

Synchrotron-based *operando* studies of Ni-based catalysts for methanation of CO₂

(1,2)H. Lichtenberg, (1,2)M.-A. Serrer, (1,2)B. Mutz, (3)J. Lefebvre, (3)S. Bajohr, (3)T. Kolb, (1,2)J.-D. Grunwaldt

(1)Institute of Catalysis Research and Technology (IKFT), (2)Institute for Chemical Technology and Polymer Chemistry (ITCP), (3)Engler-Bunte-Institute, Fuel Technology Division (EBI ceb), Karlsruhe Institute of Technology (KIT), Germany

henning.lichtenberg@kit.edu

Conversion of electric power into chemical energy carriers plays a key role in many concepts for a future energy supply based on renewable sources. ‘Power-to-X’ technologies like the methanation of CO₂ allow long-term energy storage and compensation of fluctuations in renewable energy. Structural characterization of methanation catalysts under realistic and dynamic reaction conditions [1] using methods like X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) provides valuable information for a knowledge-based optimization.

Ni-based catalysts for the methanation of CO₂ were characterized in quartz capillaries heated by a gas blower with *operando* XAS at the KIT synchrotron (XAS and CAT-ACT beamlines, [2]), and with Quick Scanning XAS at the Swiss Light Source (SuperXAS, [3]). A fluctuating H₂ supply was simulated by temporary removal of H₂ from the feed gas [4]. Within the German BMBF project “Kopernikus Power-to-X” these studies were continued at elevated pressure to approach industrial relevant conditions and by including a commercial Ni-based catalyst used in three-phase methanation of CO₂ [5]. At CAT-ACT, a set-up for combined XAS and XRD was implemented.

Operando XAS studies on Ni-based catalysts for two- and three-phase methanation of CO₂ at atmospheric pressure provided insights into deactivation mechanisms during methanation under dynamic feed conditions. The results revealed that all investigated catalysts were stable under methanation conditions at atmospheric pressure. H₂ dropouts caused partial oxidation of the catalytically active Ni⁰- to Ni²⁺-species resulting in a lower activity during subsequent methanation cycles. XRD data indicated formation of a NiO phase. No NiCO₃ reflections were observed. A regeneration of the catalysts without a loss in activity was achieved by reduction in H₂/N₂.

The combined XAS-XRD experiments provided detailed complementary structural information about the changes in Ni-based catalysts during methanation of CO₂ and under more dynamic feed conditions. All catalysts were stable during CO₂ methanation but immediately oxidized in CO₂/N₂ (H₂ dropout, technical CO₂). A regeneration to restore the initial activity was achieved by reduction in H₂/N₂. In order to further approach industrially relevant conditions (elevated pressure, low space velocity) a new high pressure *operando* cell for combined XAS-XRD is now tested, and the *operando* studies on Ni-based catalysts for two- and three-phase methanation of CO₂ will be continued to further investigate the structural changes. More complex processes like three-phase methanation will be studied in liquid phase using an *in situ* batch cell based on ref. [6].

References:

- [1] K. F. Kalz, R. Kraehnert, M. Dvoyashkin, R. Dittmeyer, R. Gläser, U. Krewer, K. Reuter, J.-D. Grunwaldt, *ChemCatChem* **2017**, *9*, 17-29.

- [2] A. Zimina, K. Dardenne, M. A. Denecke, D. E. Doronkin, E. Huttel, H. Lichtenberg, S. Mangold, T. Pruessmann, J. Rothe, T. Spangenberg, R. Steininger, T. Vitova, H. Geckeis, J.-D. Grunwaldt, *Rev. Sci. Instrum.* **2017**, 88, 113113.
- [3] O. Müller, M. Nachtegaal, J. Just, D. Lützenkirchen-Hecht, R. Frahm, *J. Synchrotron Rad.* **2016**, 23, 260.
- [4] B. Mutz, A. Gänzler, M. Nachtegaal, O. Müller, R. Frahm, W. Kleist, J.-D. Grunwaldt, *Catalysts* **2017**, 7, 279.
- [5] J. Lefebvre, N. Trudel, S. Bajohr, T. Kolb, *Fuel.* **2018**, 217, 306309.
- [6] J.-D. Grunwaldt, M. Ramin, M. Rohr, A. Michailovski, G. R. Patzke, A. Baiker, *Rev. Sci. Instrum.* **2005**, 76, 054104.