Methanolation of Olefins: A Low Pressure Alcohol Synthesis from Methanol and Olefins

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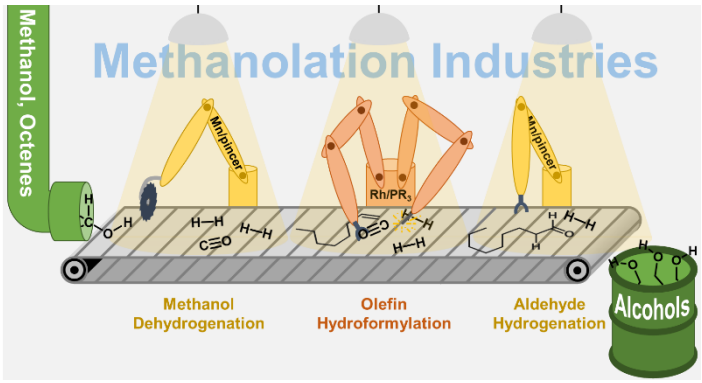
Abstract

Methanol is regarded as one of the major energy and hydrogen carrier molecules for the transition to a green future and away from fossil resources.[1] It is currently produced via heterogeneous catalysis over Cu/Zn-based catalysts at a high reaction temperature of 250 °C. An alternative to the heterogeneous system is a homogeneously catalysed reaction using earth abundant Mn-based catalysts and synthesis gas under milder reaction conditions.[2–3]
After synthesis and transportation, the methanol can be utilised in various ways. In the transport and energy sectors, it can be combusted in engines or for heat generation, or it can be used in solid oxide fuel cells. It can also be converted to other fuels in the Methanol-to-Gasoline (MtG) process or to olefins for the chemical industry in the Methanol-to-Olefins (MtO) process. If the methanol is used as a hydrogen carrier molecule, it can be reformed to CO_2 and H_2.[4–5] Recently, Leitner *et al*. showed the reversibility of the methanol synthesis from synthesis gas with a Mn/pincer catalysts in the dehydrogenation of methanol to CO and H_2.[6] This allows for an application of methanol not only as a hydrogen carrier but also as a synthesis gas carrier.
In this work, we present a tandem reaction system combining the methanol dehydrogenation to synthesis gas coupled with the hydroformylation of olefins to aldehydes and a consecutive hydrogenation of the aldehydes to alcohols. This so-called “methanolation of olefins” formally describes the addition of methanol to olefins. The homogeneous Mn/pincer catalyst is combined with the Rh-based hydroformylation catalyst in one system, providing various synergistic effects such as an unprecedented selectivity towards alcohols and a high hydroformylation rate and TON of up to 17 121 in a single batch experiment.



References

[1] A. Sonthalia, N. Kumar, M. Tomar, V. Edwin Geo, S. Thiyagarajan, A. Pugazhendhi, *Clean Technol. Envir.* **2023**, *25*, 551–575.
[2] A. Kaithal, C. Werlé, W. Leitner, *JACS Au* **2021**, *1*, 130–136.
[3] S. Stahl, N. Wessel, A. J. Vorholt, W. Leitner, *Green Chem.* **2024**, *26*, 7799–7805.
[4] V. Dieterich, A. Buttler, A. Hanel, H. Spliethoff, S. Fendt, *Energ. Environ. Sci.* **2020**, *13*, 3207–3252.
[5] M. Yang, D. Fan, Y. Wei, P. Tian, Z. Liu, *Adv. Mater.* **2019**, *31*, 1902181.
[6] A. Kaithal, B. Chatterjee, C. Werlé, W. Leitner, *Angew. Chem. Int. Ed.* **2021**, *60*, 26500–26505.

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