

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

Moritz Wolf,¹ Anna Zimina,¹ Erisa Saraçi,¹ Rabia Elbuga-Ilica,¹ Cherie Hsu,¹ Enrico Sireci,¹ Dan Zhao,¹ Revana Chanerika,² Mohamed Fadlalla,² Felix Studt,¹ Michael Claeys,² Jan-Dierk Grunwaldt¹

¹Karlsruhe Institute of Technology (KIT), Karlsruhe/Germany

²University of Cape Town (UCT), Cape Town/South Africa

Introduction

The Power-to-Liquid (PtL) route is a key technology for the defossilization of hard to abate sectors, such as aviation. It allows for production of sustainable aviation fuel (SAF) by converting green hydrogen and carbon dioxide via the reverse water-gas shift reaction and the Fischer-Tropsch (FT) synthesis. The benefits of synthetic paraffinic kerosene are well demonstrated [1]. The goal of the CARE-O-SENE [2] consortium is the accelerated and knowledge-driven development of cobalt based FT catalysts for the highly efficient and sustainable production of SAF in relevant volumes for the transformation of the aviation sector. Large mass specific surface areas are achieved in cobalt FT catalysts by employing a nano-sized active phase, which comes at the expense of the stability [3-5]. Such cobalt nanoparticles are particularly vulnerable to deactivation via sintering and chemical reaction of the active phase to inactive species, as both mechanisms are driven by minimization of surface energy.

Methodology

Model counterparts of industrial catalysts were synthesized in order to gain a deeper understanding of the catalyst behavior by gradually mimicking the different complexities in the catalyst system. At first, model systems and catalysts have been synthesized using a surfactant-free approach for well-defined nanoparticles of tunable size [6], which were deposited on model and commercial supports to study metal-support interaction and deactivation mechanisms. Further, a series of reference and FT catalysts were synthesized via flame spray pyrolysis (FSP). All catalysts were then studied using a variety of *in situ* and *operando* characterization techniques, namely X-ray diffraction (XRD) [7], X-ray absorption spectroscopy (XAS) at the CAT-ACT beamline of the KIT Light Source [8,9], and magnetometry at UCT [4]. All studies are accompanied by theoretical modelling via density functional theory (DFT).

Results and Discussion

The reduction behavior of three model systems relevant for commercial catalysts (Co, Co-Mn, Co-Mn/SiO₂) was investigated using, amongst other techniques, *in situ* XAS (Figure 1). It was found that bare cobalt oxide nanoparticles can easily be reduced to metallic Co, while complete reduction is hindered in a mixed system of Co-Mn. When using silica as a support, the reduction becomes even more challenging. XRD and microscopic characterizations revealed the dynamics between the crystalline structure of nanoparticles and their reduction behavior. Further, the interplay between complementary magnetometry, spectroscopic techniques, XRD, and theoretical considerations enable correlation of activity and selectivity during FT synthesis with the observed structural dynamics to draw conclusions on 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. Lastly, observed phase stability and transformations were compared to predictions from DFT calculation on (de)alloying of cobalt and the promoter, phase transformations of cobalt, and sintering.

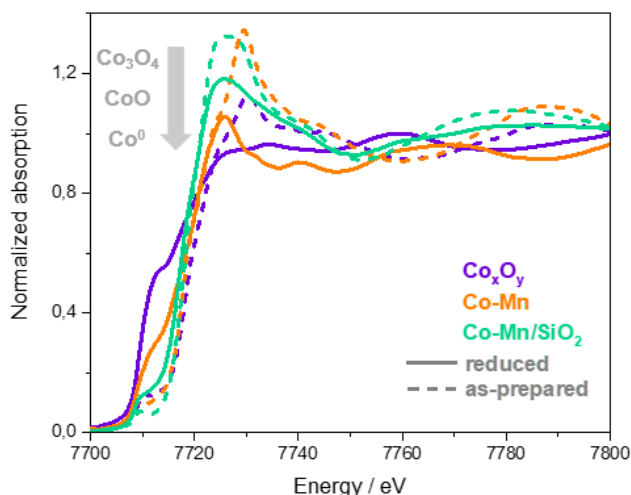


Figure 1. *In situ* XAS spectra during reduction of model FT catalyst structures at the Co K-edge.

References

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