PO-1.1 Ultra-low temperature methanol reforming using immobilized Ru-Pincer complexes (A)

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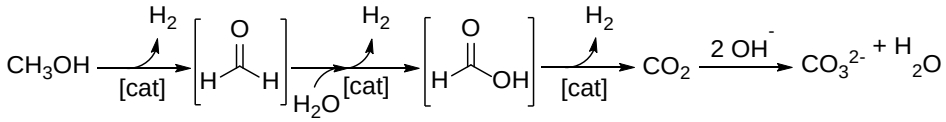
Recently, a range of noble-metal and base-metal complexes have been successfully employed for the homogeneously catalyzed dehydrogenation of methanol Hereby, one of the most active systems working at extremely low temperatures below 100 °C is catalyzed by an aliphatic Ru-pincer complex under highly basic conditions [1]. As depicted in Scheme 1, the complete aqueous phase reforming (APR) process leads to the consecutive formation of formaldehyde, formic acid and carbon dioxide and the concomitant release of one hydrogen molecule during each step. Under basic reaction conditions, the CO2 is initially captured as carbonate. The dehydrogenation of formate to CO2 was determined to be the rate-determining step since it accumulated during the reaction.[2]



Scheme 1: Overview of possible reaction intermediates in methanol dehydrogenation.

One attractive feature of these low temperature MeOH reforming catalysts is the drastically reduced formation of CO, a potential fuel cell poison. However, in order to design potential processes based on such attractive catalysts, continuous operation must be ensured. Here, the purely liquid-phase reaction would be problematic, e.g. as high base concentrations would lead to corrosion of reactor materials.
Supported Ionic Liquid Phase (SILP) materials consist of an ionic liquid, dispersed as a thin film on the inner surface of a highly porous solid material.[3] By dissolving homogeneous transition metal complexes in the ionic liquid film, the SILP concept allows tailor making of solid materials with definite properties and a controlled chemical reactivity. Since the ionic liquid is dispersed on the inner surface of the support, a dry solid material is obtained. These materials can be handled like classical heterogeneous catalysts and are highly attractive for large-scale continuous applications.

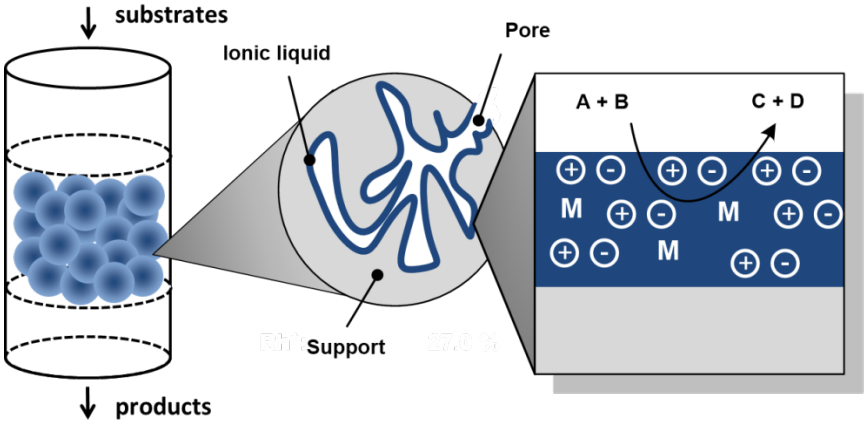


Figure 1: Schematic illustration of SILP technology for continuous gas-phase processes.

In this work, we present the first results from our immobilization studies using commercially available Ru-Pincer catalysts in standard SILP gas-phase scenarios. The SILP catalysts have been optimized by variation of the type of ionic liquid used for coating the support surface.
It is anticipated that such a technology would allow decentralized hydrogen storage and release for a variety of future applications.

[1] Nielsen, M., et al., Low-temperature aqueous-phase methanol dehydrogenation to hydrogen and carbon dioxide. Nature, 2013. 495(7439), 85.
[2] V. Strobel et al. Shining light onto the low-temperature methanol aqueous-phase reforming using homogeneous Ru-pincer complexes – operando Raman-GC studies. React. Chem. Eng. 2017, 2, 390.
[3] Supported Ionic Liquids – Fundamentals and Applications (Eds.: R. Fehrmann, A. Riisager, M. Haumann), Wiley-VCH, Weinheim, 2014.