

# Continuous Gas-Phase Hydroformylation of 1-Butene using Supported Ionic Liquid Phase (SILP) Catalysts

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**Abstract:** The concept of supported ionic liquid phase (SILP) catalysis has been extended to 1-butene hydroformylation. A rhodium-sulfoxantphos complex was dissolved in [BMIM][*n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>3</sub>] and this solution was highly dispersed on silica. Continuous gas-phase experiments in a fixed-bed reactor revealed these SILP catalysts to be highly active, selective and long-term stable. Kinetic data have been acquired by variation of temperature, pressure, syngas composition, substrate and catalyst concentration. A linear dependency in rhodium concentration

could be established over a large concentration range giving another excellent hint for truly homogeneous catalysis in the SILP system. Compared to former studies using propene, the SILP system showed significantly higher activity and selectivity with 1-butene as feedstock. These findings could be elucidated by solubility measurements using a magnetic microbalance.

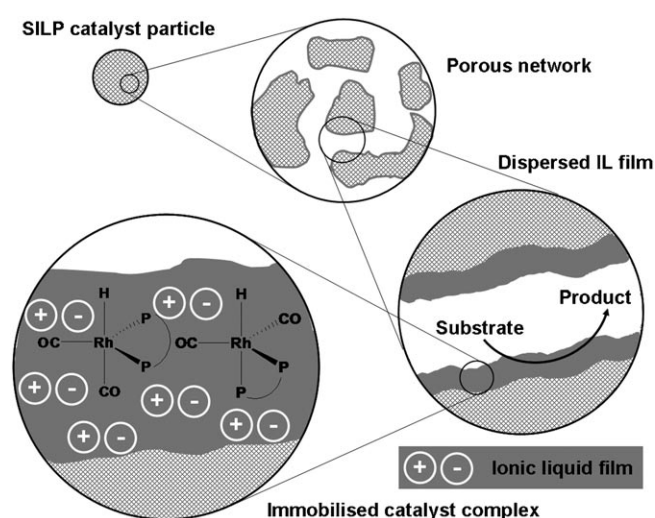
**Keywords:** hydroformylation; ionic liquids; kinetics; rhodium; supported catalysts

## Introduction

Among the biphasic catalysis concepts developed for the immobilisation of precious homogeneous catalysts the use of ionic liquids has gained significant interest over the last decade both in academia and industry.<sup>[1]</sup> Ionic liquids consist entirely of ions and have extremely low vapour pressures which makes them attractive as alternative solvents for homogeneous catalysis. Their polar, non-aqueous nature allows the stabilisation of ionic transition metal complexes as well as complexes that are susceptible to hydrolysis. The use of ionic liquids in catalysis has been reviewed recently in a number of excellent papers.<sup>[2]</sup>

Biphasic ionic liquid-organic liquid systems generally require a large amount of ionic liquid. Based on economic considerations, this is unattractive since ionic liquids will remain relatively expensive (compared to ordinary organic solvents) even though they are commercially available now.<sup>[3]</sup> 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 the precious transition metal catalyst dissolved therein to take part in the catalysed reaction. These drawbacks have re-

cently been circumvented by us and other groups using supported ionic liquid phase (SILP) systems.<sup>[4]</sup> In these systems, a thin film of ionic liquid is confined on the surface of a highly porous solid by various



**Figure 1.** Schematic representation of supported ionic liquid phase (SILP) catalysis.

methods such as, e.g., physisorption, tethering, or covalent anchoring of ionic liquid fragments. Figure 1 schematically illustrates such a catalytic SILP material containing Rh complexes dissolved in the ionic liquid film.

