. Furthermore, an increase in mono(phosphane) ligand content generally resulted in less active but more selective SILP catalysts (e.g. Entries 10 and 13). The effect on the selectivity was, however, less pronounced at very large excess of ligand, i.e. with L/Rh ratio of 21.4 (Entry 13), but remained significantly negative for the activity. Thus, the optimal L/Rh ratio for the mono(phosphane) **2** catalysts was found to be around 10.

The same ligand content trend observed for the catalysts based on ligands **1** or **2** was also observed for the catalysts containing the bidentate ligand **3** (Entries 15, 19, and 21). Additionally, for the Rh(**3**) catalysts with low L/Rh ratios of 2.5 the activity was found to be high only for the ionic-liquid-free system (Entry 14), while selectivities towards linear aldehyde were low in all reactions regardless of ionic liquid loading (Entries 14–16). This catalytic behaviour differed from the one observed with Rh(**3**) catalyst solutions in ionic liquid/organic and aqueous/organic biphasic systems, where catalysts having L/Rh ratios of 5 yielded product linearity $>$ 97%.[20] Increasing the L/Rh ratio to 10 and 20 resulted in high linearities of 94.4–96.0%, similar to the ones for biphasic catalysis. Furthermore, for L/Rh ratios of 10 the activities were reasonably high with TOFs between 25 and 41 $h^{-1}$, depending on the liquid loading (Entries 17–20). Here the optimal L/Rh ratio was also found to be 10, indicating a support–ligand interaction which reduced the effective ligand excess for all three types of ligand-based catalysts. All consecutive experiments were carried out using ligand **3** with an L/Rh ratio of 10.

With respect to the ionic liquid in the catalysts, the ionic liquid [BMIM][$PF_6$] itself was not catalytically active in the hydroformylation (Entry 1), as expected. The degree of pore filling, indicated by the ionic liquid loading ($\alpha$), had, however, a significant effect on the activity of all three catalyst systems applied, revealing a decreasing activity with increasing liquid loading. Thus, for the mono(phosphane) ligand systems the highest initial activity was obtained in the absence of ionic liquid (Entries 2, 6, and 12), which might be attributed to the formation of surface-bound rhodium species exhibiting high activities and to the absence of any mass-transport-limiting factors in these purely heterogeneous catalysts. However, for catalysts with $\alpha$ values about 0.3 (Entries 3 and 7) exceptionally low activities were obtained for ligands **1** and **2**, the reason for this being at present not clear. For Rh(**3**) catalysts the highest initial activity was also obtained in the absence of ionic liquid (Entry 17). Moreover, a linear dependence between the decrease in activity and the ionic liquid loading could be correlated with results from nitrogen absorption studies, where the catalyst pore volume was found to decrease proportionally with the different ionic liquid loadings.[21]

In contrast to the ionic liquid content, the nature of the ionic liquid anion had essentially no influence on the SILP catalyst performance. Thus, upon replacing [BMIM][$PF_6$] with the halogen-free ionic liquid [BMIM][$n$-$C_8H_{17}O$–$SO_3$] similar activities and selectivities were observed (Entries 16 and 23, and 20 and 24). Hence, in consecutive experiments catalysts containing [BMIM][$n$-$C_8H_{17}O$–$SO_3$] were applied, and the ionic liquid loading was maintained at $\alpha = 0.1$ in order to achieve high pore volume and large reaction surface area.

## Catalyst Stability Studies

### Support Pretreatment

From the results obtained in the catalyst composition studies (see above) it became obvious that ligand–support interactions probably were responsible for catalyst instability. In the case of titania catalysts, where the support contained practically no Brønsted acidic sites, long catalyst lifetimes beyond 50 h of reaction were achieved, whereas catalysts based on more Brønsted-acidic silica gel support deactivated relatively fast, indicated by loss of both activity and selectivity. In order to examine the effect of the support acidity, acidic sites on the silica gel support were reduced before use by thermal dehydroxylation of the support (500 °C, 15 h). Subsequently, using dehydroxylated silica catalysts with L/Rh ratio of 10 and ionic liquid loadings of $\alpha = 0.1$, the SILP catalyst systems proved stable over 60 h, as shown in Figure 4 for an Rh(**3**) catalyst.[15]

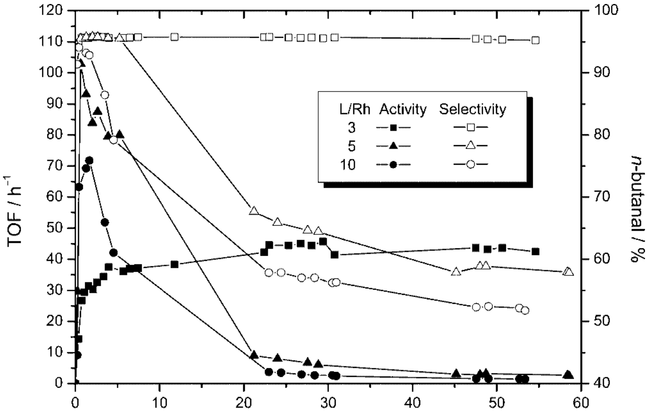


Figure 4. Propene hydroformylation activity and selectivity of Rh(**3**) silica-based SILP catalysts ($\alpha = 0.1$) as a function of **3**/Rh ratios.

