

Revealing the deactivation mechanisms of Co-based catalysts in Fischer-Tropsch synthesis by *operando* X-ray absorption spectroscopy

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Introduction

Supported Co-based catalysts have been well studied in the past decades and now are widely used in the large-scale Fischer-Tropsch synthesis (FTS), in particular for sustainable aviation fuels (SAF) production [1-3]. The Co-based catalysts, however, suffer from deactivation under harsh reaction conditions and the deactivation mechanisms are up to now still unclear due to the difficulties in monitoring structural changes of active sites under real reaction conditions. X-ray absorption spectroscopy (XAS) is a powerful technique to get insights into the oxidation states and local structures of active sites as it can be applied for the measurements at high temperatures and pressures through a reasonable design of *in-situ* reaction cells. For this purposes, a dedicated *operando* reactor system has been recently developed at the CAT-ACT beamline at KIT Light Source [4] that allows an operation close to the industrially relevant FTS conditions [5].

Results and discussion

The recent studies in revealing the deactivation mechanisms of Co-based catalysts using XAS can be summarized as following: the catalyst deactivates as the number of catalytically active sites decreases under the low temperature syngas flow due to different processes under different time scales. Many pioneers have reported [6-8] that (i) sintering of Co nanoparticles (NPs); (ii) solid state reaction of Co NPs and supports; (iii) coke or wax depositions and (iv) oxidation of Co NPs during long-term tests are the main reasons for the catalyst deactivation. For instance, through a careful evaluation of X-ray absorption near edge spectra and Fourier transformed extended X-ray absorption fine structure data on commercially representative Co-Ni-Re/ γ -Al₂O₃-FTS-catalysts, the coordination number(CN) of Co-Co was found to be increased, hinting to the fast sintering, and CoAl₂O₄ and CoC₂ phase were formed during long-term FTS operation tests [4]. The catalytically active sites, i.e., metallic Co sites, could also be oxidized to CoO_x in the presence of water, which is irreversible in FTs. These processes need to be studied in details on commercial relevant catalysts and on model structures and will support new energy-related initiatives in Germany, like the CARE-O-SENE project [9], a research collaborations with academic and industrial partners, HZB, UCT, IKTS and SASOL, focused on the production of SAFs.

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