In a number of publications we have recently demonstrated that the problem of mass transport limitation from the gas into the liquid phase can indeed be circumvented by using these SILP catalysts. Moreover, they allow the application of fixed-bed reactors for simple continuous processing when applied in combination with gaseous reaction mixtures making the separation and catalyst recycling obsolete.<sup>[5]</sup> In the case of propene hydroformylation the use of 2,7-bis-(SO<sub>3</sub>Na)-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (sulfoxantphos) **1** modified rhodium complexes in [BMIM][*n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>3</sub>] dispersed on silica resulted in very active and highly selective Rh-**1**-SILP catalysts. The catalyst lifetime exceeded 200 h time-on-stream during which a slight decrease in activity was observed. Since the selectivity towards *n*-butanal remained high at around 97%, it was concluded that possibly high-boiling side products (e.g., from an aldol condensation consecutive reaction of the formed product) accumulated in the ionic liquid film, thus diluting the effective rhodium concentration. Upon exposure of the SILP catalyst to 70 mbar vacuum these heavy species could be removed and the initial activity was regained. Consecutive application of vacuum was possible and total lifetimes of more than 700 h were obtained.<sup>[6]</sup>

In this paper we describe the extension of the SILP concept to 1-butene hydroformylation using Rh-**1**-SILP catalysts. Although pure 1-butene is not an interesting feedstock for hydroformylation due to its high price it can serve as a model for industrial C<sub>4</sub> feedstocks. The most attractive C<sub>4</sub> feedstock for hydroformylation would be the so-called Raffinate II, a mixture containing 1-butene (ca. 45%), *cis*-2-butene and *trans*-2-butene (ca. 30%) and butanes (ca. 25%).<sup>[7]</sup> Furthermore, by using a larger 1-alkene (compared to our earlier studies of propene hydroformylation) we wanted to see whether pore diffusion effects would begin to play a role in the SILP system. This question was addressed by detailed kinetic studies of the continuous gas-phase reaction of 1-butene using otherwise identical SILP systems as formerly investigated for continuous propene hydroformylation.<sup>[6]</sup>

## Results and Discussion

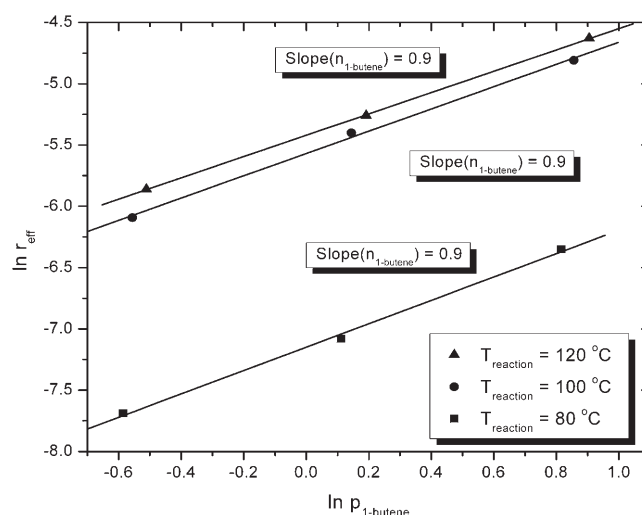
The standard SILP catalyst consisted of silica 100 (particle size 63 to 200 μm) coated with the ionic liquid [BMIM][*n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>3</sub>] ( $\alpha$  = volume IL/total pore volume = 0.1) containing the rhodium-sulfoxantphos complex with an L/Rh ratio of 10. The rhodium

loading of the SILP catalyst was varied between 0.1 and 0.9 wt % (mass Rh/total mass SiO<sub>2</sub>).

### Variation of 1-Butene Partial Pressure

The 1-butene partial pressure was varied between 0.6 and 2.4 bar in the temperature range of 80 to 120 °C at three different rhodium loadings, namely 0.1, 0.2 and 0.3 wt %. The amount of 1-butene in each experiment was well below stoichiometric conditions in order to avoid reaction rate limitation either by CO or H<sub>2</sub>. The residence time in each experiment was approximately 17 seconds. The reaction order with respect to 1-butene was determined from a differential analysis by plotting  $\ln r_{\text{eff}}$  against  $\ln p_{1\text{-butene}}$  and by taking the gradient as the reaction order. Figure 2 exemplifies the differential analysis for a rhodium loading of 0.1 wt %.

