SILP Catalysis in Gas-Phase Hydroformylation and Carbonylation

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Abstract

Supported ionic liquid phase (SILP) catalysts are new materials consisting of an ionic liquid-metal catalyst solution highly dispersed on a porous support. The use of a non-volatile, ionic liquid catalyst phase in SILP catalysts results in a stable heterogeneous-type material with selectivity and efficiency like homogeneous catalysts. The silica-supported SILP Rh-bisphosphine hydroformylation catalyst exhibited good activities and excellent selectivities in gas phase hydroformylation with stability exceeding 700 hours time-on-stream. Spectroscopic and kinetic data confirmed the homogeneous nature of the catalyst. In the Rh-SILP catalysed carbonylation of methanol the formation of undesired by-products could be suppressed by variation of residence time and gas pressure.

Introduction

The immobilisation of homogeneous catalysts by ionic liquids has been studied extensively in the last decade. The ionic nature, very low volatility and thermal stability of ionic liquids make them highly suitable for biphasic ionic liquid-organic liquid transition metal catalysis.[1] The almost unlimited combinations of cation and anion allow the synthesis of tailor made ionic liquids that can stabilise the catalytic species. Moreover, appropriate ionic liquids can enhance substrate solubility while possessing low product solubility, and thus facilitate simple product separation and complete catalyst recovery.[2]

By dispersing the ionic liquid on the large surface of a porous material a heterogenised form of a homogeneous catalyst, named Supported Ionic Liquid Phase (SILP) system, is obtained as depicted in Figure 1.[3] These SILP systems are well suited for continuous gas phase reactions, since the large surface area can minimise mass transport problems. In addition, the high dispersion of the ionic liquid catalyst solution on the support surface results in a very efficient use of ionic liquid and precious catalyst. Furthermore, the solid SILP catalysts allow the use of fixed-bed reactor technology.

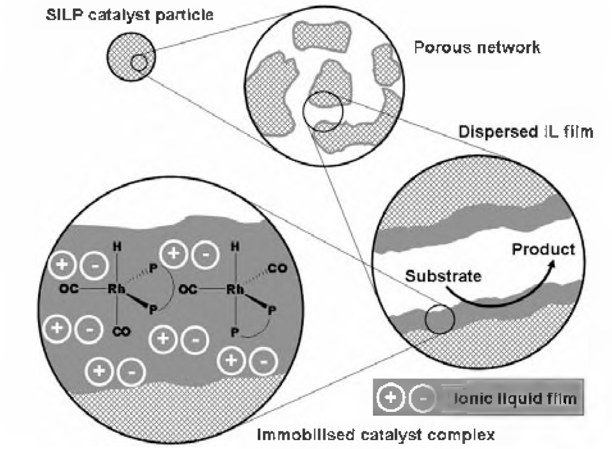
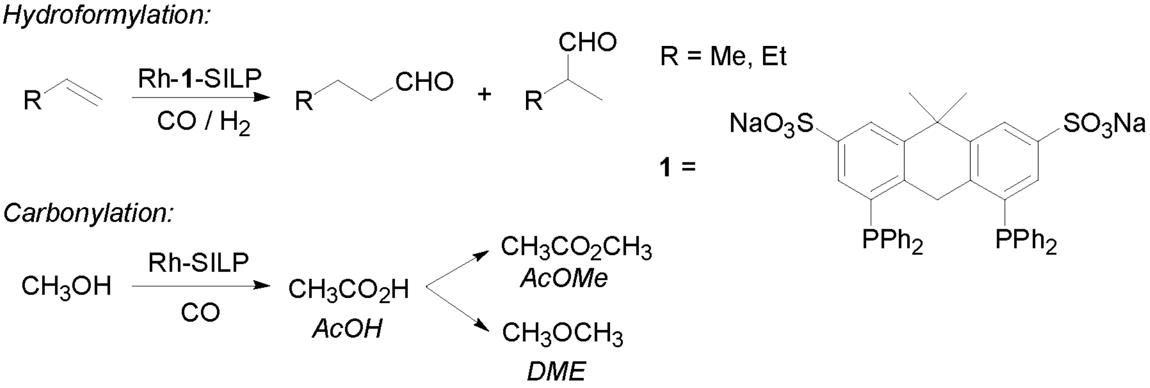


Figure 1. Schematic representation of Supported Ionic Liquid Phase (SILP) systems for catalysis.