The catalytic performance and catalyst stability, however, still proved to be significantly influenced by the ligand excess, as also shown in Figure 4. Rh(**3**) catalysts having low ligand contents (**3**/Rh ratios of 3 and 5) were initially very active compared to the catalyst with **3**/Rh ratio of 10 but less selective, and deactivated furthermore within the first 24 h of reaction resulting in very low catalytic performance (TOF = 4–5 h$^{-1}$, $n$/iso ratio = 1–1.3). In contrast, catalysts with a high ligand content (**3**/Rh ratios ≥ 10) retained the initial catalytic performance with significantly higher activity (TOF = 44 h$^{-1}$) and selectivity ($n$/iso ratio > 20) during prolonged (60 h) reactions. These results clearly indicated that a large excess of ligand was required to obtain a stable SILP catalytic system. Even after the thermal pretreatment, which induced a considerable removal of acidic surface sites, support–ligand reactions apparently still lowered the amount of effective ligand excess necessary for complex formation.

Beside the ligand content, the amount of ionic liquid also influenced the catalytic performance of catalysts based on the pretreated silica support, clearly signifying the importance of the ionic liquid solvent. Thus, varying the amount of ionic liquid loading ($\alpha = 0$–$0.5$), the catalyst systems containing no ionic liquid deactivated rapidly; only 30% of the initial activity and selectivity remained after 60 h of reaction time. The deactivation could be explained by surface diffusion of ligand **3** from the initially Rh-coordinated active state to the stronger surface-bonded state, in which the metal atom was less coordinated to the ligand but possibly more strongly coordinated to the support and thus less active and selective. Evidently, the Rh(**3**)/SILP catalysts required a certain amount of ionic liquid solvent; not only to provide a high selectivity but also to retain long-term stability during continuous processes.

Further, since the hydroformylation product selectivity with respect to aldehydes is known to depend on the available amount of ligand for coordination,[22] the simultaneous decrease in selectivity along with activity indicated that deactivation was closely related to a gradual degradation and removal of ligand from the catalyst complex system. The presence of surface–ligand interaction in the pretreated Rh(**3**) catalyst (**3**/Rh = 10) was confirmed by solid-state MAS $^{31}$P NMR spectra recorded prior to reaction, as shown in Figure 5. Here, signals corresponding to free ligand ($\delta$ = –13 ppm, 27%), surface-bonded ligand ($\delta$ = –21 ppm, 54%), and complexed ligand ($\delta$ = 31 ppm, 19%) were found.[15]

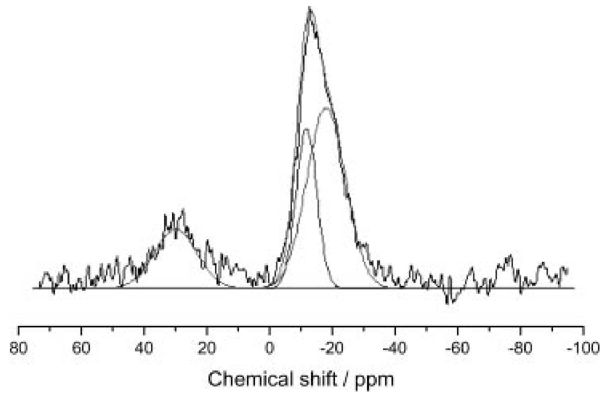


Figure 5. MAS $^{31}$P NMR spectra and deconvoluted spectra of prepared Rh(**3**)/$SiO_2$/SILP catalyst (**3**/Rh ratio = 10). $\delta_1$ = –21 ppm, 54%, support-bonded **3**; $\delta_2$ = –13 ppm, 27%, **3**; $\delta_3$ = 31 ppm, 19%, complex-bonded **3**.

Additional explanation of the observed catalytic results was obtained from in-situ FT-IR measurements of complex formation at 100 °C and atmospheric pressure. In Figure 6 the FT-IR spectra of the catalyst with **3**/Rh = 10 under (a) nitrogen, (b) after 15 min, and (c) 30 min exposure to syngas ($CO/H_2$ = 1:1) are shown. They indicate the relatively fast transformation (Scheme 2) from the pale-red dimeric complex [Rh(μ-CO)(**3**)(CO)]$_2$ (**6**) [ν(CO) = 1990 (br.) $cm^{-1}$], which is a nonactive, stable state of the catalyst, to the light-yellow precatalytic monomeric $HRh(CO)_2$(**3**) ea- and ee-isomeric complexes **7-ea** [ν(CO) = 1994, 1948 $cm^{-1}$] and **7-ee** [ν(CO) = 2035 (w), 1964 $cm^{-1}$], which co-exist in dynamic equilibrium.[15]

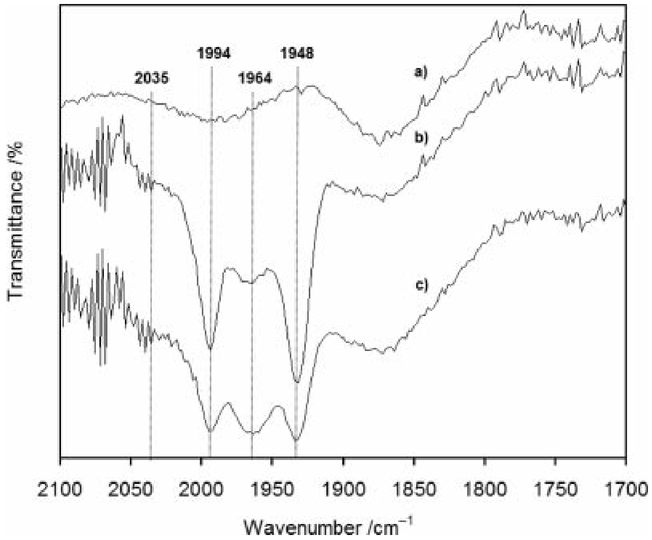


Figure 6. Part of FT-IR spectra of Rh(**3**)/$SiO_2$/SILP catalysts (**3**/Rh = 10, $\alpha$ = 0.5) at 100 °C after (a) 15 min nitrogen exposure, (b) 15 min syngas exposure, and (c) 30 min syngas exposure.

