

Homogeneous ruthenium-based water–gas shift catalysts *via* supported ionic liquid phase (SILP) technology at low temperature and ambient pressure†

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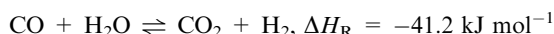
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Novel ruthenium-based supported ionic liquid phase (SILP) catalysts for the water–gas shift (WGS) reaction are reported which, compared to classical low temperature shift systems, operate at much lower temperatures and even at ambient pressure.

The water gas shift (WGS) reaction is a key reaction step in industrial hydrogen and ammonia production.¹



Currently, most industrial low-temperature-shift (LTS) catalysts are based on mixtures of solid metal oxides such as Cu, Zn and Al. LTS catalysts usually operate at temperatures above 200 °C to reach acceptable reaction rates and reasonable space-time-yields.² However, the elevated temperatures applied in today's WGS processes limit the equilibrium conversion of the exothermic WGS reaction to about 96%.³ Consequently, a relevant amount of unconverted CO remains in the product gas for thermodynamic reasons and requires additional process steps (e.g. a methanization unit in the case of ammonia synthesis) if CO-free hydrogen is required.

It has been known for a long time that homogeneous WGS catalysts can operate at much lower temperatures, thus favoring higher equilibrium conversions.³ However, all systems reported so far were applied under high CO pressures (>10 bar) and even under these conditions their catalytic activities were usually low.⁴ Furthermore, the processibility of these systems is difficult. In a technical scenario, the use of volatile solvents would require additional process steps to obtain pure hydrogen without solvent contamination. Besides that, the high pressures required for these systems restrict their use in decentralized or mobile hydrogen productions.⁵

Our group and others have recently introduced the so-called “supported ionic liquid phase” (SILP) technology.⁶ In SILP catalysts, a thin film of ionic liquid containing the dissolved homogeneous catalyst complex is dispersed on the large

internal surface of a porous support. The resulting solid combines the advantage of a heterogeneous catalyst—namely the applicability in continuous gas phase reactions using fixed bed reactors—combined with the molecular defined nature of the dissolved homogeneous catalyst. In this way the SILP catalyst technology bridges the gap between traditional homogeneous and heterogeneous catalysis. In this paper we report for the first time a new type of WGS catalyst based on this SILP concept.

The synthetic procedure applied to prepare the Ru-SILP catalyst followed a modified protocol earlier described for the preparation of SILP hydroformylation catalysts.^{7†} An aqueous solution of RuCl₃ hydrate and the ionic liquid 1-butyl-2,3-dimethylimidazolium trifluoromethane-sulfonate [BMMIM][OTf] was dispersed on the porous support material Silica Gel 100 (Merck KGaA). By removing the water *in vacuo* a dry SILP-WGS was obtained. The calculated ionic liquid film thickness on the support is 0.3 nm. In preliminary solubility studies it was found that RuCl₃ readily dissolves in even small amounts of the pure ionic liquid [BMMIM][OTf].

In a typical catalytic experiment, 4 g of the as-prepared Ru-SILP catalyst was placed in a tubular fixed bed reactor (see ESI†) and contacted with a continuous gas flow consisting of 70% N₂ (Linde AG, 99.999%), 20% H₂O (double-distilled) and 10% CO (Linde AG, 99.97%) maintaining a constant residence time of 5.5 s. The product gas mixture was analyzed by an on-line μ-GC (Varian 4900, MS5a/PPQ) that allowed sampling of the reaction gases every ten minutes.†

First catalytic experiments in the continuous, fixed-bed WGS reactor were conducted at 160 °C and atmospheric pressure. Under these conditions the system reached a turn over frequency (TOF) of 3 mol(H₂) mol(Ru)^{−1} h^{−1}, a value quite common for homogeneous systems.⁴ Remarkably, in the present SILP case it has been achieved for the first time at ambient pressure. The observed induction period is probably due to the limited CO solubility in the ionic liquid.⁸ This poor solubility is probably responsible for a slower formation of the active Ru-carbonyl catalyst from the RuCl₃ precursor over the first hours time-on-stream. The exact nature of the active species itself is still under debate.^{4a,10b} Our current research focuses on detailed *in situ* spectroscopic analysis of these active compounds.

