Combination of kinetic and structural studies of catalysts at the CAT-ACT X-ray spectroscopy beamline at KIT

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The CAT station at the CATalysis-ACTinide wiggler beamline[1] at the Karlsruhe Institute of Technology (KIT) focuses on characterization of catalytically active materials under realistic reaction conditions, e.g. in the fields of energy related applications, selective oxidation, sustainable fine chemical processes and exhaust gas after-treatment. A special infrastructure including stationary reactive gas supply, gas dosing units and on-line product analysis (mass spectrometry, infrared spectroscopy, gas chromatography) as well as *in-situ* and *operando* cells for sample environments close to industrial reactors (high temperature, elevated pressure, liquid/gas phase, etc.) are essential aspects of CAT. The XAS setup at the CAT station can be combined with advanced setups for complementary characterization techniques like X-ray diffraction[2, 3] and infrared spectroscopy[4-6]. This allows to directly correlate the information about the local molecular environment of catalytically active elements with information related to the long range order structures and adsorbed reaction species. The *in-situ* and *operando* setups installed at the CAT experimental station are of flexible design, so that users can bring their own reaction cells and gas mixing systems and integrate them into the existing infrastructure if necessary. The infrastructure for catalysis research will be complemented by an off-line catalysis lab adjacent to the experimental floor, offering sample preparation and pre- and post-characterization capabilities including kinetic studies.

As an example we show *in-situ* experiments on commercial Ni methanation catalysts performed with complementary XAS and XRD measurements using a capillary reactor at atmospheric pressure. The reduction of the catalyst in an H_2 flow was monitored *in-situ* by EXAFS and XRD during temperature programmed reduction (TPR). After the TPR a hydrogen dropout was simulated at different temperatures.

At higher temperature the Ni-Ni coordination numbers up to the third shell increased, accompanied by an increase in the intensities of the reflections of the reduced Ni phase which indicates a growth of the metallic Ni particles. After the TPR the catalyst remained stable under the applied conditions in the methanation of CO_2. Simulating a hydrogen dropout at different temperatures revealed that there might be already a slow oxidation of Ni at medium temperatures. At higher temperatures a distinct oxidation of the catalyst was observed in XANES and EXAFS spectra. Further examples are direct synthesis of hydrogen peroxide from hydrogen and oxygen, methanol and Fischer Tropsch synthesis.

The CAT station of the recently installed CAT-ACT beamline at KIT offers unique experimental possibilities for *in-situ* and *operando* studies of catalysts, as demonstrated by an

exemplary study utilizing the combination of XAS and XRD to gain further information about the correlation of structure and oxidation state under different reaction conditions.

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