A-126

From Methanol to Alcohols: Mechanistic Understanding of a Tandem Catalytic System for Resilient C1-Based Chemical Supply

J. T. Groteguth[1], S. Stahl[1], J. T. Vossen[1], J. Exo[1], T. Weyhermüller[1], C. Lyall[2], J. Lowe[2], U. Hintermair[2], W. Leitner[1,3], A. J. Vorholt[1]
[1]Max Planck Institute for Chemical Energyconversion, Mülheim an der Ruhr, Germany, [2]University of Bath, Bath, United Kingdom, [3]RWTH Aachen University, Institute of Technical and Macromolecular Chemistry, Aachen, Germany

The annual production of more than 12 million tonnes of aldehydes via olefin hydroformylation underscores the central role of this homogeneous catalytic process in the chemical industry — serving as a key entry point to alcohols, plasticizers, and a broad range of value-added chemicals.[1] However, the conventional process relies on synthesis gas (CO/H_2), whose supply is tied to large-scale, centralized infrastructure and predominantly fossil carbon sources. As the chemical industry seeks more flexible and resilient supply chains, alternative C1 feedstocks are gaining strategic importance.[2]

Methanol — increasingly accessible from renewable and distributed production routes — offers a compelling alternative. The methanolation reaction exploits methanol as an in situ syngas source, integrating methanol reforming and olefin hydroformylation into a single, atom-efficient tandem process.[2] Applied to 1-octene as a model substrate, the system delivers alcohol yields of up to 80% with outstanding linear selectivity (l:b = 93:7), a rhodium-based turnover number exceeding 17,000, and operation under mild conditions (<10 bar total pressure). Successful scale-up from 5 mL to a 250 mL miniplant demonstrates the robustness and industrial viability of the approach.[2]

Building on these results, this contribution presents mechanistic investigations of the tandem system using multinuclear operando FlowNMR spectroscopy. By directly monitoring catalyst speciation and key reaction intermediates under working conditions, this study aims to establish a molecular-level understanding that guides the rational design of future methanol-based processes for the resilient supply of carbon carriers and chemicals.

References:

[1] Shu Tao, Da Yang, Minmin Wang, Guangxun Sun, Gaoyan Xiong, Wenwen Gao, Youzhi Zhang and Yuan Pan, (2023), Single-atom catalysts for hydroformylation of olefins, CellPress, iScience, 106183, 26/3, https://doi.org/10.1016/j.isci.2023.106183, 2023-03-17, College of Chemistry and Chemical Engineering, China University of Petroleum
[2] Sebastian Stahl, Jeroen T. Vossen, Stephan Popp, Walter Leitner, Andreas J. Vorholt, (2025), Methanolation of Olefins: Low-Pressure Synthesis of Alcohols by the Formal Addition of Methanol to Olefins, Wiley VHC, Angewandte Chemie International Edition, e202418984, 64, https://doi.org/10.1002/anie.202418984, 2024-11-19, Max Planck Institute for Chemical Energyconversion