An In-Depth Investigation: Surprising Effect of the Second Liquid Phase in Homogeneously Ru-Catalyzed CO_2 Hydrogenation to Formic Acid

K. R. Ehmann[1,2], K. Dinsing[1,3], C. Ribeiro Maier[1,3], A. J. Vorholt[1], W. Leitner[1,2]
[1]Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany
[2]RWTH Aachen University, Aachen, Germany
[3]TU Dortmund University, Germany

Abstract

Carbon dioxide is an attractive C_1 building block for future chemistry, as it reduces the carbon footprint not only by using the greenhouse gas itself as a raw material, but also primarily by substituting fossil raw materials. Accordingly, the area has an increased focus in (academic) research. In the field of homogeneously catalyzed conversion of CO_2, academic research often focuses on showing a proof of concept with the selected substrates or catalysts initially. Aspects such as catalyst recycling or product separation often only play a subordinate role at first and are mostly considered in the further process development. A frequently used strategy for catalyst recycling in homogeneous catalysis is the use of liquid-liquid biphasic systems. However, many monophasic gas-liquid reaction systems are barely understood before going into multiphase systems. For this reason, we investigated the behavior of the homogeneously catalyzed hydrogenation of CO_2 to formic acid in-depth. This understanding will aid the transition to a multiphase reaction system for catalyst recycling approaches.

The model reaction system includes the organic solvent 4-methyl-2-pentanol, the additive triethylamine (needed to stabilize the formed formic acid), a Ru dppm complex (dppm: bis(diphenyl-phosphino)¬methane) as a precursor for the homogeneous catalyst, and the gaseous substrates CO_2 and H_2. The addition of water as second, immiscible solvent transfers the monophasic to a biphasic system.

The study was carried out in a miniplant with a 300 mL stirred tank reactor in batch mode. The miniplant is equipped with mass flow meters for the substrates CO_2 and H_2 and an ATR-IR probe for online detection of the product formic acid and the substrate CO_2.

The recorded concentration-time profiles of the monophasic reaction show an expected influence of the parameter total pressure as well as an unexpected inhibition of the catalyst depending on the composition of the liquid phase. The inhibitory effect can be overcome by using the second, immiscible solvent water, making the biphasic reaction system more productive than the monophasic one.

This shows, that the understanding of the monophasic reaction system is essential for identifying improvements in multiphase systems.