Development of catalyst recycling strategies for the hydroformylation of olefins using methanol as a syngas source

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Abstract

Hydroformylation of olefins is the most important homogeneously catalyzed process on an industrial scale, with a production volume exceeding 12 million tonnes per year. The resulting aldehydes can be subsequently converted into alcohols, opening up a wide range of applications.[1] Traditionally, hydroformylation is carried out using synthesis gas; however, our group recently introduced a novel approach using methanol as a source of synthesis gas, which we termed the *methanolation* reaction.[2]

The methanolation process is performed as an orthogonal tandem reaction using two different types of catalysts. The first catalyst, a Mn/Pincer complex, splits methanol *in situ* into synthesis gas. The second catalyst, a Rh/P complex, catalyzes the hydroformylation reaction. Additionally, the Mn/Pincer complex catalyzes the reduction of the resulting aldehyde to the corresponding alcohol, enabling the conversion of olefins into alcohols using methanol in a 100% atom-efficient manner.[2]

In our previous work, we achieved an alcohol yield of 80% using 1-octene as substrate, with a linear-to-branched ratio of 93:7 and a turnover number exceeding 17,000 based on rhodium, all while maintaining a total pressure below 10 bar and a partial pressure of synthesis gas in the range of 1–2 bar. Furthermore, we successfully scaled up the reaction from a 5 mL laboratory scale to a 250 mL miniplant scale.[2]

Our upcoming research focuses on the development of catalyst recycling strategies to enable the transition from a batch process to a continuous process at miniplant scale. Various techniques will be considered and tested experimentally.

Literature

[1] S. Tao, D. Yang, M. Wang, G. Sun, G. Xiong, W. Gao, Y. Zhang, Y. Pan, *iScience* **2023**, 26, 106183.

[2] S. Stahl, J. T. Vossen, S. Popp, W. Leitner, A. J. Vorholt, *Angew. Chem. Int. Ed.* **2025**, 64, e202418984.