In Table 1 the results of differential analysis from three different Rh loadings are compiled. The reaction rate of the SILP catalyst increased linearly with increasing  $p_{1\text{-butene}}$  (e.g., entries 4 to 6). The average reaction order was found to be  $1.0 \pm 0.1$  and was in good agreement with results from both literature studies in homogeneous systems and our previously reported results from SILP-catalysed propene hydroformylation. In the temperature range between 80 and 120 °C the TOFs increased significantly up to 564 h<sup>-1</sup> (entry 27). For a given temperature, the selectivity towards the linear aldehyde *n*-pentanal was neither affected by  $p_{1\text{-butene}}$  nor Rh loading (e.g., entries 1–3, 10–12, 19–21). For a given Rh loading, the selectivity decreased slightly with increasing temperature (e.g., entries 10–18). The average selectivity was



**Figure 2.** Differential analysis of 1-butene hydroformylation using Rh-**1**-SILP catalysts. 100 °C, 10 bar syngas (H<sub>2</sub>:CO = 1:1), residence time = 17 s, L/Rh = 10. Rh loading 0.2 wt %, ionic liquid loading 10 vol %.

**Table 1.** 1-Butene hydroformylation using Rh-1-SILP catalysts at different partial pressures of 1-butene.<sup>[a]</sup>

| Entry | $c_{Rh}$ [wt %] | Temperature [°C] | $p_{1-butene}$ [bar] | Conversion [%] | TOF [ $h^{-1}$ ] | $n$ -pentanal [%] | $n_{1-butene}$ |
|-------|-----------------|------------------|----------------------|----------------|------------------|-------------------|----------------|
| 1     | 0.1             | 80               | 0.6                  | 1.4            | 17.0             | 99.9              | 0.9            |
| 2     |                 | 80               | 1.2                  | 1.3            | 31.1             | 99.9              |                |
| 3     |                 | 80               | 2.4                  | 1.3            | 64.6             | 99.9              |                |
| 4     |                 | 100              | 0.6                  | 6.4            | 79.1             | 98.1              | 0.9            |
| 5     |                 | 100              | 1.2                  | 6.4            | 158.2            | 98.2              |                |
| 6     |                 | 100              | 2.4                  | 5.8            | 285.6            | 98.0              |                |
| 7     |                 | 120              | 0.6                  | 7.7            | 94.8             | 97.9              | 0.9            |
| 8     |                 | 120              | 1.2                  | 7.0            | 172.9            | 97.8              |                |
| 9     |                 | 120              | 2.4                  | 6.6            | 324.4            | 97.7              |                |
|       |                 |                  |                      |                |                  | average           |                |
| 10    | 0.2             | 80               | 0.6                  | 1.6            | 9.6              | 99.9              | 1.1            |
| 11    |                 | 80               | 1.2                  | 1.3            | 15.6             | 99.9              |                |
| 12    |                 | 80               | 2.4                  | 1.8            | 43.3             | 99.9              |                |
| 13    |                 | 100              | 0.6                  | 4.3            | 25.5             | 99.9              | 1.3            |
| 14    |                 | 100              | 1.2                  | 6.1            | 72.3             | 98.0              |                |
| 15    |                 | 100              | 2.4                  | 6.4            | 152.3            | 98.0              |                |
| 16    |                 | 120              | 0.6                  | 9.8            | 59.1             | 97.6              | 1.0            |
| 17    |                 | 120              | 1.2                  | 10.9           | 130.0            | 97.7              |                |
| 18    |                 | 120              | 2.4                  | 10.0           | 238.9            | 97.6              |                |
|       |                 |                  |                      |                |                  | average           |                |
| 19    | 0.3             | 80               | 0.6                  | 5.6            | 24.7             | 98.4              | 1.0            |
| 20    |                 | 80               | 1.2                  | 5.1            | 44.5             | 98.2              |                |
| 21    |                 | 80               | 2.4                  | 5.6            | 97.5             | 98.2              |                |
| 22    |                 | 100              | 0.6                  | 18.5           | 81.3             | 97.8              | 1.0            |
| 23    |                 | 100              | 1.2                  | 18.8           | 164.8            | 98.0              |                |
| 24    |                 | 100              | 2.4                  | 19.6           | 344.8            | 97.8              |                |
| 25    |                 | 120              | 0.6                  | 35.5           | 155.7            | 97.7              | 0.9            |
| 26    |                 | 120              | 1.2                  | 31.2           | 273.8            | 97.5              |                |
| 27    |                 | 120              | 2.4                  | 32.1           | 563.5            | 97.1              |                |
|       |                 |                  |                      |                |                  | average           |                |

<sup>[a]</sup> Reaction conditions:  $p=10$  bar, ratio  $H_2:CO=1:1$ , residence time 17 s,  $L/Rh=10$ , ionic liquid loading = 10 vol %.

found to be exceptionally high around 98 %  $n$ -pentanal under all conditions.