At 160 °C the catalyst shows significant deactivation after the full activity was reached as depicted in Fig. 1. This

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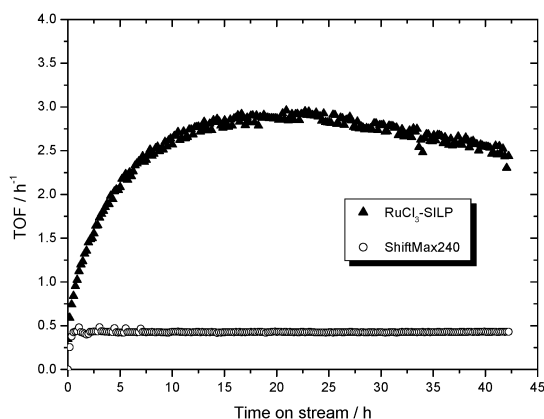


Fig. 1 Activity vs. time-on-stream plot of a RuCl_3 -SILP system (▲) in comparison to a commercial ShiftMax[®] 240 (○). $T = 160\text{ }^\circ\text{C}$, $p_{\text{total}} = 1\text{ bar}$, $p_{\text{CO}} = 0.1\text{ bar}$, $p_{\text{water}} = 0.2\text{ bar}$, balance: N_2 , $\tau = 5.5\text{ s}$, ruthenium loading $w_{\text{Ru}} = 2\text{ wt\%}$, ionic liquid loading $\alpha_{\text{IL}} = 0.1$, IL = [BMMIM][OTf]. Activity expressed as turn over frequency $\text{TOF} = \text{mol}(\text{H}_2) \text{ mol}(\text{metal})^{-1} \text{ h}^{-1}$.

deactivation can be attributed to volatile Ru-carbonyls that form at this temperature in the SILP system and get stripped from the catalyst support.⁹ This volatility of the Ru-carbonyls is even more pronounced when no ionic liquid is used. The catalyst without an ionic liquid film also shows significantly lower activity of $\text{TOF} = 0.1 \text{ mol}(\text{H}_2) \text{ mol}(\text{Ru})^{-1} \text{ h}^{-1}$ compared to $\text{TOF} = 0.3 \text{ mol}(\text{H}_2) \text{ mol}(\text{Ru})^{-1} \text{ h}^{-1}$ with a IL loading of $\alpha = 0.1$ at $120\text{ }^\circ\text{C}$.

Interestingly, the activity of this system exceeded the catalytic activity of the commercial WGS catalyst ShiftMax[®] 240 (supplied by Süd-Chemie AG) under the same mild conditions. This copper-based catalyst showed an activity of only $0.5 \text{ mol}(\text{H}_2) \text{ mol}(\text{Cu})^{-1} \text{ h}^{-1}$ after being reduced at $220\text{ }^\circ\text{C}$ in a continuous stream of 2% H_2 in nitrogen for 20 h (industrial standard procedure for activation). It has to be noted that the commercial catalyst has been optimized for rather different reaction conditions. Nevertheless this direct comparison highlights the great potential of the SILP technology for low-temperature WGS catalysis.

The activation energy of the system was calculated from a temperature variation in the range of $120\text{ }^\circ\text{C}$ to $160\text{ }^\circ\text{C}$ as depicted in Fig. 2. For the data analysis, steady-state operation points were taken that were reached about 2 h after each parameter variation.

