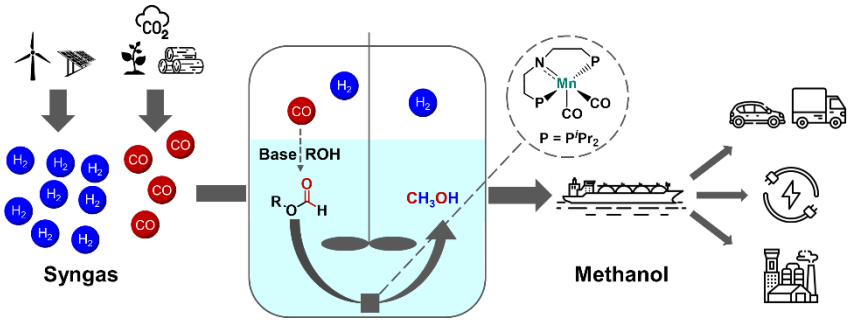
Liquid-phase Co-Reagent Free Hydrogenation of Carbon Monoxide to Methanol Using Molecular Manganese Catalysts

S. Stahl[1,2], A. J. Vorholt[1], W. Leitner[1,2]
[1]Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany.
[2]Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany

Abstract

Methanol is a central component in the chemical value chain and an important compound for energy storage either as a combustion fuel or as a hydrogen/syngas carrier.[1,2] Global methanol production is mainly based on coal and natural gas as primary feedstocks. Syngas from renewable carbon sources as the raw material can make methanol a central pivot point of a sustainable chemical value. The syngas conversion to methanol over heterogeneous catalysts is well established.[3] While these processes benefit strongly from the economies of scale they are not ideal for a decentralized small scale methanol production. Homogeneous molecular complexes in contrary, offer the possibility of small scale production. Unfortunately, the direct CO hydrogenation by homogenous catalysts has proven inefficient until the groups of Prakash and Beller employed the use of amines as co-reagents.[4-5] These systems, however suffer from incomplete conversion of the formamide intermediates and trace amounts of *N*-methylated products leading to undesired side products.



Recently, a system to produce methanol from CO alcohol-assisted catalysed by a manganese pincer complex in an effective and clean way was developed at our institute.[6] This process yields only methanol and formate ester as detected products in the liquid phase with an high activity (TON>4000) under relatively mild conditions (150°C, 60 bar). However, this system still comprises of ethanol as a co-reagent and lacks the possibility for easy product separation.

In this work, we present a co-reagent free system using the product methanol itself as the activating agent. By optimizing of various process parameters, the catalytic activity was improved while the complexity of the system was reduced. Additionally, it enables facile product separation opening the possibility for continuous operations.

References

[1] Olah, G. A., Goeppert, A., Prakash, G. K. S. *Beyond Oil and Gas: The Methanol Economy*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2009**.
[2] Bertau, M., Offermanns, H., Plass, L., Schmidt, F., Wernicke, H.- J. Methanol: *The Basic Chemical and Energy Feedstock of the Future,* Springer-Verlag: Berlin, Heidelberg, **2014**.
[3] Waugh, K. C., *Catal. Lett.* **2012**, *142*, 1153−1166.
[4] Kar, S.; Goeppert, A.; Prakash, G. K. S., *J. Am. Chem. Soc.* **2019**, *141*, 12518−12521..
[5] Ryabchuk, P., Stier, K., Junge, K., Checinski, M. P., Beller, M., *J. Am. Chem. Soc*. **2019**, *141*, 16923−16929.
[6] Kaithal, A., Werlé, C., Leitner, W., *JACS Au*. **2021**, *1*, 130-136.