High pressure and long-term operando studies for production of sustainable fuels & chemicals: Bridging industry and synchrotron

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Introduction

Power-to-liquid processes can be considered the key for renewable electricity-based liquid fuel generation. [1–3] For this purpose, green H_2 is generated *via* water electrolysis. CO_2 can be provided via "carbon capture" processes or from local CO_2-emission sources and converted together with green hydrogen and suitable catalysts.[4] In this manner hydrocarbons via Fischer-Tropsch synthesis (FTS) [2], various olefins and methanol can be synthesized.[5–7] For further improvement, characterization of these catalysts, especially *in situ* and *operando* is considered important to derive structure-activity relationships. [6,8] Particularly, operando X-ray absorption spectroscopy (XAS) is a highly promising tool as structural changes can be observed in heterogeneous catalysts at work. Especially the study of active sites is of significant importance, mainly in view of growing demand for energy storage using CO_2 as feedstock and for renewable electrical energy.[6,9] However, in order to determine simultaneously catalyst performance and structure at a molecular level, compromises in terms of reaction conditions need to be undertaken, e.g. with respect to catalyst mass, product formation/detection, pressure and temperature. As ideal case, a dedicated system has been recently developed at the CAT-ACT beamline (at KIT Light Source) [10] that allows operation even close to the industrially relevant conditions,[6] e.g. during long-term Fischer-Tropsch-Synthesis (FTS) from green H_2 and CO /CO_2 (see Figure 1).[9]

Results and discussion

The high pressure and high temperature setup was developed and installed on the CAT-ACT Beamline.[6] Co-Ni-Re/ γ-Al_2O_3-FTS-catalysts were investigated at 250°C and 30 bar for more than 300h. In parallel with the operando measurements, the products were investigated by online μ-GC and offline GC-FID. Further characterization methods such as XRD, Raman spectroscopy, temperature programmed reduction-and oxidation were performed off-line as complementary characterization. Through this study, the catalytic activity and selectivity were extensively analyzed. Three time-on-stream ranges were investigated to understand the various deactivation levels and mechanisms of the catalyst. The study shows that considering the high stability of the

catalysts, the main reason of catalyst deactivation is due to macroscopic effects such as pore blocking and diffusion limitation. The formation of carbon species was confirmed from XAS analysis and investigated using various characterization methods such as Raman spectroscopy, TPH and TPO. It was found that the formation of atomic carbon, surface carbides, hydrocarbons, graphitic carbon deposits and hydrogen resistant carbon species, led to the increased limitation of pore diffusion.
The study underlines the importance of *operando* techniques, especially those under real reaction conditions. The study allowed the understanding of catalyst deactivation phenomena. Moreover, this *operando* setup can be applied to various further processes at high pressure and temperature (e.g. methanol, DME, higher alcohol synthesis). Based on this obtained information, we further aim to synthesize an optimized model catalyst for FTS and analyze it, in particular, for activity and selectivity. As part of the energy transition, there are several initiatives in Germany to fund research collaborations focused on the production of sustainable aviation fuel (see: CARE-O-SENE, https://care-o-sene.com/de_de/).

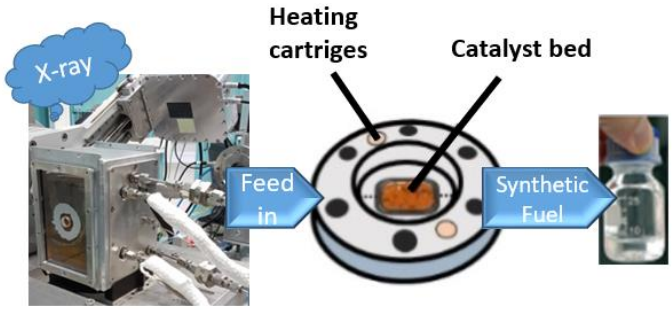

Figure 1: Scheme of high pressure setup and *operando* high-pressure cell for combined X-ray absorption spectroscopy and –diffraction.[6]

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