Re-exposure of the **7-ea/7-ee** isomeric mixture to inert gas slowly regenerated the dimer **6** reversibly, while air treatment presumably led to irreversible complex degradation and oxidation of excess ligand. The degradation product was dark yellow and had a broad CO band at ν(CO) = 1972 $cm^{-1}$. Importantly, the complex formation in the Rh(**3**)/$SiO_2$/SILP catalysts having **3**/Rh ratio of ≥ 10 were very similar to what previously has been reported for Rh(**3**) and analogous Rh(xanthene-based ligand) systems in ionic liquids[16] and organic solvents,[23] as shown in Table 3. Thus, it seemed reasonable to conclude that the Rh(**3**) complex was formed in the ionic liquid film and that the examined SILP hydroformylation reactions were indeed of purely homogeneous nature.[15]

In the FT-IR spectra recorded of the analogous catalysts with **3**/Rh ratios of 3 and 5, the degradation product was (in sharp contrast to the catalysts with high ligand content) irreversibly formed independent of the gas treatment, and was significantly more pronounced for catalysts with **3**/Rh = 3 than for catalysts having **3**/Rh = 5. This clearly suggested that an insufficient excess of ligand **3** was present in these systems with low ligand content to maintain the equilibrium between the modified hydrido complex **7** and the unmodified hydrido complex **8** in favour of complex **7**, as shown in Scheme 2. This was in excellent accordance with the relative catalyst selectivities and stabilities measured, since the unmodified hydrido complex provided low selectivity (*n*/iso ratio ≈ 2) and facilitated formation of inactive clusters at the modest CO partial pressure applied. Hence, it seemed unambiguously justified that the SILP catalyst stability was directly connected to the complex degradation reaction, which additionally seemed to be correlated to the amount of accessible ligand available for complex formation in the systems.

The content of acidic support OH groups (mostly Brønsted sites) contained in the partly dehydroxylated silica support was evaluated by ammonia temperature-programmed desorption (TPD) to be 69 μmol OH/g support, corresponding to 26% of the original content present in the untreated support. This was in relatively good agreement with the remaining fraction of 35% Si–OH groups (Q3, $\delta$ ≈ 100 ppm) relative to Si–O–Si groups (Q4, $\delta$ ≈ 111 ppm) measured by solid-state MAS $^{29}Si$ NMR spectroscopy for analogous samples. Therefore, it seemed reasonable to assume that the applied pretreatment decreased the amount of acidic support OH groups only by dehydroxylation of surface silanol groups thereby causing no significant structural changes of the support. This was further affirmed by the identical $T_{max}$ values obtained for ammonia desorption (i.e. desorption sites are identical), and by the practically unchanged BET surface area and pore volume after dehydroxylation.

As a consequence, it should therefore be anticipated that highly stable SILP catalysts could only be obtained in those cases where the ligand content was sufficient to compensate the loss induced by the surface bonding as shown in Table 4. This was in excellent agreement with the experimental data from the catalytic reactions, thus clearly showing that the relative content of acidic support OH groups most probably was the key factor determining the long-term stability for silica-support-based Rh(phosphane)/SILP catalysts.[15]

Table 4. Effective L/Rh ratios in SILP-catalysed hydroformylation using pretreated silica.

| L/Rh | $c_{L,eff}$ [μmol $g^{-1}$] | free L [%] | $(L/Rh)_{eff}$ |
|---|---|---|---|
| 3 | 58 | 0 | <1 |
| 5 | 97 | 30 | 1.5 |
| 10 | 194 | 65 | 6.5 |

Table 3. Comparison of IR ν(CO) bands in $HRh(CO)_2(L)$ complexes in different systems.

| Complex system | Solvent | ν(CO) ea isomer [$cm^{-1}$] | ν(CO) ee isomer [$cm^{-1}$] | Ref. |
|---|---|---|---|---|
| Rh(**3**)/$SiO_2$/SILP | [BMIM][$n$-$C_8H_{17}O$–$SO_3$] | 1994, 1948 | 2035(w), 1964 | [15] |
| $HRh(CO)_2$(**3**) | [BMIM][$PF_6$] | 1985, 1935 | 2032, 1967 | [16] |
| $HRh(CO)_2$(xantphos) | benzene | 1991, 1941 | 2036, 1969 | [23] |
| $HRh(CO)_2$(thixantphos) | cyclohexane | 1999, 1953 | 2040, 1977 | [23] |

### Deactivation/Reactivation Assessment

All the stability measurements of the Rh(**3**)/SILP catalyst discussed so far were initially studied at 100 °C and 10 bar syngas pressure ($H_2/CO = 1:1$) over a period of up to 36 h. This time on-stream was further extended to 180 h to test the long-term stability of the Rh(**3**) dehydroxylated catalyst system.[24]