The whole temperature variation experiment was started with a catalyst system being already 65 h time-on-stream at $120\text{ }^\circ\text{C}$. In this way it was possible to exclude any falsification of the obtained kinetic data by the initial catalyst activation effects. During the experimental run shown in Fig. 2, it was possible to adjust a whole set of steady-state-conditions from which the apparent activation energy E_A was determined to be 84 kJ mol^{-1} . This value indicates clearly that the SILP catalyst was operating in the kinetic regime without mass transport limitations. The fact that the catalytic activity was almost identical after 65 h time-on-stream and after 82 h time-on-stream under the same reaction conditions indicates that the kinetic data obtained in the experiment were not influenced by any catalyst deactivation process.

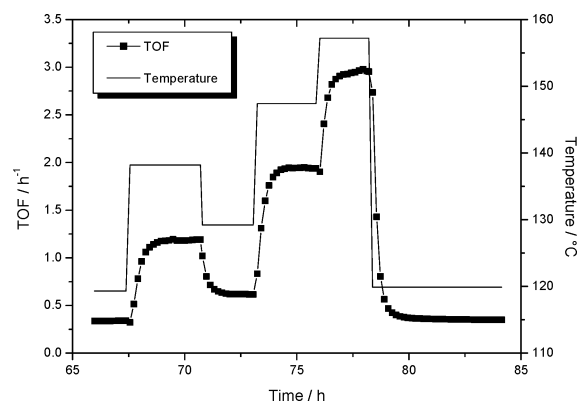


Fig. 2 Temperature variation in the water gas shift reaction using a RuCl_3 -SILP catalyst system. $T = 120$ to $160\text{ }^\circ\text{C}$, $p_{\text{total}} = 1\text{ bar}$, $p_{\text{CO}} = 0.1\text{ bar}$, $p_{\text{water}} = 0.2\text{ bar}$, $\tau = 5.5\text{ s}$, ruthenium loading $w_{\text{Ru}} = 2\text{ wt\%}$, ionic liquid loading $\alpha_{\text{IL}} = 0.1$, IL = [BMMIM][OTf]. Activity expressed as turn over frequency $\text{TOF} = \text{mol}(\text{H}_2) \text{ mol}(\text{Ru})^{-1} \text{ h}^{-1}$.

In additional experiments it was found that deactivation due to stripping of volatile ruthenium compounds as seen from Fig. 1 is only observed at temperatures above $150\text{ }^\circ\text{C}$. At $140\text{ }^\circ\text{C}$, RuCl_3 -SILP systems showed stable operations for at least 150 h time on stream. An end-of-run ICP analysis of the used SILP catalyst showed some ruthenium leaching that has not been quantified yet. Additional NMR studies showed no traces of ionic liquid being removed from the support.

The water content of the reaction mixture had a pronounced effect on the activity, with higher water content leading to higher activity. From the differential analysis of $\ln(r_{\text{eff}})$ versus $\ln(p_i)$ an apparent reaction order with respect to water of 1.05 was calculated. This behavior could be explained by a mechanism of homogeneous WGS catalysts in which the addition of water is the crucial step in the initiation of the proposed catalytic cycle.¹⁰ In contrast, the partial pressure of CO had virtually no effect on the catalyst activity: an apparent order of 0.01 was calculated.

In none of the experiments formation of side products like methane or dimethylether could be detected *via* μGC analysis. This high selectivity under very mild reaction conditions is remarkable.

It is also noteworthy that all kinetic data reported here were obtained from a single catalytic experiment and thus from exactly the same catalytic material under steady state conditions. All data were confirmed in additional runs yielding excellent reproducibility.

In conclusion, these results exemplify in a particularly promising manner the advantages of supported ionic liquid phase catalysis. The combination of homogeneous dissolved RuCl_3 , extremely low-volatile ionic liquid [BMMIM][OTf] and porous silica support leads to a catalytic material that promotes the WGS reaction under ambient pressure and at low temperatures. Clearly, the activity as well as the lifetime of such catalysts has to be further improved.[‡] Nevertheless, further catalyst improvement can open the door to mobile fuel cell applications and decentralized hydrogen production processes with enhanced efficiency.

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- † Under technical syngas conditions (13% CO₂, 8% CO, 4% N₂, balance H₂) the SILP catalysts remains almost inactive.
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