

Novel approach of advanced characterization, dedicated synthesis and theoretical modelling on commercially relevant Fischer-Tropsch catalysts for production of sustainable fuels & chemicals: Bridging industry and academia

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Power-to-liquid processes can be considered the key for renewable electricity-based liquid fuel generation [1,3]. For this purpose, green H₂ is generated *via* water electrolysis, CO₂ can be provided via "carbon capture" processes or from local CO₂-emission sources and converted together with suitable catalysts [4]. In this manner hydrocarbons via Fischer-Tropsch synthesis (FTS) [2], various olefins and methanol can be synthesized [5-7]. The CARE-O-SENE consortium [8] that connects German and South African partners is driven to accelerate the development of cobalt-based FT catalysts for green and efficient production of sustainable aviation fuel (SAF). For efficient development, systematic characterization of Co-based catalysts, especially *in-situ* and *operando* is essential to derive structure-activity relationships in reliable manner [6,9]. X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), magnetometry and Raman spectroscopy are a highly promising tool as structural changes of active species, support and adsorbents can be observed in heterogeneous catalysts at work. Especially the study of active sites and their interaction with promoters and support is of significant importance, mainly in view of growing demand for energy storage using CO₂ as feedstock and for renewable electrical energy [6,10]. However, in order to determine simultaneously catalyst performance and its 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 pilot case, a dedicated system has been developed at the CAT-ACT beamline at KIT Light Source [11] that allows operation close to the industrially relevant conditions [6] e.g. during long-term Fischer-Tropsch synthesis (FTS) from green H₂ and CO /CO₂ [10].

The high pressure and high temperature setup was developed and installed on the CATACT beamline and verified during the study on Co-Ni-Re/ γ -Al₂O₃ FTS catalysts at 250°C and 30 bar for more than 300 h, the products were analyzed by online μ -GC and offline GC-FID [6]. Moreover, this *operando* setup can be applied to various other processes at high pressure and temperature (e.g. methanol, DME, higher alcohol synthesis). In following, advanced studies of commercially relevant materials for FTS and model structures to mimic the atomic structure of active cobalt, promoter and support were performed and combined with theoretical modelling. The cobalt FT catalyst with oxidic supports have a nano-scale active phase with large mass specific surface area, however, nano-structuring and strong metal-support interaction would lead to deactivation due to sintering and/or forming metal-support compounds [12-15]. Recent study showed that further reason of catalyst deactivation is a macroscopic effect such as pore blocking causing diffusion limitation. 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. Further investigations such as *in-situ* XRD [16], Raman spectroscopy, temperature programmed reduction/oxidation and TEM will be performed complementary to gain deeper insight into the behavior of cobalt, promoter and support during the reaction. The dedicated and controlled synthesis, complementary characterization of model structures and model catalysts could close the knowledge gap between the fundamental research and industrial application. Furthermore, these insights can be transferred into deeper understanding with respect to promotion, metal-support interaction, long-term stability and deactivation phenomena to improve the commercially-relevant catalysts in the overall FT process to efficiently produce SAF.

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