### Variation of Rhodium Concentration

At 100 °C four different SILP catalysts with rhodium loadings of 0.1, 0.2, 0.3 and 0.9 wt % were studied. Table 2 compiles the results with respect to activity

**Table 2.** 1-Butene hydroformylation using Rh-1-SILP catalysts at different Rh loadings.<sup>[a]</sup>

| Entry | $c_{Rh}$ [wt %] | $r_{eff}$ [ $10^{-3}$ bars $^{-1}$ ] | Conversion [%] | TOF [ $h^{-1}$ ] | $n$ -pentanal [%] |
|-------|-----------------|--------------------------------------|----------------|------------------|-------------------|
| 28    | 0.1             | 7.7                                  | 6.6            | 271              | 98.0              |
| 29    | 0.2             | 15.0                                 | 13.2           | 263              | 98.0              |
| 30    | 0.3             | 20.6                                 | 18.1           | 252              | 97.9              |
| 31    | 0.9             | 27.7                                 | 24.3           | 159              | 97.6              |

<sup>[a]</sup> Reaction conditions:  $T=100$  °C,  $p=10$  bar, ratio  $H_2:CO=1:1$ ,  $p_{1-butene}=1.9$  bar, residence time 16 s,  $L/Rh=10$ , ionic liquid loading = 10 vol %.

and selectivity. Increasing the Rh loading had a pronounced effect on the reaction rate, which increased almost linearly with  $c_{Rh}$  up to a rhodium loading of 0.3 wt % (entries 28 to 30). In this concentration range the TOF of each SILP system remained unchanged, indicating that each rhodium centre showed the same activity and no cluster formation occurred.

When using a rhodium loading of 0.9 wt % (entry 31) the observed reaction rate showed a non-linear behaviour. The TOF of 159  $h^{-1}$  was significantly lower compared to the rhodium loadings of 0.1 to 0.3 wt % (TOFs between 252 and 271  $h^{-1}$ ). This reduced activity might be caused by mass transport limitations from the gas into the liquid phase, starting to compete with the rate of reaction. The latter could be induced by the very high Rh and – in particular – by the very high ligand concentration leading to a strong increase of ionic liquid film viscosity. In all cases the selectivity was still high with 98 %  $n$ -pentanal being formed so that the formation of active, ligand free Rh clusters appears unlikely. For the range of Rh loadings between 0.1 and 0.3 wt %, the reaction rate showed first order dependency in rhodium concentration.

### Variation of H<sub>2</sub> and CO Partial Pressure

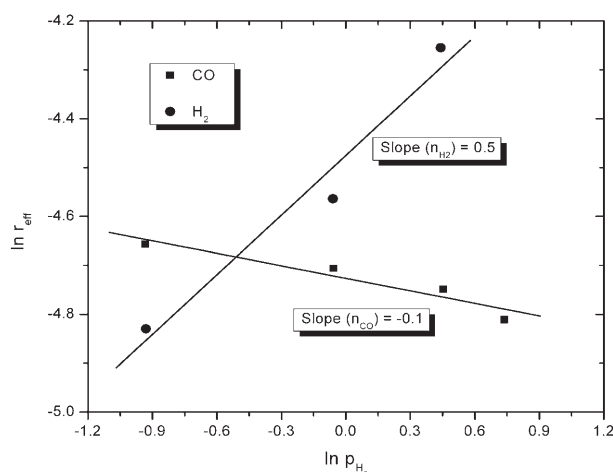
The effect of partial pressure of hydrogen and carbon monoxide was studied using a standard Rh-SILP catalyst with 0.2 wt % Rh loading. In the region of 0.4 to 2.1 bar partial pressure of CO a negative slope of  $-0.1$  was found as depicted in Figure 3.

