

First application of supported ionic liquid phase (SILP) catalysis for continuous methanol carbonylation†

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A solid, silica-supported ionic liquid phase (SILP) rhodium iodide Monsanto-type catalyst system, [BMIM][Rh(CO)₂I₂]-[BMIM]-SiO₂, exhibits excellent activity and selectivity towards acetyl products in fixed-bed, continuous gas-phase methanol carbonylation.

Rhodium catalyzed carbonylation of methanol with carbon monoxide, the dominating industrial process for production of acetic acid (and methyl acetate), exceeded 8.3×10^6 tons in 2000.¹ More than 60% of the total production is based on the homogeneous liquid phase Monsanto process, employing [Rh(CO)₂I₂]⁻ complex anions as the catalyst.² Recently, also an analogous iridium-based process has been developed and commercialized (Cativa process).³

The established Monsanto continuous, batch process involves catalyst recirculation where the reactants and products are removed by flash distillation under reduced pressure and the catalyst solution returned to the reactor with part of the reaction mixture.⁴ This procedure both limits the throughput of product per mole of rhodium of the process, and demands controlled reaction conditions in order to avoid formation of inactive species, such as [Rh(CO)₂I₄]⁻, and irreversible loss of rhodium as insoluble rhodium(III) iodide.^{3a} Conditions in the reactor (particular the rhodium and water concentration) also have to be preserved within a certain margin to prevent catalyst precipitation and to ensure high production rates. This generally places a limit on plant productivity and results in increased recycle and separation costs, higher corrosion rates (due to increased hydrogen iodide formation), and difficulty in product purification.²

Alternatively to the Monsanto process, several heterogeneous catalyst systems^{2,3b,5} useful for continuous flow liquid- and gas-phase processes have been prepared by confinement of rhodium iodide complexes onto supports (*e.g.* carbon, inorganic oxides, zeolites, polymers and ionic exchange resins) by anchoring, ligand tethering or *via* ion-pair interactions. However, the heterogeneous catalysts have generally proven to be less active than the corresponding homogeneous system, suffering from rhodium metal leaching (particular in liquid-phase reactions) or loss of metal carbonyl compounds by vaporization and insufficient

reaction heat removal (especially gas-phase reactions), and/or hampered by decomposition of the support materials during operation at elevated temperatures. Catalysts with [Rh(CO)₂I₂]⁻ anions supported on polymeric vinyl pyridine resins exhibit, however, high stability⁶ and reactivity.⁷ This heterogeneous catalyst system has been commercialized (Chiyoda-UOP Acetica process) for slurry phase methanol carbonylation using a bubble column-type reactor design.²

Ionic liquids have attracted much interest as media for catalysts immobilization⁸ mainly due to their lack of vapor pressure, making the catalytic system easy separable and recyclable. Moreover, the versatile chemical and physical properties of ionic liquids⁹ have also advanced their use. In this context, acetic acid production by a Monsanto-type process employing ionic liquids containing [Rh(CO)₂I₂]⁻ have recently been claimed for both liquid-phase¹⁰ and gas-phase¹¹ carbonylation processes. In the liquid-phase process the reaction is performed in a conventional continuous, stirred batch reactor with successive (and troublesome) product flash-separation and catalyst recycling, while the gas-phase process uses a more simplified bubble-column reaction system with the non-volatile catalyst solution remaining in the reactor during the process. In both reactions the ionic liquid provides a medium with high catalyst solubility which effectively removes generated reaction heat. However, despite the advantages of using non-volatile ionic liquid catalysts such systems require rather large amounts of relatively expensive ionic liquids and precious catalysts, which may impede their industrial implementation. Furthermore, bulk ionic liquid systems may suffer from slow diffusion due to the relatively high viscosity of the ionic liquids, causing the main part of the reaction to proceed in the inter-phase or in the diffusion layer of the catalyst layer, rather than in the bulk solvent as would be strongly preferred. Thereby, the productivity of the process is limited since a large part of the rhodium complexes are not participating in the reaction.

