

Semi-continuous Biphasic System for the Synthesis of Formates via Catalytic CO₂-Hydrogenation: Integrated Reaction and Catalyst Separation for CO₂-Scrubbing Solutions

C. Westhues*, M. Scott*, G. Franciò*, W. Leitner*/**

*Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Aachen, Germany, **Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr, Germany

Abstract

Since the last decades the utilization of carbon dioxide as chemical feedstock has been an important research field.^[1] Especially, the homogeneously catalyzed hydrogenation of CO₂ into formic acid and its derivatives has been widely studied and many proficient molecular catalysts are now available.^[2] However, product separation and catalyst recycling remain challenging and just a few examples have been reported.^[3] In our recent research efforts, we developed an effective biphasic system for the hydrogenation of aqueous scrubbing solutions of CO₂ to formate-amine-adducts (Figure 1, left).^[4,5]

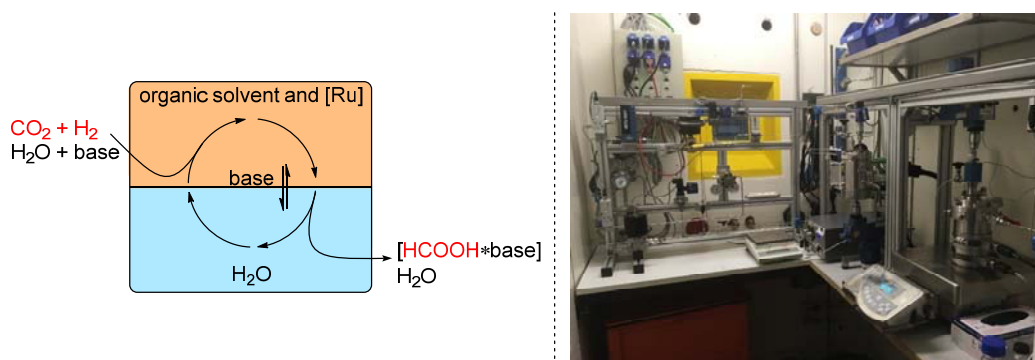


Figure 1: Illustration of the biphasic system (left) and the semi-continuous setup (right).

Amine containing aqueous solutions saturated with CO₂ have been hydrogenated in the presence of a Ru-catalyst dissolved in a hydrophobic organic solvent. The most productive system has been achieved with the common scrubbing agent methyl diethanolamine (MDEA) as the base and methyl-isobutylcarbinol (MIBC) as the catalyst phase. Excellent productivities as well as effective catalyst retention and recycling were obtained using a largely automated reactor set-up (Figure 1, right).^[6]

References:

- [1] J. Artz, T. E. Muller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* **2018**, *118*, 434.
- [2] a) W. Leitner, *Angew. Chem. Int. Ed.* **1995**, *34*, 2207; b) Y. Himeda, *Eur. J. Inorg. Chem.* **2007**, *2007*, 3927.
- [3] a) J. J. Anderson, D. J. Drury, J. E. Hamlin, A. G. Kent, WO 8602066, BP Chemicals Limited, **1986**; b) T. Schaub, R. A. Paciello, *Angew. Chem. Int. Ed.* **2011**, *50*, 7278.
- [4] M. Scott, B. Blas-Molinos, C. Westhues, G. Franciò, W. Leitner, *ChemSusChem* **2017**, *10*, 1085.
- [5] J. Kothandaraman, A. Goepfert, M. Czaun, G. A. Olah, G. K. S. Prakash, *Green Chem.* **2016**, *18*, 5831.
- [6] W. Leitner, G. Franciò, M. Scott, C. Westhues, J. Langanke, M. Lansing, C. Hussong, E. Erdkamp, *Chem. Ing. Tech.* **2018**, DOI: 10.1002/cite.201800040, in press