One of the first examples of liquid SILP catalysis was reported by Mehnert and co-workers on the hydroformylation of 1-hexene in batch autoclave mode using silica as support material.[4] 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.

In this work the advantages of SILP catalysis are exemplified for the Rh-diphosphine catalysed, continuous gas-phase hydroformylation of propene and 1-butene as well as for the carbonylation of methanol using a novel Rh-iodine complex as depicted in Scheme 1.



Hydroformylation

Long-term stability

Preliminary measurements using the Rh-**1** SILP were initially studied at 100 °C and 10 bar syngas pressure (H_2:CO 1:1) over a period of up to 36 hours.[5] This time-on-stream was further extended to 180 hours to test the long-term stability of the Rh-1 dehydroxylated catalyst system.[6] 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 constant it was excluded that deactivation was caused by catalyst decomposition, as observed in previous studies when using low L/Rh ratios.[7] ICP 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.

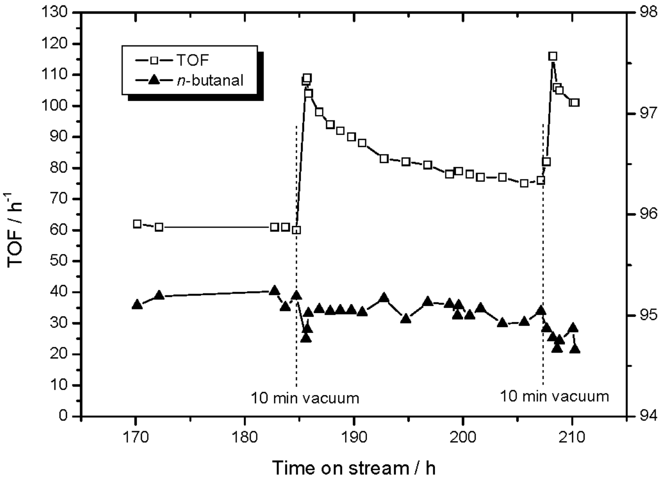


Figure 2. Reactivation of Rh-**1**-SILP catalyst by consecutive application of vacuum. 100 °C, 10 bar syngas pressure (H_2:CO = 1:1), Rh loading 0.2 wt%, $p_{propene}$ = 1.8 bar, τ = 0.38 s.

To confirm this hypothesis, the gas flow was temporary stopped after 180 hours time-on-stream and the reaction setup was evacuated to 70 mbar for 10 min at 100 °C. When the experiment was continued after this procedure, the activity had indeed increased from 60 to 108 h^{-1}. Within the next 20 hours of reaction the TOFs decreased again from 108 h^{-1} to 76 h^{-1} and the selectivity re-established at 95 % n-butanal. A second vacuum period of 10 min resulted in improved TOFs, as depicted in Figure 2. 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 re-saturated 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-ethyl-hexanal and 2-ethyl-hexanol to be of relevance, as traces of these high boiling side products were observed at particular high conversions. To confirm this hypothesis, the SILP catalyst was removed from the reactor and washed with cyclohexane. GC analysis of the wash solution indicated the presence of 2-ethyl-hexanal and 2-ethyl-hexanol.

For 1-butene hydroformylation a similar activity decrease was observed.[8] Due to the higher boiling temperature of the side products the vacuum was reduced from 70 mbar to 1 mbar. In analogy to the propene experiments the SILP catalyst could be reactivated by this vacuum procedure.

Kinetic investigations

In the first kinetic experiments the propene concentration was varied by changing the propene partial pressure in the feed gas (at constant total pressure) between 0.9 and 3.2 bar at temperatures in the range of 65 to 140 °C. The differential analysis is shown in Figure 3 from which the rate constants k and the reaction order with respect to propene partial pressure were determined.