Supported Ionic Liquid Phase (SILP) catalyst systems are solid catalysts containing an ionic liquid film, the size of a diffusion layer, of a homogeneous catalyst solution confined on the surface of a porous, high-area support material. SILP catalysts have recently been introduced¹² for several liquid- and gas-phase reaction systems, *e.g.* hydroformylation, hydrogenation, Heck aryl coupling, and hydroamination, and demonstrated¹³ to be a truly, heterogeneous analogue of the homogeneous Rh catalyst systems in gas-phase, fixed-bed propene hydroformylation. Fixed-bed SILP process designs demand smaller amounts of expensive metal catalyst and ionic liquid than existing batch technology. The applicability for gas-phase processes further distinguishes the SILP catalysis

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technology from processes applying heterogeneous catalysts (*e.g.* the Acetica process), which are restricted to liquid reactions.

In this work, we have developed a new silica supported ionic liquid phase (SILP) Monsanto catalyst system¹⁴ useful for conducting continuous, fixed-bed gas-phase methanol carbonylation at industrially relevant reaction conditions. The developed SILP rhodium iodide complex catalyst system, [BMIM][Rh(CO)₂I₂]-[BMIM]I-SiO₂, 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.

The SILP rhodium iodide complex catalyst system, [BMIM][Rh(CO)₂I₂]-[BMIM]I-SiO₂, 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)₂I₂] (Scheme 1). By using the dimer as metal precursor the Monsanto catalyst anion [Rh(CO)₂I₂]⁻ was formed directly during catalyst preparation (as previously shown¹⁵ by ESI-MS analysis of diluted methanol solution), without formation of byproducts contaminating the ionic liquid catalyst solution.

FT-IR spectra of the prepared SILP catalyst (Fig. 1) confirmed the conversion of the dimer [Rh(CO)₂I₂] complex to the Monsanto *cis*-[Rh(CO)₂I₂]⁻ complex anion, by the change of the characteristic strong carbonyl stretching bands originating from the dimer ($\nu_{\text{CO}} = 2075, 2043, 2028 \text{ cm}^{-1}$)¹⁶ to bands assignable to the complex anion at $\nu_{\text{CO}} = 2076$ and 2006 cm^{-1} .

The CO bands in the [BMIM][Rh(CO)₂I₂] SILP catalyst system were, however, found to be shifted towards higher frequencies than previously found¹⁵ in CH₂Cl₂ solution ($\nu_{\text{CO}} = 2062$ and 1990 cm^{-1}), as a result of decreased back-bonding from the rhodium metal to the CO ligands. The lower frequencies are also usually found for the [Rh(CO)₂I₂]⁻ anion in organic solutions containing ion pairs of [R₄Y][Rh(CO)₂I₂] (where R = butyl, Y = N or R = phenyl, Y = P, As),¹⁷ or for anions confined on polymeric pyridinium^{6,7} and pyrrolidinium^{5c} ion-exchange resins ($\nu_{\text{CO}} \approx 2060$ and 1990 cm^{-1} slightly dependent on the solvent or resin, respectively). The relatively lower degree of metal to CO back bonding is obtained as a result of a decreased electron density around the metal center (*i.e.* lower nucleophilicity), presumably caused by bonding interaction between the metal center and acidic protons ($\text{p}K_{\text{a}} = 21\text{--}23$)¹⁸ in the [BMIM]⁺ ionic liquid cation of the catalyst (particularly the proton in the C₂-position). Analogous proton–rhodium metal interactions in apolar solvents between the Monsanto anion and more acidic alkylammonium- or 4-alkylpyridinium cations (typically $\text{p}K_{\text{a}} = 10\text{--}11$), have previously been reported^{5b,17} to induce identical CO band shifts.

