

Supported Ionic Liquid-Phase (SILP) Catalysts in Continuous Flow Processes

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In recent years, development of new and approved strategies to immobilize homogeneous catalysts using room-temperature ionic liquids have received significant interest.¹ In this context, a concept using heterogenized, homogeneous ionic liquid catalyst systems, i.e. supported ionic liquid-phase (SILP) catalysts, have been examined for Rh-phosphine catalyzed hydroformylation,² and hydrogenation³ as reaction examples. Generally, SILP catalysts are comprised of a small amount of ionic liquid containing dissolved transition metal complexes, which are heterogenized on a high-area solid support by either physisorption or by anchoring of ionic liquid fragments. Hence, although the catalyst is a solid it performs as a homogeneous catalyst, i.e. reaction takes place in the highly dispersed ionic liquid.

The applications of ionic liquid solvents in SILP catalyst systems benefit from unique advantages which are not provided by analogous supported catalyst systems containing traditional solvents, e.g. non-volatility, large thermal-/liquid-phase window and adjustable properties. Consequently, processes applying SILP catalysts can be conducted at unusual conditions using fixed-bed reactor designs in continuous operation mode, thus offering simple and complete product separation. In addition, use and handling of large amounts of often toxic, volatile organic solvents (VOCs) are avoided.

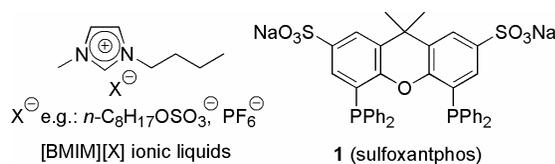


Figure 1: 1-butyl-3-methylimidazolium ionic liquids and bisphosphine ligand **1** (sulfoxantphos).

In continuous-flow gas-phase propene hydroformylation using SiO₂-based SILP Rh-**1** catalysts with various L/Rh ratios and different amounts of [BMIM] ionic liquids (e.g. [BMIM][PF₆] or [BMIM][n-C₈H₁₇OSO₃], ionic liquid loading □ as the ratio of ionic liquid volume/support pore volume, Figure 1), the catalytic performance during 4-5 h reactions (Figure 2) was found to be strongly influenced by the ligand and ionic liquid content, but less influenced by the choice of ionic liquid. Importantly, high reaction selectivity resulting in *n*/*iso* ratios ≥ 20 was only obtained using catalyst systems containing ionic liquid as well as high L/Rh ratios. In addition, the catalyst *in-situ* pre-reaction giving the catalytically active Rh-**1** components, appeared to be slower in [BMIM][n-C₈H₁₇OSO₃] than for the [BMIM][PF₆], suggesting differences in the solubility of Rh-precursor and/or **1** in the fluids. In accordance with this, no difference in pre-reaction was observed in the reactions using catalysts without supported ionic liquid.

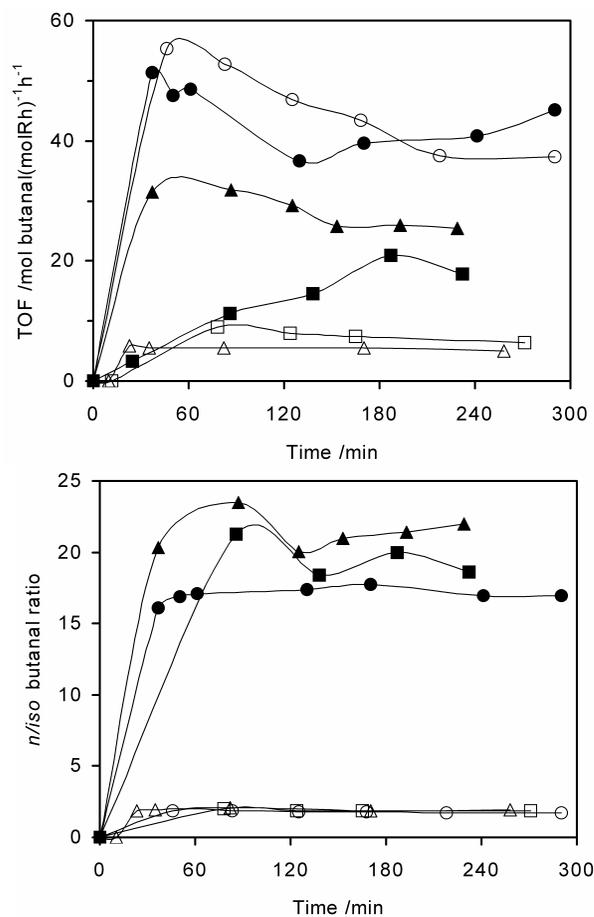


Figure 2: Propene hydroformylation activity (top) and selectivity (bottom) of SiO₂ SILP Rh-**1** catalyst with L/Rh ratios of 2.5 (open symbols) and 10 (closed symbols) containing no ionic liquid (circles, □ = 0), [BMIM][PF₆] (triangles, □ = 0.5) or [BMIM][n-C₈H₁₇OSO₃] (squares, □ = 0.5).

Noticeable, the described SiO₂-based SILP catalysts were deactivated in prolonged use resulting in low activities and selectivities. The deactivation could, however, be suppressed using alternative supports, e.g. TiO₂-based catalysts, which remained stable over a 60-hours period but proved less active and selective than the analogous SiO₂-based catalysts. Combined, the results indicate that a high ligand content together with the presence of ionic liquid solvents are prerequisites for obtaining selective Rh-phosphine SILP catalysts systems, while SILP catalyst stabilities are support dependent.

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