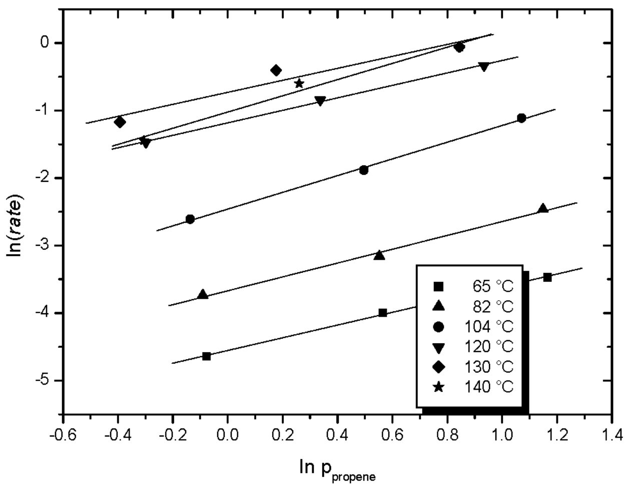


Figure 3. Differential analysis of the Rh-**1**-SILP catalysed hydroformylation at various propene partial pressures and temperatures. 10 bar total pressure, H_2:CO = 1:1, Rh loading 0.2 wt%, τ = 0.9 s.

The first order dependency was similar to traditional organic and aqueous Rh-phosphine catalysed hydroformylation systems.[9] The differential analysis for 1-butene hydroformylation using the same Rh-SILP catalyst system indicated a first order reaction as well. Interestingly, the obtained activity was around 2.5 times higher than for propene hydroformylation which can be attributed to better solubility of 1-butene in the ionic liquid and capillary condensation under reaction conditions.

For 1-butene hydroformylation 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 4. In the region of 0.4 to 1.6 bar partial pressure of H_2, a positive trend was observed.

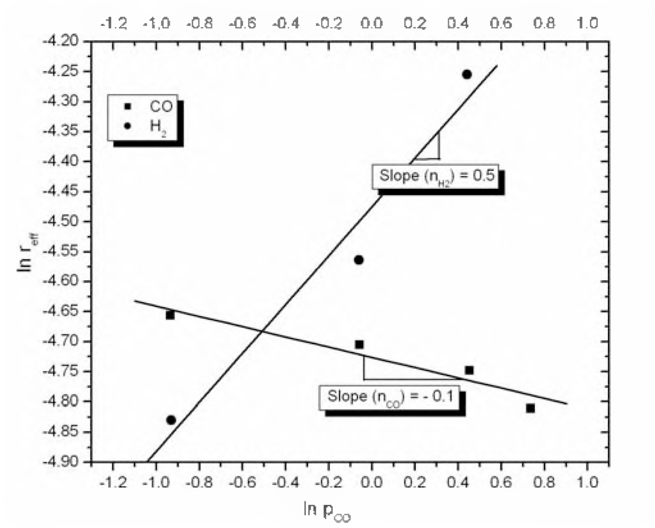


Figure 4. Syngas variation in 1-butene hydroformylation using Rh-**1**-SILP catalysts. 100 °C, 10 bar syngas (H_2 : CO = 1 : 1), $p_{1\text{-butene}}$ = 1.1 bar, τ = 17 s, L/Rh = 10. Rh-loading 0.2 wt%, α = 0.1.

This behaviour of the SILP catalyst is in accordance with the hydroformylation mechanism described by Wilkinson.[10] Addition of hydrogen to the catalyst system 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.

For 1-butene hydroformylation three different SILP catalysts with rhodium loadings of 0.1, 0.2 and 0.3 wt% were studied at 100 °C. Table 1 compiles the results with respect to activity and selectivity.

Table 1. 1-Butene hydroformylation using Rh-**1**-SILP catalysts at different Rh loadings. T = 100 °C, p = 10 bar syngas (H_2 : CO = 1 : 1), $p_{1\text{-butene}}$ = 1.9 bar, τ = 16 s, L/Rh = 10.