The SILP catalyst system was applied for water-free gas-phase carbonylation of methanol§ at reaction conditions resembling typical industrial conditions at two different gas space velocities. In Fig. 2 the catalyst activity (as TOFs) for formation of the desired acetyl products acetic acid (AcOH) and methyl acetate (AcOMe)

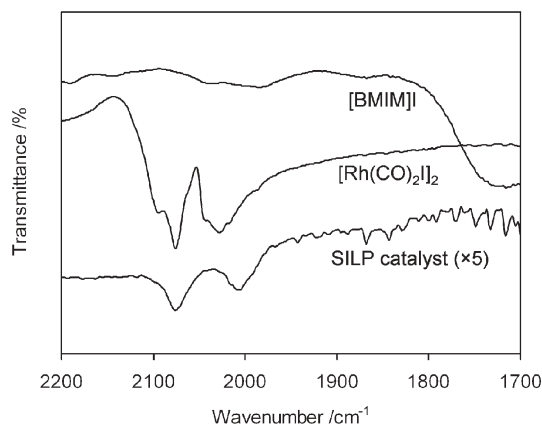


Fig. 1 FT-IR spectra (KBr disk) of [BMIM]I, [Rh(CO)₂I₂], and the SILP [BMIM][Rh(CO)₂I₂]-[BMIM]I-SiO₂ catalyst.

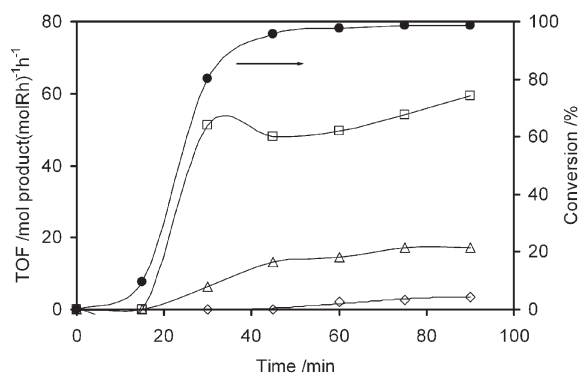
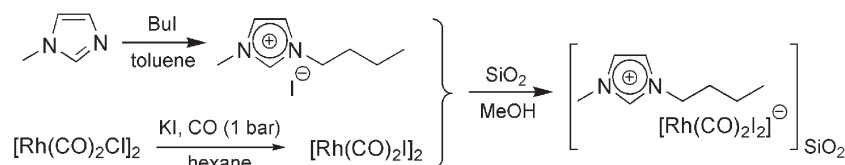


Fig. 2 Turn-over frequencies (TOFs) for product formation (AcOH: Δ , AcOMe: \square , DME: \diamond) and methanol conversion (\bullet) of SILP [BMIM][Rh(CO)₂I₂]-[BMIM]I-SiO₂ catalyst in continuous, gas-phase methanol carbonylation *versus* reaction time ($T_{\text{r}} = 180 \text{ }^{\circ}\text{C}$, $P_{\text{r}} = 20 \text{ bar}$, $F_{\text{CO}} = 50 \text{ nm}^3 \text{ min}^{-1}$, F_{liq} (MeOH : MeI = 75 : 25 wt%) = 0.69 g h^{-1}).

and the byproduct dimethyl ether (DME), are shown for the first 1.5 h of reaction with the low gas velocity at 20 bar pressure. Here, essentially 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 $21.0 \text{ mol L}^{-1} \text{ h}^{-1}$, with a high selectivity towards the ester relative to the acid (ester/acid ratio of about 3.5) and DME byproduct (Table 1, entry 1).

The obtained production rate (Table 1) is practically the same as previously obtained¹¹ using an analogous bubble-column reaction system (water-free) containing about 10^2 times the volume of ionic liquid catalyst solution, clearly signifying 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%) is significantly lower than what previously was found for the large-volume reaction system (up



Scheme 1 Preparation of SILP [BMIM][Rh(CO)₂I₂]-[BMIM]I-SiO₂ catalyst.

Table 1 Methanol carbonylation^a with SILP [BMIM][Rh(CO)₂I₂]-[BMIM]I-SiO₂ catalyst

Entry	P_r /bar	Conv. ^b (%)	TOF ^c /mol mol ⁻¹ h ⁻¹		Production rate ^d /mol L ⁻¹ h ⁻¹		Product selectivity (%)		
			AcOR	DME	AcOR	DME	AcOH	AcOMe	DME
1	20	99	76.5	3.4	21.0	0.9	21.4	74.4	4.2
2	10	45	69.7	1.5	19.1	0.4	4.7	93.1	2.2
3 ^e	10	20	32.1	3.3	8.8	0.9	14.1	76.7	9.2