In the extended reaction period the selectivity towards linear butanal remained constant around 95% (*n*/iso = 19), whereas the TOFs slightly decreased over time, corresponding to a total loss in activity of 17% or 0.1% per hour. Since the selectivity remained unchanged it was excluded that deactivation was caused by catalyst decomposition, as observed in the previous studies when using low L/Rh ratios.[7,14,15] ICP (inductively coupled plasma) analyses of the exit gas streams condensed by liquid nitrogen further established the rhodium contents to be below the detection limit of 3 ppm. Instead, the formation of high-boiling side-products, dissolving in the ionic liquid layer during reaction causing a lowering in the effective rhodium concentration, was suspected to be the reason of the slow activity decrease measured. Furthermore, the film thickness might be increased and smaller pores flooded, which would lead to a lower reaction surface. To confirm this hypothesis, the gas flow was temporary stopped after 180 h on-stream and the reaction setup evacuated for 10 min at 100 °C. When the experiment was continued after this procedure, the activity had indeed increased by 80% from initially 60 to 108 $h^{-1}$. Within the next 20 h of reaction the TOFs decreased again from 108 $h^{-1}$ to 76 $h^{-1}$ and the selectivity was re-established at 95% *n*-butanal. A second vacuum period of 10 min resulted in improved TOFs, as depicted in Figure 7. In both cases the observed "overshooting" of the activity directly after evacuation might be caused by either simultaneous removal of CO ligand of the Rh complex leading to higher activity or a rearrangement of the active surface due to sudden evaporation of dissolved heavies. In the first case a lower selectivity would be expected which was indeed observed directly after the evacuation. Thereafter, the catalyst solution was resaturated with CO gas and both the activity and the selectivity approached the initial levels.

The findings from the evacuation experiment confirmed the interpretation that the observed slight deactivation over time was not due to catalyst decomposition, as an accompanying decrease in activity and selectivity otherwise would have been observed. Instead, we expected the formation of 2-ethylhexanal and 2-ethylhexanol to be of relevance, as traces of these high-boiling side products were observed at particular high conversions.

To support this interpretation the deactivated catalyst was removed from the reactor and the pale yellow catalyst particles placed in two round-bottomed flasks containing cyclohexane and ethanol, respectively. Immediately, the ethanol solution became orange whereas the cyclohexane solution remained colourless, indicating that the ethanol wash led to removal of the ionic catalyst phase from the support while the cyclohexane wash did not. Both solutions were subsequently analysed by means of GC-MS (ethanol solution after distillation and separation of nonvolatile ionic liquid fragments), where content of small amounts of by-products 1-butanol, 2-ethylhexanal, and 2-ethylhexanol were confirmed, as expected. Additionally, IR analysis of both used and unused Rh/SILP catalysts was carried out. The used catalyst showed an absorbance band at 1730 $cm^{-1}$ (corresponding to the C=O stretching frequency) clearly indicating the presence of aldehydes in the catalyst.

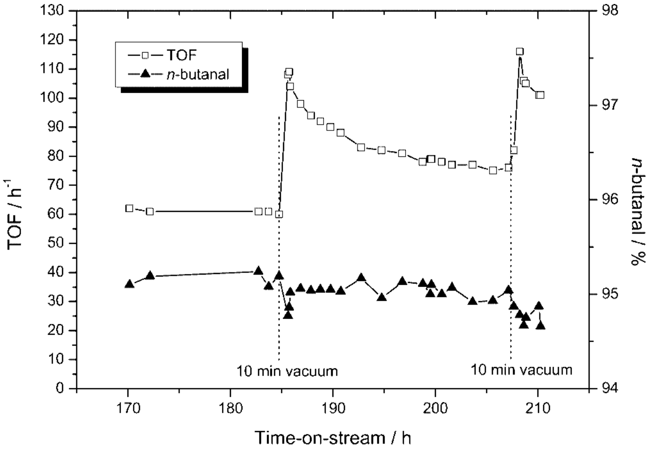


Figure 7. Reactivation of Rh(**3**)/$SiO_2$/SILP catalyst by consecutive application of vacuum. 100 °C, 10 bar syngas.

## Kinetic Studies

Long-term stability and kinetic experiments have been conducted in order to further prove the findings from the catalyst composition studies with Rh(**3**) catalysts. For these studies a continuous reactor setup equipped with online gas chromatography, described in detail previously, has been applied.[24] The general rate law for the hydroformylation of propene was assumed to be

$$r = k \cdot p^{n}_{\text{propene}} \cdot p^{x}_{H_2} \cdot p^{y}_{CO}$$

### Differential, Integral, and Arrhenius Analysis

In the first kinetic experiments the substrate concentration was varied by changing the propene partial pressure $p_{\text{propene}}$ in the feed gas (at constant total pressure) between 0.9 and 3.2 bar at temperatures in the range of 65–140 °C. In Figure 8 the obtained results are compiled.

As expected, the highest catalyst activities (corresponding to TOFs of about 500 $h^{-1}$) and the lowest selectivities (down to 88% linearity) were obtained at high propene partial pressure and high temperature. However, the activities at 140 °C were not as high as expected assuming a normal Arrhenius temperature dependence, which was attributed to the formation of high-boiling by-products dissolved in the ionic liquid layer, thus lowering the effective catalyst concentration (see "deactivation/reactivation assessment"). The rate constants *k* were derived from differential analyses of the data, and the reaction with respect to propene partial

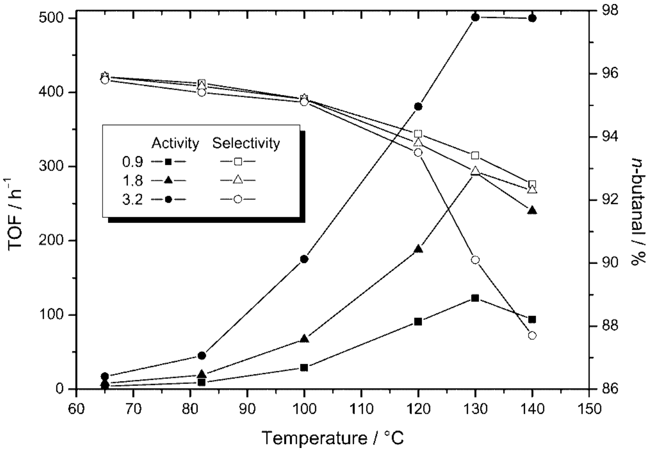


Figure 8. Activity and selectivity in Rh(**3**)/$SiO_2$/SILP-catalysed propene hydroformylation as a function of temperature and propene partial pressure.

pressure was determined to be of first order (i.e. $n = 1$). This dependency was similar to traditional organic and aqueous (phosphane)Rh-catalysed hydroformylation systems.[19]

At a constant propene partial pressure of 2.1 bar the residence time inside the catalyst bed was varied by altering the total reactant flow, as shown in Figure 9.