In the region of 0.4 to 1.6 bar partial pressure of H<sub>2</sub>, a positive trend was observed. This behaviour of the SILP catalyst is in accordance with the hydroformylation mechanism described by Wilkinson.<sup>[8]</sup> Addition of hydrogen is assumed to be the rate-limiting step for most systems, whereas the initial step of the catalytic cycle is hampered by high partial pressures of CO. The selectivity towards *n*-pentanal was not influenced by the syngas composition and an average value of 98 % was determined from the data.

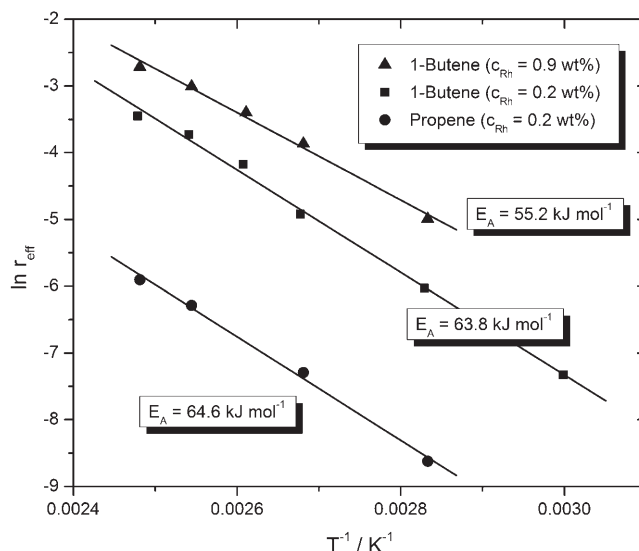
### Variation of Temperature; Activation Energy

The standard SILP catalyst was studied in the temperature range between 60 and 130 °C for two rhodium loadings: 0.2 wt % and 0.9 wt %. In Figure 4 the results from an Arrhenius analysis are shown. The formal, effective activation energy  $E_{A,eff}$  was calculated to be  $63.8 \text{ kJ mol}^{-1}$  in the case of 0.2 wt % catalyst loading. The value was in good agreement with the previously determined  $E_{A,eff} = 63.2 \text{ kJ mol}^{-1}$  for propene hydroformylation.<sup>[6]</sup>

Both values indicate that the SILP system was operating in the kinetic regime and no severe pore diffusion influence occurred under these conditions. Interestingly, the effective rate in butene hydroformylation was always higher than the one obtained in propene hydroformylation.



**Figure 3.** Syngas variation in 1-butene hydroformylation using Rh-1-SILP catalysts. 100 °C, 10 bar syngas (H<sub>2</sub>:CO = 1:1),  $p_{1\text{-butene}} = 1.1 \text{ bar}$ , residence time = 17 s, L/Rh = 10. Rh loading 0.2 wt %, ionic liquid loading 10 vol %.



**Figure 4.** Arrhenius plot for Rh-1-SILP-catalysed hydroformylation of propene and 1-butene. 10 bar syngas (H<sub>2</sub>:CO = 1:1),  $p_{\text{alkene}} = 1.1 \text{ bar}$ , residence time = 17 s, L/Rh = 10. Rh loading 0.2 wt %, ionic liquid loading 10 vol %.

The empirical rate law for rhodium loading below 0.3 wt % can be written as

$$r_{\text{eff}} = k_{\text{eff}} \cdot p_{1\text{-butene}} \cdot p_{\text{CO}}^{-0.1} \cdot p_{\text{H}_2}^{0.5} \cdot c_{\text{Rh}} \quad (\text{for } c_{\text{Rh}} < 0.3 \text{ wt } \%)$$

When using the SILP catalyst with a rhodium loading of 0.9 wt % the  $E_{A,eff}$  was calculated to be  $55.2 \text{ kJ mol}^{-1}$ . The lower value may indicate some additional influence on the overall reaction rate. It is estimated that the rate of the gas-film transition in the catalyst pores may become an influencing factor at the high catalyst and ligands loadings. Additionally, the temperature dependent change in film viscosity may contribute to the observed rate dependency on temperature.