Entry	c_{Rh} / wt%	r_{eff} / 10^{-3} bar s^{-1}	Conversion / %	TOF / h^{-1}	n-pentanal / %
1	0.1	7.7	6.6	271	98.0
2	0.2	15.0	13.2	263	98.0
3	0.3	20.6	10.1	252	97.9

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%. In this concentration range the TOF of each SILP system remained almost constant, indicating that each rhodium centre showed the same activity and no cluster formation occurred. 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 average reaction order was determined to be 0.9 with respect to c_{Rh}.

Activation energy

From the independent propene pressure and residence time experiments the activation energy was calculated from Arrhenius plots to be 63.3 ± 2.1 kJ mol^{-1}. In 1-butene hydroformylation the standard SILP catalyst was studied in the temperature range between 60 and 130 °C for three rhodium loadings: 0.1, 0.2 and 0.3 wt%. The formal, effective activation energy $E_{A,eff}$ was calculated to be 63.8 kJ mol^{-1} in the case of 0.2 wt% catalyst loading. All values indicate that the SILP system was operating in the kinetic regime and no severe pore diffusion influence occurred under these conditions.

Comparison between propene and 1-butene

Remarkable, a clear enhancement in both activity and selectivity can be noticed when comparing SILP-catalysed hydroformylation of 1-butene and propene. Table 2 presents the experimental data for both substrates at 100 and 120 °C.

Table 2. Comparison between Rh-**1**-SILP catalysed hydroformylation of propene and 1-butene. 10 bar syngas (H_2 : CO = 1 : 1), τ = 17 s, L/Rh = 10. Rh-loading 0.2 wt%, ionic liquid loading 10 vol%.

Entry	Substrate	$p_{substrate}$ bar	Temperature °C	TOF h^{-1}	C_4H_8/ C_3H_6 [a)]	n-aldehyde %
4	C_3H_6	2.1	100	103	2.5	95.6
5	C_4H_8	1.9	100	260		98.0
6	C_3H_6	2.1	120	308	2.1	94.8
7	C_4H_8	1.9	120	647		97.6

a) ratio of activities for 1-butene and propene.

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 2.1 times up, whereas the selectivity also increased from ca. 95 % to ca. 98 % n-aldehyde (entries 4/5 and 6/7). This surprising result raised the question whether capillary condensation inside the pores of the support may account for the increased activity and selectivity. To verify this hypothesis the solubility of propene and 1-butene in the SILP system was measured using a magnetic suspension microbalance. The results for two different support materials are summarised in Table 3.

Table 3. Gas solubility of propene and 1-butene determined by magnetic suspension balance. Comparison of different support material and type of ionic liquid.

Entry	Support	Ionic liquid	$S_{1\text{-butene}}$ 10^{-5} mol g^{-1}	$S_{propene}$ 10^{-5} mol g^{-1}	C_3H_6/C_4H_8 [a)]
8	SiO_2	BO[b)]	19.8	8.4	2.4
9	PG[c)]	BO[b)]	3.8	1.5	2.5
10	SiO_2	EE[d)]	4.3	2.0	2.2
11	SiO_2/PG [e)]	BO	5.2	5.6	
12	SiO_2	BO/EE[f)]	4.6	4.3	

a) ratio of $S_{propene}$ / $S_{1\text{-butene}}$, b) BO=[BMIM][n-$C_8H_{17}OSO_3$], c) PG= porous glass, d) EE= [EMIM][n-$C_2H_5OSO_3$], e) solubility ratio for silica and porous glass, f) solubility ratio for [BMIM][n-$C_8H_{17}OSO_3$] and [EMIM][n-$C_2H_5OSO_3$] Reaction conditions: 10 bar syngas (H_2 : CO = 1 : 1), residence time = 17 s, L/Rh = 10. Rh-loading 0.2 wt%, ionic liquid loading 10 vol%.

