ISGC 2022

N°309 / OC
TOPIC(s) : Homogenous, heterogenous and biocatalysis

Production of formic acid from carbon dioxide in a liquid-liquid biphasic system with self-separating pure product phase

AUTHORS

Kira EHMANN / MAX PLANCK INSTITUTE FOR CHEMICAL ENERGY CONVERSION, STIFTSTRASSE 34-36, MUELHEIM AN DER RUHR
Arne NISTERS / MAX PLANCK INSTITUTE FOR CHEMICAL ENERGY CONVERSION, STIFTSTRASSE 34-36, MUELHEIM AN DER RUHR
Walter LEITNER / MAX PLANCK INSTITUTE FOR CHEMICAL ENERGY CONVERSION, STIFTSTRASSE 34-36, MUELHEIM AN DER RUHR
Corresponding author : Andreas VORHOLT / andreas-j.vorholt@cec.mpg.de

PURPOSE OF THE ABSTRACT

Climate change is recognized as a global topic since several years. One strategy to deal with this topic is the use of carbon dioxide as C1 building block. The conversion of CO2 waste emissions to value-added products offers the possibility to close the carbon cycle [1]. One reaction using CO2 as building block is the hydrogenation of carbon dioxide to formic acid. For this reaction lots of reaction systems with homogeneous catalysts are reported [2]. Most of these miss the aspect of separating and recycling the catalyst, which is essential for establishing CO2-based value chains. One approach towards facile catalyst recycling are liquid-liquid biphasic systems. The product phases of known biphasic systems for CO2 hydrogenation usually consist not only of the reaction product formic acid and the required amine, but also of an additional solvent, which subsequently needs to be removed energy-intensively [3].

Therefore, in the present study, we present a simple catalytic system comprising only a hydrophobic solvent for the catalyst phase and an amine as base. Based on the previously in our group used catalyst phase of cis?[Ru(dppm)2Cl2] in 4-methyl-2-pentanol (MIBC), the first aim was to find a polar tertiary amine which forms in combination with formic acid a second liquid phase [4]. A change in the phase behavior of simulated reaction mixtures from mono- to biphasic simply by CO2 conversion to formic acid can be observed while using N-methyldiethanolamine (MDEA) as amine (Figure 1). NMR measurements confirmed that one phase consists mainly of the solvent MIBC and the other phase of amine and formic acid. Thus, the product and the catalyst phase would self-separate in catalysis if high acid to amine ratios (AAR) are achieved. Several reactions parameters of Ru-catalyzed carbon dioxide hydrogenation to formic acid were screened to find suitable conditions for the occurrence of the self-separating effect via catalysis. Besides finding suitable reaction conditions, it was possible to improve the productivity of the system. With these reaction conditions in hand, the recyclability of the catalyst phase has been successfully proven, resulting in a total turnover number of 5590 after four recycling runs.

FIGURES

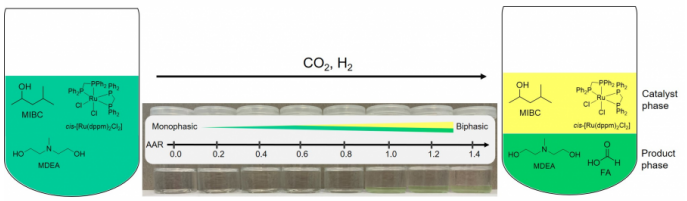

FIGURE 1

Illustration of the reaction system

Illustration of the reaction system with self-separating product phase for high acid to amine ratios (AAR).

FIGURE 2

KEYWORDS

CO2 hydrogenation | biphasic catalysis | homogeneous catalysis

BIBLIOGRAPHY

[1] M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, ChemSusChem 2011, 4, 1216–1240.

[2] K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, Chem. Rev. 2018, 2, 372–433.

[3] a) R. G. Beevor, D. J. Gulliver, M. Kitson, R. M. Sorrell, The production of formate salts of nitrogenous bases., 1990, EP0357243A2. b) T. Schaub, R. A. Paciello, Angew. Chemie Int. Ed. 2011, 32, 7278–7282. c) A. Behr, P. Ebbinghaus, F. Naendrup, Chem. Eng. Technol. 2004, 5, 495–501. d) J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah, G. K. Surya Prakash, Green Chem. 2016, 21, 5831–5838. e) C. Guan, Y. Pan, E. P. L. Ang, J. Hu, C. Yao, M.-H. Huang, H. Li, Z. Lai, K.-W. Huang, Green Chem. 2018, 18, 4201–4205.

[4] M. Scott, B. Blas Molinos, C. Westhues, G. Franciò, W. Leitner, ChemSusChem 2017, 6, 1085–1093.