

## **Methanolation of Olefins: Versatile low-pressure synthesis of various alcohols from olefins and methanol**

Sebastian Stahl<sup>1,2</sup>, Jeroen T. Vossen<sup>1,2</sup>, Jan Mädicke<sup>1,2</sup>, Stephan Popp<sup>1,2</sup>, Walter Leitner<sup>1,2</sup>, Andreas J. Vorholt<sup>1</sup>

<sup>1</sup>Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

<sup>2</sup>Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany

### **Abstract**

Methanol is considered a central molecular pivot between renewable energy and the chemical value chain. Such “green” methanol can be produced at sites with a large green energy capacity and transported within existing infrastructure to locations where it is in demand.[1] As a carbon source for the chemical industry, methanol can be implemented in existing processes or open opportunities for emerging applications.[2] One field that has seen little attention to date is the utilization of methanol as liquid equivalent of synthesis gas (CO/H<sub>2</sub>). Leitner et al. showed the reversibility of the methanol synthesis from synthesis gas with a homogeneous Mn/pincer catalyst in the dehydrogenation of methanol to CO and H<sub>2</sub>. [3] In our recent work we paired this synthesis gas liberating reaction with the reductive hydroformylation of olefins to alcohols as this utilizes the CO/H<sub>2</sub> ratio of 1:2 as produced from methanol.[4]

This so-called “methanolation of olefins” formally describes the addition of methanol to olefins in a 100% atom economic manner without the need for external pressurized synthesis gas. The homogeneous Mn/pincer catalyst is combined with the Rh-based hydroformylation catalyst in one system, providing various synergistic effects. Unprecedented selectivity towards alcohols, excellent regioselectivities for the simple ligands employed and a high hydroformylation rate and TON of more than 17 121 in a single batch experiment were demonstrated with Rh concentrations in the low ppm range.

This process eliminates the need for high-pressure equipment or synthesis gas infrastructure due to the low overall reaction pressure. This drastically reduces the investment costs thus making it more accessible to a wide range of potential users on the laboratory and industrial scale and integrates “green” methanol as a sustainable synthesis gas source into the production of important intermediates and products of the present and future chemical industry. We now aim to demonstrate the broad applicability to structurally diverse substrates with high demand in different branches of the chemical industry.

### **Literature**

[1] Olah, G. A., Goeppert, A., Prakash, G. K. S. *Beyond Oil and Gas: The Methanol Economy*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2009**.

[2] V. Dieterich, A. Buttler, A. Hanel, H. Spliethoff, S. Fendt, *Energ. Environ. Sci.* **2020**, *13*, 3207–3252.

[3] A. Kaithal, B. Chatterjee, C. Werlé, W. Leitner, *Angew. Chem. Int. Ed.* **2021**, *60*, 26500–26505.

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