When using the standard 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*-$C_8H_{17}OSO_3$] was 2.4 times higher compared to the propene solubility (entry 8). In order to exclude capillary condensation a porous glass with a larger pore diameter of 30 nm was used (entry 9). Approximately the same ratio in solubility was observed. 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 10). This might give a hint that capillary condensation already occurred for propene as substrate. In an additional experiment the ionic liquid was changed from [BMIM][*n*-$C_8H_{17}OSO_3$] to [EMIM][*n*-$C_2H_5OSO_3$] in order to study the influence of the alkyl chain length at the anion. The same solubility ratio was observed as well (entry 10), but compared with [BMIM][*n*-$C_8H_{17}OSO_3$] the solubility for both 1-butene and propene was lower by a factor of 4.3 and 4.6, respectively (entry 12).

Carbonylation

For conducting continuous, fixed-bed gas-phase methanol carbonylation at industrial relevant reaction conditions, we have developed a new silica supported ionic liquid phase (SILP) Monsanto catalyst system. The developed SILP rhodium-iodide complex catalyst system, SiO_2-[BMIM][$Rh(CO)_2I_2$]-[BMIM]I **4**, requires use of less catalyst material and allow a simple process design - without recirculation and pressure change of the catalyst system – compared to conventional and ionic liquid-based carbonylation systems.[11]

The SILP rhodium-iodide complex catalyst system **4** was prepared by one-step impregnation of a silica support using a methanolic solution of the ionic liquid [BMIM]I and the dimer $[Rh(CO)_2I]_2$ **5**. By using the dimer **5** as metal precursor the Monsanto catalyst anion $[Rh(CO)_2I_2]^-$ **6** was formed directly during catalyst preparation without formation of by-products contaminating the ionic liquid catalyst solution.

Spectroscopic studies

FT-IR spectra of the prepared SILP catalyst confirmed the conversion of the dimer complex **5** to the Monsanto cis-**6** complex anion. Figure 5 shows the change of the characteristic strong carbonyl stretching bands originating from the dimer **5** (νCO = 2075, 2043, 2028 cm^{-1}) to bands assignable to the complex anion **6** at νCO = 2076 and 2006 cm^{-1}.

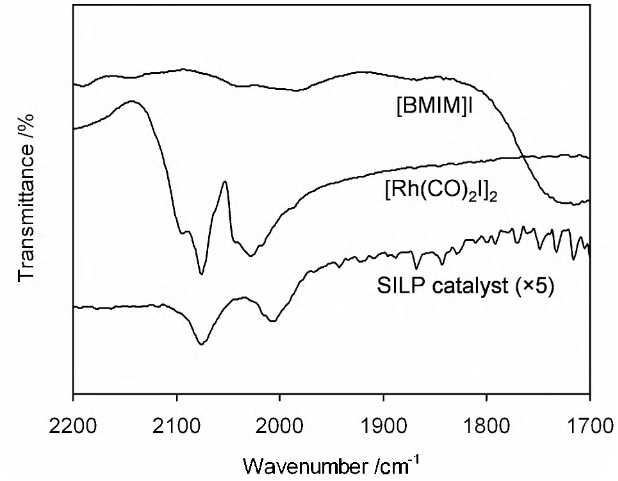


Figure 5. FT-IR spectra (KBr disk) of [BMIM]I, $[Rh(CO)_2I]_2$, and the SILP $[BMIM][Rh(CO)_2I_2]$–[BMIM]I catalyst.

Kinetic studies

With the SILP system **4** complete conversion of methanol was obtained with a TOF for acetyl products of 76.5 h^{-1} and space time yield (i.e. production rate) of 21.0 mol L^{-1} h^{-1}. The selectivity towards the ester relative to the acid (ester/acid ratio of about 3.5) and DME by-product was high as shown in Table 4.

Table 4. Methanol carbonylation using SILP $[BMIM][Rh(CO)_2I_2]$–[BMIM]I catalyst.

