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Operando XAS studies on catalysts for energy related processes

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Synchrotron based in situ and operando X-ray absorption spectroscopy (XAS) has evolved into a powerful tool to analyze structural changes of catalysts under realistic reaction conditions as a basis for structure activity relationships. The design of appropriate sample cells is crucial to achieve the best compromise between high quality data acquisition and sample environments similar to those in industrial reactors. The following three selected examples illustrate the high potential of this technique for various relevant energy related applications. Data were acquired at DESY, ESRF and ANKA.

Methanol, one of the most important industrial bulk chemicals, can be used as fuel additive or precursor for clean fuels and is attractive for chemical energy and hydrogen storage due to its high energy density. Industrially, methanol is produced from synthesis gas over Cu/ZnO catalysts which have been studied since decades but still are not fully understood. Operando XAS provides a unique insight into these materials: Upon variation of the reduction potential of a synthesis gas mixture Cu k-edge XAS spectra of Cu/ZnO methanol synthesis catalysts indicate dynamic, reversible changes in the catalyst structure which strongly correlate with changes in catalytic activity. The changes in Cu particle morphology are clearly reflected in the coordination numbers extracted from the EXAFS data, whereas evidence of significant alloying of copper and zinc is only found under severe reduction conditions [1].

Hydrogenation of CO2 to methane using sustainable H2 (e.g. from water splitting) is an attractive process in the field of ‘‘power to gas’’ technologies for storage of renewable energy in the form of chemical energy. To investigate the influence of dynamic reaction conditions resulting from fluctuations in renewable power XAS spectra of Ni based catalysts were recorded under changing reaction atmospheres. The Ni k- absorption spectra and on-line product gas analysis show that H2 drop outs during methanation, simulated by temporarily removing H2 from the H2/CO2 feed gas, not only lead to an interruption in methane production but also to fast bulk-like oxidation of the Ni particles and to a slight but continuous decrease in catalytic performance during subsequent methanation cycles due to residual partly oxidized Ni, necessitating a reactivation step to restore the initial activity and initial state of the catalyst [2].

The Water Gas Shift (WGS) reaction is an important process for production and purification of clean hydrogen (e.g. in the production of clean hydrogen rich synthesis gas from gasified biomass) and fuel cell applications where CO acts as a catalyst poison. In membrane reactors WGS reactions can proceed in a single stage, as an alternative to the industrially well-established two-step process (High and Low Temperature Shift using iron and copper catalysts). For this application Rh K-XAS spectra of a hydrogen selective membrane and a flame made Rh/ceria catalyst in a novel micro-structured membrane reactor specially designed for measurements under WGS conditions were recorded while simultaneously analyzing the product and permeate stream. The results provide an insight into the structure-performance relationships of Rh/CeO2 catalysts under different WGS reaction conditions and during reduction [3].

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