

New perspectives for Fischer-Tropsch synthesis: development and advanced characterization of next-generation catalysts

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Introduction

Power-to-X technologies (PtX) significantly impact energy transition by converting excess (renewable) electricity into valuable energy carriers or chemicals, enabling efficient energy storage and significant carbon emission reduction.^{1,2} Fischer-Tropsch synthesis (FTS) is considered as a key reaction for the production of clean transportation fuels and chemicals. The catalyst-assisted process can convert H₂, generated *via* water electrolysis, and CO₂, provided *via* "carbon capture", to long-chain hydrocarbons.

Complex multi-component catalysts are often used in industrial FTS. Deep understanding of catalyst behavior and uncovering structure-activity relations is in the core of knowledge-based design of efficient catalysts in terms of activity and stability. In this respect, advanced characterization can yield valuable insights and accelerate the fundamental research and industrial development. Using model catalysts and structures for advanced characterization is important to elucidate the dynamics between catalyst components (active metal / promoters / support) and catalyst behavior, especially in terms of reducibility and metal-dispersion.⁴ For the synthesis of model catalysts, different methods like incipient wetness impregnation (IWI), co-precipitation, flame spray pyrolysis etc. can be used. Considering different atomic structures produced by different methods, the structure-activity relation can be explored in detail, including the metal-support interaction and the role of promoters. Flame Spray Pyrolysis (FSP) is an appealing method to synthesize model cobalt-based FTS catalysts with controllable crystalline phase and chemical structure.³ *In-situ* and *operando* characterization of FTS catalysts is essential to observe structure-activity relationship under working conditions.⁵ We have further applied *operando* X-ray absorption spectroscopy (XAS) to track structural changes of active sites of heterogeneous catalysts at work under these demanding reaction conditions. For these purposes a dedicated *operando* reactor has been developed and commissioned at the CAT-ACT beamline at KIT Light Source that allows to perform XAS measurements and FTS reaction close to the industrially relevant conditions simultaneously.⁶ Understanding of the reduction mechanism of Co-based catalysts and correlating it with the activity is the one of the main goals of this study.

As part of the energy transition, there are several funding initiatives in Germany that focus on the production of sustainable aviation fuels. This study focuses on industrially relevant catalysts within the CARE-O-SENE project⁷ and pilot results.

Materials and Methods

A series of reference catalysts/samples and FTS catalysts were synthesized *via* FSP and IWI. Our high-pressure and high-temperature *operando* setup (cf. ref. 5) was developed further

and installed at the CAT-ACT beamline.⁶ In-situ reduction of FSP- and IWI-prepared model structures was investigated. XAS spectra were recorded at the Co K-edge (7709 eV).

Results and Discussion

The reduction behavior of three model structures simulating the structure of commercially relevant catalysts (Co, Co-Mn and Co-Mn/SiO₂) was investigated using *in situ* XAS (Figure 1). It was found that FSP-prepared pure Co-nanoparticles can be easily reduced to metallic Co. However, in a mixed system of Co/Mn, the Mn prevents Co to completely reduce. The additional presence of silica (often used as support in Co-based FTS catalysts) resulted in nanoparticles that are even more difficult to reduce. Complementary XRD and TEM

characterizations revealed the dynamics between the crystalline structure of nanoparticles and their reduction behavior. Additional advanced characterization methods like magnetometry and in-situ XRD and theoretical considerations provide complementary information on catalyst behavior.⁸ The observed structural dynamics of the catalysts during reduction will be correlated to activity/selectivity with the aim to draw structure-activity relationships. These insights can be transferred into deeper understanding and improving commercially relevant catalysts with

respect to metal-support interaction and deactivation phenomena.

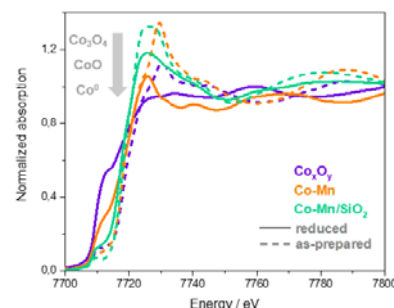


Figure 1. In-situ XAS spectra during reduction of model FTS catalyst structures at the Co K-edge.

Significance

The study is of significant importance in view of growing demand for sustainable aviation fuels using CO₂ and renewable electrical energy.^{1,7} To bridge the existing knowledge gap between the academic research and industrial application is highly demanded.

References

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