Entry	Pressure bar	Conversion % a)	TOF h^{-1} b)		Productivity mol L^{-1} h^{-1} c)		Selectivity %		
13			AcOR	DME	AcOR	DME	AcOH	AcOMe	DME
14	20	99	76.5	3.4	21.0	0.9	21.4	74.4	4.2
15	10	45	69.7	1.5	19.1	0.4	4.7	93.1	2.2
16	10 d)	20	32.1	3.3	8.8	0.9	14.1	76.7	9.2

Reaction conditions: T = 180 °C, reaction time = 1.5 h, F_{CO} = 50 ncm^3 min^{-1}, F_{liq} (MeOH:MeI = 75:25 wt %) = 0.69 g h^{-1}. a) Determined within 1-5 %. b) Catalyst activities are determined as turn-over-frequencies (TOFs) at steady-state conversions and reported in mol product per mol rhodium per hour with TOF_{AcOR} = TOF_{AcOH} + TOFAcOMe. c) Production rates calculated as TOF × n_{Rh} × V_{IL}^{-1}, assuming that the volume of the supported ionic liquid catalyst solution is the same as the initial ionic liquid volume. d) F_{CO} = 100 ncm^3 min^{-1}, F_{liq} = 1.38 g h^{-1}.

The obtained production rate was practically the same as previously obtained using an analogous bubble-column reaction system (water-free) containing about 102 times the volume of ionic liquid catalyst solution. This result emphasised the efficiency of the highly dispersed ionic liquid catalyst layer in the SILP catalyst. In contrast, the low reaction selectivity towards acetic acid (about 21 %) was significantly lower than what was previously found for the large-volume reaction system (up to 96 % acetic acid). This was most likely a result of a relatively longer residence time of the reactant gas in the SILP system. Accordingly, reaction at low space velocity at a pressure of 10 bar (entry 15) resulted in increased formation of acetic acid (and DME, 9 %) relatively to ester (ester/acid ratio of 5.4) than found at twice the gas space velocity (entry 14, ester/acid ratio = 19.8). Moreover, the formation of DME was reduced to about 2 % by applying a combination of low reaction pressure and long contact time of the gas with the supported ionic liquid catalyst phase (i.e. low gas space velocity), thus providing a mixed acetyl reaction product with high purity (about 98 %) which can be further hydrolysed into acetic acid if required.

Conclusion

In this work we have demonstrated the long-term stability of homogeneous rhodium catalysts, which have been immobilised by the use of the new supported ionic liquid phase (SILP) technique. In propene and 1-butene hydroformylation the activity decreased slightly due to formation of high boiling side-products. These heavies could easily be removed from the catalyst by a vacuum procedure after which the initial activity could be regained. The selectivity was not influenced and remained constant around 95 % n-butanal and 98 % n-pentanal. Both propene and 1-butene showed a first order reaction dependency. The influence of 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 for rhodium catalysed hydroformylation. The variation of rhodium loading showed a linear dependency of rate with catalyst loading between 0.1 and 0.3 wt% adding evidence that the catalyst is indeed a homogeneous complex dissolved in an ionic liquid film on a support. The activation energy was determined to be 63.3 kJ mol-1 (63.8 in case of 1-butene).

In methanol carbonylation, the introduced SILP Monsanto catalysts allowed complete conversion of methanol within 90 min. Formation of side products could be suppressed by variation of CO pressure and residence time. FT-IR spectra of the SILP catalyst indicated bonding interaction between protons in the imidazolium cation and the rhodium metal centre in the $[Rh(CO)_2I_2]^-$ anion, thereby lowering the nucleophilicity of the metal. Hence, an even higher catalyst activity may be realised by employing ionic liquids containing cations with lower ability for hydrogen bonding (i.e. with lower Kamlet-Taft α parameter) like, e.g. 1,2,3-trialkyl imidazolium cations. This proposition is currently under investigation.

In perspective, we believe that the knowledge gained in this and previously published work will accelerate significantly the successful development of new SILP catalysts and future SILP catalysis applications (e.g. other C-C-couplings, hydrogenations etc.). The SILP concept is most advantageous for continuous gas-phase reactions, where the combination of well-defined catalyst complexes, low-volatile ionic liquids and solid, porous supports can enhance the process economics with respect to product separation and catalyst recovery. If mechanical and chemical removal of the ionic liquid film can be prevented, the SILP technology can also be applied in multiphase slurry reactions. We therefore anticipate that the SILP catalysis concept will help bridging the gap between homogeneous and heterogeneous catalysis and will lead to improved catalytic processes in the future.

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