

***Operando* X-ray absorption spectroscopy as a first step towards a knowledge-based optimization of Fischer-Tropsch catalysts**

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Introduction

Power-to-liquid processes can be considered the key for renewable electricity-based liquid fuel generation. [1,2] For this purpose, H₂ generated *via* water electrolysis and CO₂ provided *via* "carbon capture" are converted together on a suitable catalysts [3] and hydrocarbons, various olefins and methanol can be synthesized *via* Fischer-Tropsch process (FTS)[2]. For catalyst improvement, *in-situ* and *operando* characterization of FTS catalysts is considered essential to derive structure-activity relationships. [4] In this respect, *operando* X-ray absorption spectroscopy (XAS) can be used to observe structural changes of active sites of heterogeneous catalysts at work. The study is of significant importance, mainly in view of growing demand for energy storage using CO₂ as feedstock and renewable electrical energy.[5] For this purposes, a dedicated *operando* reactor system has been recently developed at the CAT-ACT beamline at KIT Light Source [6] that allows an operation close to the industrially relevant FTS conditions [4].

Results and discussion

The high-pressure and high-temperature setup was developed in house [5] and installed at the CAT-ACT beamline.[6] As a pilot study, commercial Co-Ni-Re/ γ -Al₂O₃-FTS-catalysts were investigated at 250°C and 30 bar for more than 300h. The products were investigated by online μ -GC and offline GC-FID to trace the catalytic activity and selectivity. The study showed that considering the high stability of the catalysts, the main reason of catalyst deactivation is due to macroscopic effects such as pore blocking by reaction products and diffusion limitation. The formation of carbon species was confirmed from XAS analysis and investigated by complementary 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 increased limitation of pore diffusion. Based on this obtained information, we aim to prepare a model FTS catalyst and further optimize it for improved activity and selectivity. For the synthesis of model catalysts, different methods like wet-impregnation, co-precipitation, flame spray pyrolysis etc. are used. Considering different atomic structures produced by different methods, the structure-activity relation is explored in detail, including the metal-support interaction and the role of promoters using *operando* spectroscopy. Part of the findings, will support new energy-related initiatives in Germany, like the Care-o-Sene project [7], a research collaborations focused on the production of sustainable aviation fuel.

References

- [1] Kalz, K.F.; Kraehnert, R.; Dvoyashkin, M.; Dittmeyer, R.; Gläser, R.; Krewer, U.; Reuter, K.; Grunwaldt, J.-D.; *ChemCatChem* **2017**, 9, 17–29.
- [2] Moodley, D.; Botha, T.; Crous, R.; Potgieter, J.; Visagie, J.; Walmsley, R.; Dreyer, C.; *Catl. Sustain. Environm.* (in press **2022**).
- [3] Osman, A.I.; Hefny, M.; Abdel Maksoud, M.I.A.; Elgarahy, A.M.; Rooney, D.W.; *Environ. Chem. Lett.* **2021**, 19, 797–849.
- [4] Loewert, M.; Serrer, M.-A.; Carambia, T.; Stehle, M.; Zimina, A.; Kalz, K.F.; Lichtenberg, H.; Saraçi, E.; Pfeifer, P.; Grunwaldt, J.-D.; *React. Chem. Eng.* **2020**, 5, 1071–1082.
- [5] Pandit, L.; Serrer, M.-A.; Saraçi, E.; Boubnov, A.; Grunwaldt, J.-D.; *Chem. Methods* **2022**, 2.
- [6] Zimina, A.; Dardenne, A. K.; Denecke, M.A.; Doronkin, D.E.; Huttel, E.; Lichtenberg, H.; Mangold, S.; Pruessmann, T.; Rothe, J.; Spangenberg, T.; Steininger, R.; Vitova, T.; Geckeis, H.; Grunwald, J.-D.; *Rev. Sci. Instrum.* **2017**, 88, 113113.
- [7] www.care-o-sene.com, accessed on 20.01.2023.