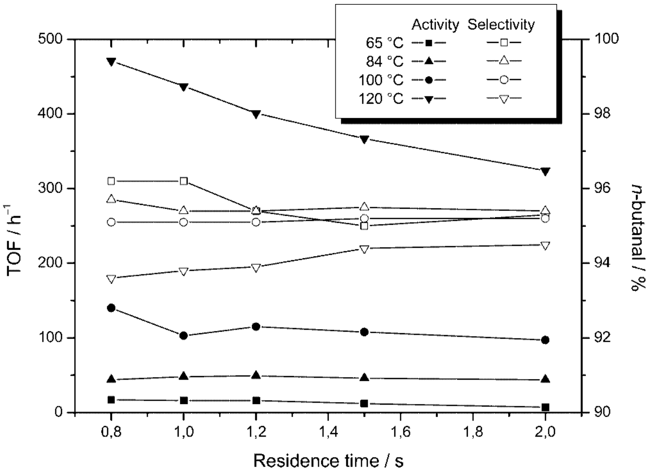


Figure 9. Activity and selectivity in Rh(**3**)/$SiO_2$/SILP-catalysed propene hydroformylation as a function of residence time.

The selectivity for the desired linear aldehyde was only influenced by temperature and not by residence time. Shorter residence times generally resulted in lower conversions, as expected. However, under nondifferential conditions at higher conversions the observed TOFs decreased slightly with longer residence times, due to lower mean levels of propene present in the reactor. An integral analysis of the data revealed the rate constants $k$ for the temperature range between 65 and 120 °C.

From the independent propene pressure and residence time experiments the activation energy was calculated from Arrhenius plots to be $63.3 \pm 2.1$ kJ·mol$^{-1}$. This value indicated that the Rh(**3**)/$SiO_2$/SILP catalyst was operating under kinetically controlled reaction conditions and added further proof to the homogeneous nature of the Rh/SILP catalyst as confirmed by spectroscopic studies (vide supra). In Table 5 the result obtained with the Rh(**3**)/SILP catalyst is compared with results for other rhodium-catalysed hydroformylations using sulfonated ligands in aqueous media and supported aqueous media.

Table 5. Comparison of results for Rh(**3**)/$SiO_2$/SILP hydroformylation with literature results.

| Substrate | Catalyst | $E_A$ [kJ·mol$^{-1}$] | Solvent | Support | Ref. |
|---|---|---|---|---|---|
| Propene | $HRh(CO)_2$(**3**) | 63.2 | IL[a] | $SiO_2$ | [20] |
| Propene | $HRh(CO)(L)_3$[b] | 77.0 | water | – | [21] |
| 1-Octene | $HRh(CO)(L)_3$[b] | 65.9 | water | – | [22] |
| 1-Octene | $HRh(CO)(L)_3$[b] | 71.0 | water | $SiO_2$ | [23] |
| Linalool | $HRh(CO)(L)_3$[b] | 60.7 | water | $SiO_2$ | [24] |
| 1-Dodecene | $HRh(CO)(L)_3$[b] | 72.8/70.9[c] | water[d] | – | [25] |

[a] Ionic liquid = [BMIM][$n$-$C_8H_{17}O$–$SO_3$]. [b] L = TPPTS. [c] Two different algorithms were used for data analysis. [d] CTAB (cetyltrimethylammonium bromide) surfactant used.

The activation energy of propene using Rh/SILP catalysts is slightly lower than the one determined by Mao et al. for $HRh(CO)(TPPTS)_3$ in water,[25] while the activation energy compared with $HRh(CO)(TPPTS)_3$ in supported aqueous phase (SAP) catalysis of higher alkenes[26–29] is in good agreement. This comparison provides additional evidence that the Rh/SILP catalyst truly acts as a homogeneous catalyst in the ionic liquid film immobilised on the silica.

## Variation in Syngas Composition and Total Pressure

In order to further assess the effect of parametrical changes to the Rh(**3**)/SILP hydroformylation system, the ratio between the partial pressures of hydrogen and carbon monoxide ($p_{H_2}/p_{CO}$ ratio) has been varied between 0.25 and 4 (at constant total pressure) in reactions performed at 65 and 100 °C.[24] Increasing the hydrogen partial pressure had a profound effect on the catalyst activity for both temperatures, as depicted in Figure 10.

