ESRF	**Experiment title:** Operando grazing incidence small angle X-ray scattering and grazing incidence X-ray diffraction analysis for development of a new generation of Fischer-Tropsch catalysts	**Experiment number**: CH-4981
Beamline: ID03	**Date of experiment**: from: 03/05/2017 to: 09/05/2017	**Date of report**: 2018-01-10
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Report:

Fischer-Tropsch synthesis (FTS), which produces long chain hydrocarbons via the use of biomass or natural gas derived synthetic gas (a mixture of H_2 and CO), is currently of great interest due to the due to the environmental concerns and fossil fuels shortage. Co-based FTS catalysts are more economically viable due to the mechanical strength, high selectivity and less susceptibility to attrition in comparison to traditional iron-based systems. The active phase in the catalysts is thought to be metallic Co^0 and among factors determining its activity are nanoparticle (NP) size and distribution, type of support and crystal structure.[1,2]

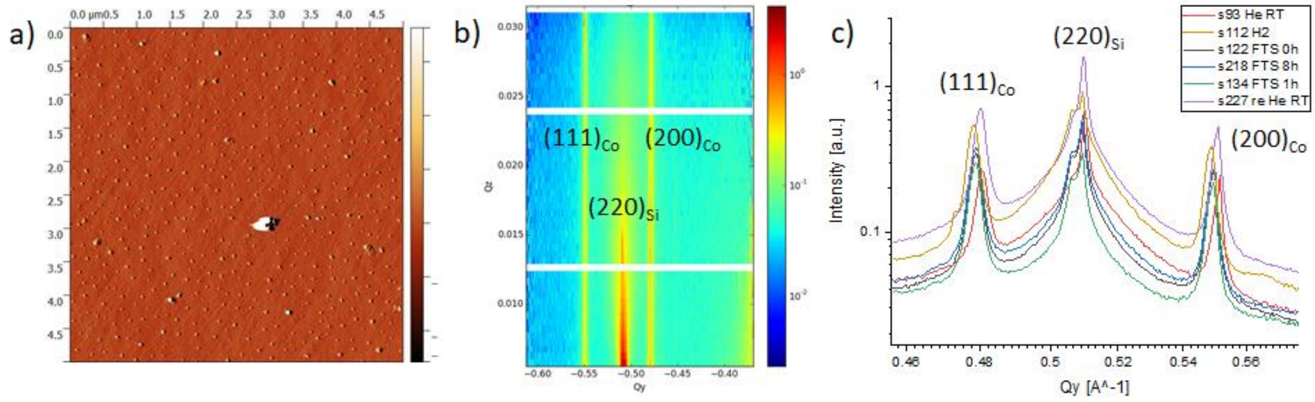

Figure 1. a) AFM image of the planar Co-SiO_2/Si catalyst where NPs are forming nanoarray. b) 2D GIXD image of the reduced catalyst where crystalline peaks from Co NPs are clearly visible. c) 1D GIXD in-plane projections (Qy) during operando FTS reaction.

In this project, we studied the nano(re)structuring behaviour of a series of supported cobalt nanoparticles prepared using reverse micelle encapsulation[3] (Fig. 1a). 2D GIXD patterns were collected using Maxipix 2D camera with pixel resolution of 55µm in both lateral directions and incident X-ray beam wavelength of 0.0827 nm. For the measurements, the FTS catalyst was placed in the flow reactor with the reactor volume of 15 ml connected to the Residual Gas Analyser (RGA) for the analysis of the reaction gas products during all stages of the FTS.

A typical 2D GIXD pattern from supported Co NP of 15 nm reveals two peaks around 0.48 and 0.55 $Å^{-1}$ that correspond to 111 and 200 reflexes of fcc phase for metallic Co (Fig. 1b). The most intensive peak around 0.51 $Å^{-1}$ can be indexed as 220 of monocrystalline Si support (Fig. 1c). We could not observe the signal from native SiO_2 layer that forms on the surface of Si and has a thickness of few nm as calculated from XPS in our previous work.[3] A significant reversible shift in the crystalline peak positions of Co has been detected (Fig. 2a). This could be due to the defects formation including stacking faults or/and interstitial carbon.[4] It has to be noted that size of the NPs does not change considerably according to the FWHM values (Fig. 2b). From Figure 2c, it can be seen that the investigated catalyst is active in FTS, confirming the validity of the approach used for the operando GIXD study.

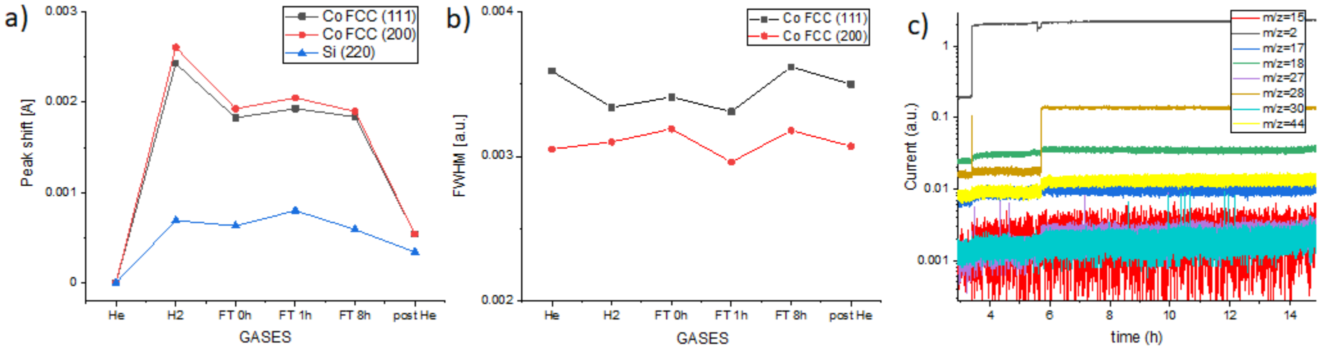

Figure 2. a) Shift in crystalline peak position during operando FTS catalyst testing. b) FWHM values for the crystalline peaks obtained from the deconvolution of the 1D GIXD profiles during operando FTS catalyst testing. c) RGA traces of the products formed during FTS. The m/z values are given in the legend.

Structural analysis of the model planar Co FTS catalysts with highly monodispersed NP size distribution was performed using surface sensitive operando GIXD method. The results obtained provide insight into defects accumulation and phase composition of the cobalt NPs during reduction and FTS catalysts formation and allow to correlate these structural changes with catalyst activity. The obtained results help to better understand the structural transformations in supported Co NP during exposure to various gas environments, which is of high importance for the understanding of true active species during FTS reaction.

References

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(3) Odarchenko, Y. et al. *Faraday Discuss.* **2018**. DOI: 10.1039/C8FD00007G

(4) Price, S. W. T. et al. *Sci. Adv.* **2017**, *3* (3), e1602838.