

Operando Surface X-ray Diffraction on Cobalt Single Crystal Model Catalyst for the Fischer-Tropsch Synthesis under Realistic Conditions

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The synthesis of hydrocarbons from hydrogen and carbon monoxide over cobalt catalyst is a highly relevant process as an alternative route to produce fuel with lower sulfur content than the one obtained from fossil sources.

Since decades the (0001) surface of cobalt single crystal has been used to model active sites of real catalysts, made of Co nanoparticles deposited on oxide support, because the (0001) surface is the most abundant facets. The hexagonal close-packed (0001) surface under reaction conditions was investigated *in situ* with surface science techniques. Significant results were obtained with high pressure Scanning Tunneling Microscopy, at pressure ranging from few mbars up to few bars, showing the effects of the pressure together with the H₂:CO ratio. Synthesis performed at 4 bar induced a massive surface reconstruction of the cobalt surface within the three first hours of reaction [1]. At pressure in the mbar range with high syngas ratio (H₂ rich feeds), the surface morphology remains unchanged with respect to the surface in vacuum [2]. However, authors from the same group using the same experimental apparatus investigated the Co(0001) surface evolution in pure CO at pressure in the mbar range; they observed surface reconstruction induced by the presence of carbidic carbon, together with cobalt carbide formation within few hours of reaction [3]. The roughening and C-induced transformations may affect the catalyst activity by creating new active sites [4]. Those transformations have been shown, by Density Functional Theory calculation, to be thermodynamically feasible under realistic CO-coverage and to offer preferential adsorption site for monomers [5].

In this context, *Operando* Surface X-ray Diffraction (SXR) and X-ray Reflectivity (XRR) are suitable techniques to obtain an averaged information over the beam size and investigate surface transformations and roughening of the catalyst at the early stages of the reaction. Studies were performed at the ID03 beamline of the European Synchrotron, using a flow catalytic reactor developed in collaboration with Leiden University. The setup includes a vacuum compartment allowing surface cleaning and preparation of reproducible surface state as starting point. To explore the surface morphology and structure as a function of gas composition and sample temperature, we acquired *in situ* SXR data of the Co(0001) surface under various syngas H₂:CO ratio. First results confirmed that the surface remains in metallic state under realistic conditions and no surface carbide formation was observed after few hours. Cobalt oxide was formed in pure CO and it is easily reduced in usual reaction conditions (H₂:CO=3:1, T = 220 C). No sign of graphitic neither carbidic carbon was found on the surface. Those results do not allow to conclude yet about the CO dissociation on Co(0001), since the gas feed contains ppm level of H₂O and O₂ contamination. We built up a phase diagram stability of the cobalt oxide as a function of syngas ratio and temperature. This preliminary result will help us in the understanding of the surface states during the activation process of the catalyst.

References:

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