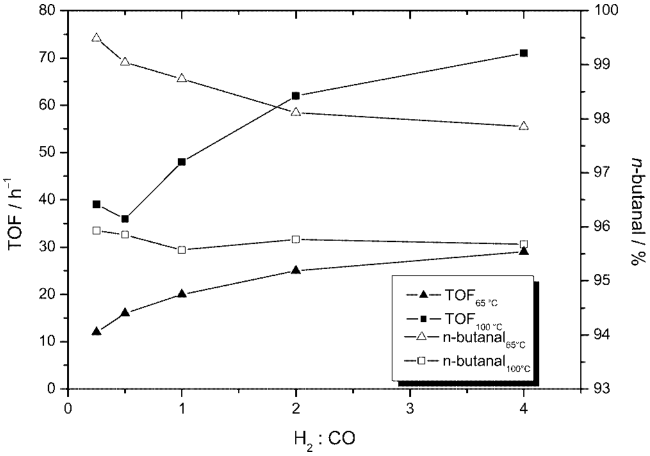


Figure 10. Activity of Rh(**3**)/$SiO_2$/SILP catalyst at different syngas compositions ($H_2$/CO ratios) and temperatures. 10 bar syngas pressure.

The positive effect of a high relative hydrogen pressure is well known in homogeneous hydroformylation[30] and can be derived from the generally accepted Wilkinson mechanism for ligand-modified rhodium catalysis,[31] in which the pre-equilibrium between dimer **6** and monomer **7** is shifted towards the active monomer **7** at higher partial pressures of hydrogen. Furthermore, the observed negative influence of high carbon monoxide partial pressures was also in accordance with this mechanism, in which the formation of catalytically active species requires the loss of CO during the cycle.[30,32] Thus, these findings provided further verification of the homogeneous nature of the Rh/SILP catalyst system.

At 100 °C the catalyst selectivity for *n*-butanal was practically independent of the $H_2$/CO ratio ($< 0.5\%$ variation), while the syngas ratio significantly influenced the selectivity at the lower temperature of 65 °C providing high selectivity of about 98% with an $H_2$/CO ratio of 4. Moreover, at 65 °C with a large excess of CO gas ($H_2/CO = 0.25$) *n*-butanal was formed exclusively with 99.5% selectivity (*n*/iso = 193). Such high selectivity has not previously been reported for Rh(**3**) catalyst systems in either homogeneous or biphasic reaction systems, normally performed in batch autoclaves. These results indicate the high potential of the SILP concept for obtaining a better mechanistic understanding in homogeneous catalysis, as exceptionally low steady-state conversions (impossible to realise in batch mode) can be adjusted in fixed-bed reactors. Additionally, the fixed-bed SILP catalytic concept allows a variety of reaction parameters to be altered over a broad range by using only small amounts of precious catalyst.

At a reaction temperature of 100 °C, the effect of the total syngas pressure $p_{\text{total}}$ on the catalyst performance was further examined by changing the pressure between 10 and 30 bar at fixed $p_{H_2}/p_{CO}$ pressure ratios.[24] From these pressure variations the reaction order with respect to hydrogen was determined to be $x = 0.4$ and the reaction order with respect to carbon monoxide to be $y = -0.4$. The selectivity remained nearly unchanged around 93% *n*-butanal for all experiments. By combining the obtained pressure dependencies for all of the three gases involved the general rate law for the propene hydroformylation using Rh(**3**)/$SiO_2$/SILP catalysts could therefore been established as

$$r = k \cdot p^{1}_{\text{propene}} \cdot p^{0.4}_{H_2} \cdot p^{-0.4}_{CO}$$

## Effect of Carbon Dioxide Cofeeding

Carbon dioxide gas is known to have high solubilities in most ionic liquids, lowering their viscosity and thus enhancing the diffusion of other gases.[33] In recent publications, the effect of super- and sub-critical $CO_2$ on hydrogen and oxygen solubilities has been reported.[34] In order to study the effect of $CO_2$ addition on the SILP-catalysed hydroformylation of propene, inert gas helium was replaced by a $CO_2$ cofeed corresponding to partial pressures between 1.8 and 36.4 bar.

From the results in Table 6 it became obvious that $CO_2$ indeed had a positive effect on the performance of the SILP catalyst. The initial activity obtained using helium could be increased by 2% at 1.8 bar $CO_2$ gas up to 35.1% at 36.4 bar $CO_2$ pressure. In contrast, the initial selectivity was not influenced by the $CO_2$ addition and remained constant around 94.5% throughout the experiments, and hydrogenation by-products could not be detected by GC analysis.

## Concluding Remarks

In this Microreview, we have described important progress in the very promising field of SILP catalysis, exemplified by the hydroformylation of propene. The long-term stability of Rh(**3**)/[BMIM][*n*-$C_8H_{17}O$–$SO_3$] catalysts supported on partly dehydroxylated silica was demonstrated, and clear spectroscopic evidence for the homogeneous nature of the catalysis in the supported ionic liquid layer was presented. Moreover, the prerequisite for obtaining active, highly selective, and Rh(**3**)/SILP hydroformylation catalysts with long-term stability was established to involve both the presence of an ionic liquid solvent and the content of a relatively large excess of phosphane ligand to compensate for some detrimental surface activity. The activation energy of $63.3 \pm 2.1$ kJ·mol$^{-1}$ added evidence that the catalyst was indeed homogeneous, i.e. a complex dissolved in an ionic liquid film on a support. Furthermore, the Rh/SILP catalyst performed similarly to a homogeneous catalyst with regard to variation in syngas composition. The presented work further confirms the high technical potential of the SILP catalysis concept as it allows the combination of homogeneous catalysis and its advantages with heterogeneous, fixed-bed technology. In this way, the SILP concept might provide a better mechanistic understanding of homogeneous catalysis (with only a small amount of precious catalyst) as reaction studies may be carried out at steady-state conversions unattainable by traditional batch reactions.