^a Reaction conditions: $T_r = 180$ °C, reaction time = 1.5 h, $F_{CO} = 50$ nm³ min⁻¹, F_{liq} (MeOH : MeI = 75 : 25 wt%) = 0.69 g h⁻¹.
^b Determined within 1–5%. ^c Catalyst activities are determined as turn-over frequencies (TOFs) at steady-state conversions and reported in mol product per mol rhodium per hour with $TOF_{AcOR} = TOF_{AcOH} + TOF_{AcOMe}$. ^d Production rates calculated as $TOF \times n_{Rh} \times V_{IL}^{-1}$, assuming that the volume of the supported ionic liquid catalyst solution is the same as the initial ionic liquid volume. ^e $F_{CO} = 100$ nm³ min⁻¹, $F_{liq} = 1.38$ g h⁻¹.

to 96% acetic acid), most likely as 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 (Table 1, entry 3) 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 2, ester/acid ratio = 19.8). Moreover, the formation of DME proved to be 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 hydrolyzed into acetic acid if required.

In conclusion, the introduced SILP Monsanto catalysts are different from present catalytic alcohol carbonylation technologies by using an ionic liquid as reaction medium, and by offering a highly efficient use of the ionic liquid catalyst phase containing the precious metal catalyst, having it dispersed on a robust, inert, porous high-area support material as a liquid film the size of a diffusion layer. Moreover, the fixed-bed SILP process design requires a smaller reactor size than existing technology in order to obtain the same productivity, which makes the SILP carbonylation concept potentially interesting for technical applications. The shift in CO stretching frequencies in the FT-IR spectra of the SILP catalyst indicated bonding interaction between protons in the imidazolium cation and the rhodium metal center in the [Rh(CO)₂I₂]⁻ anion, thereby lowering the nucleophilicity of the metal. Hence, assuming the rate determining step in the carbonylation reaction to be the oxidative addition of methyl iodide to the metal center, as normally found,⁴ an even higher catalyst activity may be realized by employing ionic liquids containing cations with lower ability for hydrogen bonding (*i.e.* with lower Kamlet-Taft α parameter)¹⁹ like, *e.g.* 1,2,3-trialkylimidazolium cations. This proposition will be examined in future work.

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Notes and references

‡ *Catalyst preparation.* The Monsanto-type SILP catalyst was initially prepared as earlier described,¹⁵ whereas the [BMIM][Rh(CO)₂I₂] ionic liquid was synthesized by stirring a dry, degassed methanolic solution (8 ml) containing 16.5 mg [Rh(CO)₂I₂]¹⁷ (0.029 mmol) metal precursor and 302.5 mg ionic liquid [BMIM]I (1.137 mmol) (*i.e.* with excess of ionic liquid) under argon atmosphere for 24 h. Subsequently, 0.600 g thermally pretreated (500 °C, 15 h, in air) silica support (silica gel 100, Merck; BET surface area: 304 m² g⁻¹; pore volume: 1.01 cm³ g⁻¹; mean pore diameter

(monomodal): 13.2 nm) was added, whereafter the suspension was left with slow stirring for an additional 4 h before the volatile solvent was removed under reduced pressure at room temperature. The residue consisting of fine red-brown SILP catalyst particles was finally dried *in vacuo* overnight (0.1 mbar, 60 °C) and further kept under CO atmosphere at ambient pressure prior to use.

§ *Gas-phase methanol carbonylation.* In catalyst tests 1.00 g of SILP catalyst (containing 0.0437 mmol Rh) was placed as fixed catalyst bed in the tubular reactor, pressurized with CO gas at a constant flow (F_{CO}) to a constant reaction pressure (P_r) while heated to a constant reaction temperature (T_r) of 180 °C (the rest of the test system was heated to *ca.* 160 °C). Then, at the preset reaction pressure and temperatures the reactor was bypassed, and the vaporized liquid methanol-methyl iodide feed (75 : 25 wt%) introduced into the bypassed reactant gas at a constant flow (F_{liq}) resulting in a CO/methanol ratio of approximately 8. When the reactant gas mixture composition became constant (determined by FID-GC analysis) the reaction was initiated by passing the reactant gas stream through the SILP catalyst bed.

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