### Comparison of Propene and 1-Butene Hydroformylation

Remarkable, a clear enhancement in both activity and selectivity can be noticed when comparing SILP-catalysed hydroformylations of 1-butene and propene. Table 3 presents the experimental data for both substrates at 100 and 120 °C.

The SILP catalyst showed a 2.5-fold higher activity when using 1-butene instead of propene at 100 °C. At 120 °C the activity was up 2.1 times, whereas the selectivity also increased from ca. 95 % to ca. 98 % *n*-aldehyde (entries 32/33 and 34/35). Therefore, the solubility of propene and 1-butene in the SILP system was measured using a microbalance. The results for

**Table 3.** Comparison between Rh-1-SILP-catalysed hydroformylation of propene and 1-butene.<sup>[a]</sup>

| Entry | Substrate                     | $p_{\text{substrate}}$ [bar] | Temperature [°C] | TOF [h <sup>-1</sup> ] | C <sub>4</sub> H <sub>8</sub> /C <sub>3</sub> H <sub>6</sub> <sup>[b]</sup> | <i>n</i> -aldehyde [%] |
|-------|-------------------------------|------------------------------|------------------|------------------------|-----------------------------------------------------------------------------|------------------------|
| 32    | C <sub>3</sub> H <sub>6</sub> | 2.1                          | 100              | 103                    | 2.5                                                                         | 95.6                   |
| 33    | C <sub>4</sub> H <sub>8</sub> | 1.9                          | 100              | 260                    |                                                                             | 98.0                   |
| 34    | C <sub>3</sub> H <sub>6</sub> | 2.1                          | 120              | 308                    | 2.1                                                                         | 94.8                   |
| 35    | C <sub>4</sub> H <sub>8</sub> | 1.9                          | 120              | 647                    |                                                                             | 97.6                   |

<sup>[a]</sup> Reaction conditions: 10 bar syngas (H<sub>2</sub>:CO = 1:1), residence time = 17 s, L/Rh = 10. Rh loading 0.2 wt %, ionic liquid loading 10 vol %.

<sup>[b]</sup> Ratio of activities for 1-butene and propene.

two different support materials are summarised in Table 4.

When using the SILP standard system prepared from a silica 100 support with an average pore diameter of 4 nm the difference in molar solubility between propene and 1-butene resembled the observed difference in activity very well. In the pressure regime between 0 and 2.6 bar the 1-butene solubility in the ionic liquid [BMIM][*n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>3</sub>] was 2.4 times higher compared to the propene solubility (entry 36). A porous glass with a larger pore diameter of 30 nm was also studied (entry 37). Approximately the same ratio in solubility for 1-butene vs. propene was observed (entry 37). However, the molar solubility of both propene and 1-butene was up to 5.6 times higher when using silica gel as support instead of porous glass (entry 40). This might give a hint that, in the smallest pores of a SILP silica 100 system capillary, condensation occurs for both propene and 1-butene as substrate. In an additional experiment the ionic liquid was changed from [BMIM][*n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>3</sub>] to [EMIM][*n*-C<sub>2</sub>H<sub>5</sub>OSO<sub>3</sub>] in order to study the influence of the alkyl chain length at the anion. The same solubility ratio was observed as well (entry 38), but compared with [BMIM][*n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>3</sub>] the solubility for both 1-butene and propene was lower by factors of 4.3 and 4.6, respectively (entry 40).