In perspective, we believe that the knowledge gained in this work could accelerate significantly the successful development of new SILP catalysts and future SILP catalysis

Table 6. Rh(**3**)/$SiO_2$/SILP catalyst performance in propene hydroformylation with $CO_2$ cofeed.

| $p_{He}$ [bar] | TOF [h$^{-1}$] | *n*-Butanal [%] | $p_{CO_2}$ [bar] | TOF [h$^{-1}$] | *n*-Butanal [%] | Δ(TOF)[a] [%] | Δ(*n*-Butanal)[b] [%] |
|---|---|---|---|---|---|---|---|
| 1.8 | 15.9 | 94.8 | 1.8 | 16.2 | 94.0 | 2.0 | 0.9 |
| 7.3 | 20.4 | 94.8 | 7.3 | 21.6 | 94.2 | 6.1 | 0.6 |
| 13.6 | 25.9 | 95.1 | 13.6 | 28.1 | 94.5 | 8.3 | 0.7 |
| 36.4 | 34.9 | 94.7 | 36.4 | 46.7 | 94.6 | 35.1 | 0.1 |

[a] $\Delta = [(TOF_{CO_2} - TOF_{He})/TOF_{He}] \cdot 100\%$. [b] $\Delta = [(n\text{-Butanal}_{CO_2} - n\text{-Butanal}_{He})/n\text{-Butanal}_{He}] \cdot 100\%$.

applications (e.g. other C–C couplings, hydrogenations etc.). Here, advent of task-specific ionic liquids (TSILs)[35] may also provide new opportunities for catalyst immobilisation and stabilisation in the ionic phase. From our work it becomes quite obvious that the combination of well-defined catalyst complexes, nonvolatile ionic liquids and solid, porous supports offers much more than traditional supported liquid-phase catalysis[36] using water or organic solvents which clearly suffers from evaporation of the supported solvent.[37] We therefore anticipate that the SILP catalysis concept may be able to contribute significantly to future developments aiming for highly selective, heterogenised homogeneous catalysts.

## Acknowledgments

This work was supported by the framework "Smart ligands – smart solvents" of ConNeCat financed by the German Federal Ministry for Education and Research (BMBF). Financial support by the Deutsche Forschungsgemeinschaft, DFG (M. H.), the Danish Research Council for Technology and Production, FTP, and the Villum Kann Rasmussen Foundation (A. R.) is gratefully acknowledged. The authors thank H. Gerhard, B. S. K. Gorle, B. Melcher, and C. Ernst, University of Erlangen-Nürnberg, and U. Maymann and A. Kustov, Technical University of Denmark, for their contributions in connection with analyses and SILP catalyst preparation. Furthermore, O. B. Lapina, Boreskov Institute of Catalysis (Novosibirsk, Russia) and G. Henze, University of Dortmund, are acknowledged for performing MAS NMR measurements and ICP analyses, respectively.

---

[1] a) J. D. Holbrey, K. R. Seddon, *Clean Prod. Proc.***1999**, *1*, 223; b) T. Welton, *Chem. Rev.* **1999**, *99*, 2071; c) J. Dupont, C. S. Consorti, J. Spencer, *J. Braz. Chem. Soc.* **2000**, *11*, 337; d) R. Sheldon, *Chem. Commun.* **2001**, 2399; e) H. Olivier-Bourbigou, L. Magna, *J. Mol. Catal. A: Chem.* **2002**, *182–183*, 419; f) O. Stenzel, H. G. Raubenheimer, C. Esterhysen, *J. Chem. Soc., Dalton Trans.* **2002**, 1132; g) H. Zhao, S. V. Malhotra, *Aldrichim. Acta* **2002**, *35*, 75.

[2] a) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772; b) C. M. Gordon, *Appl. Catal., A* **2001**, *222*, 101; c) P. J. Dyson, *Transition Met. Chem.* **2002**, *27*, 353; d) D. Zhao, M. Wu, Y. Kou, E. Min, *Catal. Today* **2002**, *74*, 157; e) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667.

[3] a) P. Wasserscheid, H. Waffenschmidt, P. Machnitzki, K. W. Kottsieper, O. Stetzler, *Chem. Commun.* **2001**, 451; b) F. Favre, H. Olivier-Bourbigou, D. Commereuc, L. Saussine, *Chem. Commun.* **2001**, 1360; c) P. Wasserscheid, T. Welton (Eds.), *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, Germany, **2003**.

[4] P. Wasserscheid, M. Eichmann, *Catal. Today* **2001**, *66*, 309.

[5] Selection of ionic liquid suppliers: a) Acros Organics (www.acros.com); b) Fluka (www.fluka.com); c) Merck (www.merck.com); d) Sigma–Aldrich (www.sigma-aldrich.com); e) Solvent Innovation (www.solvent-innovation.com); f) Strem (www.strem.com); g) Wako (www.wako-chem.co.jp).

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

[7] a) A. Riisager, K. M. Eriksen, P. Wasserscheid, R. Fehrmann, *Catal. Lett.* **2003**, *90*, 149; b) A. Riisager, P. Wasserscheid, R. van Hal, R. Fehrmann, *J. Catal.* **2003**, *219*, 252.

[8] a) A. Riisager, B. Jørgensen, P. Wasserscheid, R. Fehrmann, *Chem. Commun.*, in press. b) A. Riisager, R. Fehrmann, *Patent Application 2005/00735*, **2005** (assigned to DTU).

[9] a) C. P. Mehnert, E. J. Mozeleski, R. A. Cook, *Chem. Commun.* **2002**, 3010; b) A. Wolfson, I. F. J. Vankelecom, P. A. Jacobs, *Tetrahedron Lett.* **2003**, *44*, 1195.

[10] H. Hagiwara, Y. Sugawara, K. Isobe, T. Hoshi, T. Suzuki, *Org. Lett.* **2004**, *6*, 2325.

