

The influence of the support on Pd-based catalysts in direct DME synthesis

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Abstract

The syngas to dimethyl ether (STD) process on bifunctional catalysts is of great interest for the valorization of CO₂ and syngas from biomass gasification. Dimethyl ether (DME) economics (conventionally based on fuel use) is attracting growing interest, in parallel with the development of various pathways for conversion to hydrocarbons (fuels and chemicals such as olefins, oxygenates, aromatics, and liquefied petroleum gas) and H₂ production. DME is commercially produced from syngas (CO / H₂) in a two-step process *via* dehydration of methanol. This two-step process typically employs Cu/ZnO/Al₂O₃ catalysts for methanol synthesis in combination with a solid acid (for example, γ -Al₂O₃ or zeolites) for its dehydration. Taking advantage of favorable thermodynamics, the single-step STD process leads to higher syngas conversions and entails further economic and technical advantages. This necessitates the design of specific bifunctional catalysts with high methanol synthesis and dehydration activity as well as high stability against deactivation. Recently, Pd-based compounds have emerged as interesting alternatives providing improved reaction rates, methanol selectivity or thermal stability [1, 2, 3]. For example, Pd/ZnO in combination with a solid acid was shown to be a suitable catalyst for hydrogenation of CO or CO₂ to DME [3]. The activity of these catalysts was ascribed to the formation of an intermetallic PdZn phase during reductive catalyst pretreatment [3].

In this study, a series of Pd/Zn nanoparticles with different Pd/Zn ratio were obtained by reductive stabilization [3] and anchored on a hierarchical H-ZSM-5 zeolite for bifunctional PdZn/ZnO-based STD catalysts. We demonstrate the influence of the Pd/Zn ratio and the dehydration catalyst on the catalytic performance in the hydrogenation of CO to DME. Alternatively, Pd/CeO₂ was obtained by colloidal, liquid-phase synthesis providing a catalyst with high reaction rates in the STD process when combined with γ -Al₂O₃. The reaction rates were highly dependent on the preparation procedure and catalysts supported on commercial ceria revealed much lower reaction rates. Nanoparticles and catalysts were characterized by various analytical tools including powder X-ray diffraction, inductively coupled plasma optical emission spectroscopy, electron microscopy (SEM/EDS, STEM-HAADF/EDS), and N₂ physisorption. Catalytic tests were carried out in a continuous, fixed-bed laboratory reactor employing CO-rich syngas (CO/H₂ 1 : 1).

[1] T. Pinheiro Araújo, C. Mondelli, M. Agrachev, T. Zou, P. Willli, K. Engel, R. Grass, W. Stark, O. Safonova, G. Jeschke, S. Mitchell, J Pérez-Ramírez, *Nature Commun.* 13, 5610 (2022) 13; [2] M. Gentzen, D. Doronkin, T. Sheppard, J.-D. Grunwaldt, J. Sauer, S. Behrens, *Applied Catalysis A* 562, 206 (2018); [3] M. Gentzen, D. Doronkin, T. Sheppard, A. Zimina, H. Li, J. Jelic, F. Studt, J.-D. Grunwaldt, J. Sauer, S. Behrens, *Angew. Chem. Int. Ed.* 58, 15655 (2019).