## Conclusions

In the present work we have extended the concept of supported ionic liquid phase (SILP) catalysis to the gas phase hydroformylation of 1-butene using continuous fixed bed reactors. The SILP catalyst showed the same characteristics of a truly homogeneous complex as previously described for propene hydroformylation. A first order in 1-butene partial pressure was obtained from differential analysis. The variation of rhodium loading showed a linear dependency of rate with catalyst loading between 0.1 and 0.3 wt % and for this regime a full rate law was established. The first order with respect to rhodium indicated that the reaction was not limited by mass transport from the gas into the liquid phase. The hydrogen partial pressure was found to have a positive effect on the reaction rate, whereas the carbon monoxide partial pressure had a slightly negative one. All three observations are in accordance with the mechanism of homogeneous Rh-catalysed hydroformylation. The activation energy was derived from an Arrhenius plot to be 63 kJ mol<sup>-1</sup>. Since this value is in good agreement with literature data in both homogeneous and biphasic systems<sup>[9]</sup> it is assumed that the 1-butene hydroformylation using Rh-SILP catalysts is not influenced by pore diffusion effects inside the catalyst particle. Fur-

**Table 4.** Gas solubility of propene and 1-butene determined by magnetic suspension balance. Comparison of different support materials and types of ionic liquid.<sup>[a]</sup>

| Entry | Support                             | Ionic liquid         | Solubility <sub>1-butene</sub> [10 <sup>-5</sup> mol g <sup>-1</sup> ] | Solubility <sub>propene</sub> [10 <sup>-5</sup> mol g <sup>-1</sup> ] | C <sub>3</sub> H <sub>6</sub> /C <sub>4</sub> H <sub>8</sub> <sup>[b]</sup> |
|-------|-------------------------------------|----------------------|------------------------------------------------------------------------|-----------------------------------------------------------------------|-----------------------------------------------------------------------------|
| 36    | SiO <sub>2</sub>                    | BO <sup>[c]</sup>    | 19.8                                                                   | 8.4                                                                   | 2.4                                                                         |
| 37    | PG <sup>[d]</sup>                   | BO <sup>[c]</sup>    | 3.8                                                                    | 1.5                                                                   | 2.5                                                                         |
| 38    | SiO <sub>2</sub>                    | EE <sup>[e]</sup>    | 4.3                                                                    | 2.0                                                                   | 2.2                                                                         |
| 39    | SiO <sub>2</sub> /PG <sup>[f]</sup> | BO                   | 5.2                                                                    | 5.6                                                                   |                                                                             |
| 40    | SiO <sub>2</sub>                    | BO/EE <sup>[g]</sup> | 4.6                                                                    | 4.3                                                                   |                                                                             |

<sup>[a]</sup> Reaction conditions: 10 bar syngas (H<sub>2</sub>:CO = 1:1), residence time = 17 s, L/Rh = 10. Rh loading 0.2 wt %, ionic liquid loading 10 vol %.

<sup>[b]</sup> Ratio of solubility<sub>propene</sub>/solubility<sub>1-butene</sub>.

<sup>[c]</sup> BO = [BMIM][*n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>3</sub>].

<sup>[d]</sup> PG = porous glass.

<sup>[e]</sup> EE = [EMIM][*n*-C<sub>2</sub>H<sub>5</sub>OSO<sub>3</sub>].

<sup>[f]</sup> Solubility ratio for silica and porous glass.

<sup>[g]</sup> solubility ratio for [BMIM][*n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>3</sub>] and [EMIM][*n*-C<sub>2</sub>H<sub>5</sub>OSO<sub>3</sub>]

thermore, the coefficient of 1-butene diffusion from the gas into the ionic liquid phase is orders of magnitude lower than the gas diffusion coefficient of 1-butene.<sup>[10,11]</sup>

At a rhodium loading of 0.9 wt % a lower TOF and an activation energy of 55 kJ mol<sup>-1</sup> were observed, indicating additional effects to pure chemical kinetics. It is assumed that, under these conditions, the high ligand concentration in the liquid film affects the viscosity of the latter and decreases thereby the gas-film mass transport rate.

Compared to the reaction of propene the SILP catalyst exhibited significantly higher activity and selectivity in 1-butene hydroformylation. The solubilities of propene and 1-butene were measured and found to match very well the observed difference in activity. However, between two different supports and two different ionic liquids the solubility changed for both propene and 1-butene in an analogous fashion. These effects may be due to capillary condensation effects, a point that will attract our specific attention in future studies.