[11] S. Breitenlechner, M. Fleck, T. E. Müller, A. Suppan, *J. Mol. Catal. A: Chem.* **2004**, *214*, 175.

[12] K. Yamaguchi, C. Yoshida, S. Uchida, N. Mizuno, *J. Am. Chem. Soc.* **2005**, *127*, 530.

[13] a) Y. Yang, H. Lin, C. Deng, J. She, Y. Yuan, *Chem. Lett.* **2005**, *34*, 220; b) Y. Yang, C. Deng, Y. Yuan, *J. Catal.* **2005**, *232*, 108.

[14] A. Riisager, R. Fehrmann, P. Wasserscheid, R. van Hal in *Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities – Transformations and Processes* (Eds.: R. D. Rogers, K. R. Seddon), ACS Symposium Series, **2005**, vol. 902, chapter 23, p. 334.

[15] A. Riisager, R. Fehrmann, S. Flicker, R. van Hal, M. Haumann, P. Wasserscheid, *Angew. Chem. Int. Ed.* **2005**, *44*, 185.

[16] S. M. Silva, R. P. J. Bronger, Z. Freixa, J. Dupont, P. W. N. M. van Leeuwen, *New J. Chem.* **2003**, *27*, 1294.

[17] a) L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1999**, *18*, 4765; b) L. A. van der Veen, M. D. K. Boele, F. R. Bregman, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk, C. Bo, *J. Am. Chem. Soc.* **1998**, *120*, 11616; c) L. A. van der Veen, P. H. Keeven, G. C. Schoemaker, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Lutz, A. L. Spek, *Organometallics* **2000**, *19*, 872.

[18] P. Wasserscheid, "Transition Metal Catalysis in Ionic Liquids", in *Ionic Liquids in Synthesis* (Eds.: P. Wasserscheid, T. Welton), Wiley-VCH, Weinheim, Germany, **2003**.

[19] P. W. N. M. van Leeuwen, C. Claver (Eds.), *Rhodium Catalyzed Hydroformylation, Catalysis by Metal Complexes Series*, Springer, Heidelberg, **2000**.

[20] M. Schreuder Goedheijt, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Mol. Catal. A: Chem.* **1998**, *134*, 243.

[21] A. Riisager, M. Haumann, unpublished results.

[22] C. D. Frohning, C. W. Kohlpaintner, "Synthesis Gas Chemistry", in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1996**.

[23] a) L. A. van der Veen, M. D. K. Boele, F. R. Bregman, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk, C. Bo, *J. Am. Chem. Soc.* **1998**, *120*, 11616; b) L. A. van der Veen, P. H. Keeven, G. C. Schoemaker, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Lutz, A. L. Spek, *Organometallics* **2000**, *19*, 872.

[24] A. Riisager, R. Fehrmann, M. Haumann, B. S. K. Gorle, P. Wasserscheid, *Ind. Eng. Chem. Res.* **2005**, *44*, 9853.

[25] C. Yang, Z. S. Mao, Y. Wang, J. Chen, *Catal. Today* **2002**, *74*, 111.

[26] R. M. Desphande, P. Purwanto, H. Delmas, R. V. Chaudhari, *Ind. Eng. Chem. Res.* **1996**, *35*, 3927.

[27] U. J. Jáuregui-Haza, E. Pardillo-Fontdevila, P. Kalck, *Catal. Today* **2003**, *79–80*, 409.

[28] M. Benaissa, U. J. Jáuregui-Haza, I. Nikovc, A. M. Wilhelm, H. Delmas, *Catal. Today* **2003**, *79–80*, 419.

[29] Y. Zhang, Z. S. Mao, J. Chen, *Catal. Today* **2002**, *74*, 23.

[30] a) G. Gregorio, G. Montrasi, M. Tampieri, P. Cavalieri dÓro, G. Pagani, A. Andreetta, *Chim. Ind. (Milan)* **1980**, *62*, 389; b) P. Cavalieri d'Oro, L. Raimondi, G. Pagani, G. Montrasi, G. Gregorio, A. Andreetta, *Chim. Ind. (Milan)* **1980**, *62*, 572.

[31] a) J. F. Young, J. A. Osborn, F. A. Jardine, G. Wilkinson, *J. Chem. Soc., Chem. Commun. (London)* **1965**, 131; b) D. Evans, J. A. Osborn, G. Wilkinson, *J. Chem. Soc. A* **1968**, 3133; c) D. Evans, G. Yagupsky, G. Wilkinson, *J. Chem. Soc. A* **1968**, 2660.

[32] S. S. Divekar, R. M. Desphande, R. V. Chaudhari, *Catal. Lett.* **1993**, *21*, 191.

[33] a) L. A. Blanchard, Z. Gu, J. F. Brennecke, *J. Phys. Chem. B* **2001**, *105*, 2437; b) J. L. Anthony, E. J. Maginn, J. F. Brennecke, *J. Phys. Chem. B* **2002**, *106*, 7315.
[34] a) M. Solinas, A. Pfaltz, P. G. Cozzi, W. Leitner, *J. Am. Chem. Soc.* **2004**, *126*, 16142; b) D. G. Hert, J. L. Anderson, S. N. V. K. Aki, J. F. Brennecke, *Chem. Commun.* **2005**, 2603.
[35] J. H. Davis Jr., *Chem. Lett.* **2004**, *33*, 1072.
[36] K. T. Wan, M. E. Davis, *Nature* **1994**, *370*, 449.
[37] A. Beckmann, F. J. Keil, *Chem. Eng. Sci.* **2003**, *58*, 841.

Received: September 28, 2005