

High pressure *operando* XANES and EXAFS investigation during the synthesis of dimethyl ether over a bifunctional PdZn catalyst prepared by a colloidal route

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Dimethyl ether (DME) is an important base chemical and used in a wide range of applications, one of the most important being “green” diesel fuel substitute. DME is produced from synthesis gas, which can be obtained via gasification of biomass-derived feedstocks, thus, allowing strong reduction of CO₂ emissions compared to the use of fossil fuels. DME can be produced in one step over bifunctional catalysts containing transition metals and acidic sites [1]. The susceptibility of commonly used Cu/ZnO/Al₂O₃ catalysts to deactivation is the main motivation for the development of new syngas-to-DME (STD) catalysts. Pd-Zn catalysts are extremely interesting alternatives as they are fairly stable and exhibit high catalytic activity. Up to now hardly any structural investigations on these materials have been conducted. Here we report on studies under *operando* conditions; an elevated pressure of 20 bar was used to detect also the catalytic performance in parallel.

PdZn-based nanoparticles were synthesized *via* reductive stabilization of Pd (II) acetylacetonate with diethyl zinc, supported on γ -Al₂O₃ and calcined. XAS measurements in terms of XANES and EXAFS were performed using a quartz capillary microreactor (6 mg of catalyst, sieved) heated by a hot air blower at the CAT-ACT beamline at KIT [2]. During the reductive activation of the PdZn catalyst (heating in 5% H₂/He to 250 °C, 50 ml/min, 1 bar, 1 °C/min) XANES data were continuously recorded, and, finally, EXAFS at 250 °C at both the Pd K- and Zn K- edge. Afterwards, the gas feed was switched to 15% H₂, 15% CO in He (18 ml/min) and the microreactor was pressurized stepwise to 20 bar. After 1 h time-on-stream XANES and EXAFS spectra were recorded.

Ex situ XAS identified PdO and ZnO in the as-received calcined catalyst sample. *In situ* XANES revealed complete reduction of PdO to PdH_x within 2-3 minutes after exposure to H₂ at 20 °C. The PdH_x phase was decomposed upon further heating already at 45 °C. At the same time gradual reduction of ZnO started and a stoichiometric PdZn alloy was formed at 180 °C. Afterwards, additional Zn-species were reduced, which were most probably located on the surface of the alloyed particles with a final Pd⁰:Zn⁰ ratio 1:1.3. EXAFS analysis clearly indicated formation of PdZn alloy nanoparticles under reducing H₂ atmosphere with a Pd-Zn distance of 2.58 ± 0.03 Å and a Pd-Pd distance of 2.76 ± 0.03 Å corresponding to a bimetallic PdZn phase. *Operando* EXAFS data recorded one hour after applying DME synthesis conditions at 20 bar confirmed intermetallic PdZn particles being the active phase. At the same time, the production of methanol and DME was monitored by online mass spectrometry and confirmed a stable catalytic activity during the entire experiment.

In summary, Pd/Zn-based model catalysts were developed for single-step DME synthesis. *In situ* XANES spectroscopy was used to quantitatively monitor the reduction of Pd and Zn oxides and the evolution of PdZn alloyed nanoparticles. *Operando* EXAFS, conducted for the first time at high pressure during DME synthesis, confirmed the stability of the PdZn phase which correlates well to the exceptional catalyst stability observed in laboratory tests.

References:

[1] M. Gentzen et al., *Catal. Sci. Technol.* **6** (2016) 1054

[2] A. Zimina et. al., *Rev. Sci. Instrum.* **88** (2017) 113113