## Experimental Section

### General Remarks

All syntheses were carried out using standard Schlenk techniques under argon (99.999%). Rh(acac)(CO)<sub>2</sub>, xanthene and MeOH (HPLC grade) were purchased from Aldrich and used without further purification. The synthesis of sulfoxantphos ligand **1** was carried out according to literature procedures.<sup>[12]</sup> Silica gel 100 (63 to 200 µm) was purchased from Merck and was thermally pre-treated at 450 °C for 24 h. Porous glass (PG) was obtained from VitraBio GmbH and was pre-treated at 450 °C for 24 h. Carbon monoxide (99.7%), hydrogen (99.99%) and 1-butene (99.5%) were purchased from Linde. The ionic liquids were purchased from Solvent Innovation GmbH. The water content was measured with a Karl Fischer titration and the ionic liquids were dried under high vacuum at 50 °C overnight.

### SILP Catalyst Preparation

Rh(CO)<sub>2</sub>(acac) (0.0512 g, 0.2 mmol) was dissolved in 20 mL dried MeOH and stirred for 10 min. The ligand sulfoxantphos (1.57 g, 2 mmol) was added and the orange solution was stirred for another 10 min. Afterwards, 1 mL (1.06 g) of ionic liquid was added to the solution. After stirring for 30 min, 10 g calcinated silica were added and the solution was stirred for 60 min. The MeOH was removed under vacuum and a pale red powder was obtained. The supported ionic liquid phase catalyst was stored under argon until further use.

### Kinetic Experiments

The continuous reactor set-up used in our laboratories for the SILP-catalysed hydroformylation has been described in

detail previously.<sup>[6]</sup> The supported ionic liquid phase (SILP) catalyst was filled into the reactor and the complete rig was evacuated at room temperature. The rig was pressurised with 50 bar helium and left under pressure for 30 min while monitoring the pressure. If no pressure drop was observed, the reactor was heated to the reaction temperature under helium pressure. The complete set-up was evacuated and flushed with helium three times before syngas and 1-butene were fed into the system. 1-Butene was taken out of a reservoir in the liquid state and fed into a heated evaporator *via* an HPLC pump to control the molar flow of the substrate. Both carbon monoxide and hydrogen flows were adjusted by means of mass-flow controllers (MFC, 5850 S series, Brooks Instruments). The preheated gases were combined with the propene in the mixing unit which was filled with glass beads in order to ensure proper mixing and isothermal conditions. The gas mixture could then either enter the reactor or exit the system *via* a bypass. The reactor consisted of a stainless steel tube (10 mm diameter, 220 mm length) equipped with a bronze sinter plate for catalyst placement. After the reactor, the gas mixture passed a 7 µm filter in order to avoid decontamination of the tubing with catalyst or solid particles. A back-pressure regulator valve (Samson) was used to maintain the desired reaction pressure and outlet gas flow. After the regulator valve, the gas stream was split and a minor flow was passed through a 134 µL sampling loop mounted on a gas chromatograph (HP 5890 II plus). Samples were taken at regular intervals by injecting the volume of the sampling loop *via* a 6-port valve into the GC.

### Gas Chromatography

The conversion of 1-butene as a function of process conditions was measured using the on-line GC technique. An HP 5890 GC equipped with a Pona column (50 m, 0.2 mm diameter, 0.25 µm coating) and a flame ionisation detector (FID) pre-calibrated for 1-butene, *n*-pentanal and isopentanal (allowing the peak areas to be transferred into 1-butene conversion) was applied: Injector temperature 150 °C, split ratio 43:1, helium carrier gas flow 2.4 mL min<sup>-1</sup>, detector temperature 250 °C. To detect possible high boiling by-products (heavy species), the following temperature program was used: initial temperature 50 °C, initial time 5 min, heating ramp of 50 °C min<sup>-1</sup>, final temperature 150 °C, final time 3 min, cooling ramp 50 °C min<sup>-1</sup>, final temperature 50 °C.

### Microbalance Measurements

The solubility of propene and 1-butene in the ionic liquid films of the SILP catalysts was measured using a magnetic suspension balance from Rubotherm Präzisionsmesstechnik GmbH. Samples were analysed at 80 °C and in the pressure range between 0 and 9.0 (propene) and 0 and 3.5 bar (1-butene). Densities of the two gases were taken from the NIST data base.

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