



Experiment Report Form

	Experiment title: "Understanding of carbide formation onto working supported metal catalysts for Fischer-Tropsch Synthesis"	Experiment number: CH4944
Beamline: ID20	Date of experiment: from: 16/11/2016 to: 22/11/2016	Date of report:
Shifts: 18	Local contact(s): Dr. Blanka Detlefs	<i>Received at ESRF:</i> 28/12/16
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Brief Description

In the so-called Fischer-Tropsch synthesis (FTS) a mixture of carbon monoxide and hydrogen is converted into different hydrocarbon chains by a catalytic surface polymerization reaction. FTS has experienced a renaissance in recent years, as a result of higher environmental awareness, the ever-increasing worldwide demand for transportation fuels, and depleting oil reserves. This technology provides the opportunity to exploit different feedstock sources, such as natural gas (gas-to-liquid, GTL), coal (coal-to-liquid, CTL), and biomass (biomass-to-liquid, BTL) [1]. An illustrative example being of the commercial impact of FTS technology is the construction of the Shell Pearl GTL facility in Qatar making use of TiO₂-supported cobalt catalysts. However, catalyst deactivation over time is one of the main issues in FTS, with the formation of carbides (bulk, sub-surface and surface) and deposition of carbon species (graphitic, aliphatic or aromatic) onto the catalyst surface, being the most significant aspects of deactivation [2,3]. Despite more than 80 years of research on FTS catalysts, our fundamental understanding regarding the effect of carbide species on the performance of FTS catalysts and the deposition mechanisms of carbon [1-5] remains elusive. This is partly due to the difficulty of performing *in-situ* spectroscopic measurements at relevant industrial conditions (i.e., elevated temperature and pressure). The aim of this proposal is to obtain new physicochemical insights into the formation of carbides on supported cobalt nanoparticles (taking TiO₂ as the relevant porous support) during FTS. The ultimate goal is to design a new generation of improved FTS catalysts, which requires a better understanding of the deactivation process of the Co/TiO₂ catalyst material.

Experiment Procedure

The first experiment that was performed during this beamtime, was the *ex-situ* measurement of metal carbide standard material (Co₂C), which was provided by American Elements, this material was previously

characterized by XRD. Two different *in-situ* experiments were performed during this allocated beamtime: a) carburization reaction at 503 K and 1 bar, and b) FTS reaction (CO hydrogenation reaction) at 493 K and 10 bar, both reactions over un-promoted Co-based catalyst. The Co/TiO₂ FTS catalyst, tested during this beamtime, contained ~ 14.1 wt% of Co. The *in-situ* experiments consisted of two parts: i) reduction (activation) in H₂ atmosphere (1 bar) by heating up to 773 K for 2 h, and ii) carburization/FTS reaction. Before reduction, the Co L_{2,3}-edge, C K-edge, and XRD patterns were measured (at room temperature) in order to identify the different species presented in the catalyst before the activation process. After the complete reduction of cobalt was achieved, a second set of measurements (Co L_{2,3}-edge, C K-edge and XRD patterns) were acquired in order to identify the changes induced in the catalyst material during the reduction process. In the case of carburization reaction, the reaction was performed at 503 K and 1 bar. The catalyst was cooled down from 773 K (reduction temperature) to 503 K, and was exposed to a pure CO flow (1 ml/min) the temperature in the capillary was decreased to room temperature every 6 h in order to do measurements at low temperature; after the data acquisition, the temperature was raised to 503 K to continue with the reaction, and measurements at reaction conditions were performed. The carburization reaction was done for 36 h, and a second carburization reaction was performed for 11 h (in order to double check the results obtained in the first experiment) (Figure 1 and 2). FTS reaction was completed at 493 K and 10 bar. The syngas was fed with a H₂/CO rate of 0.5 (0.5 ml/min of H₂ and 1 ml/min of CO). After 8 h, the measurements at room temperature were collected, and after the measurements the temperature was increased to 493 K (reaction conditions). The FTS reaction was executed for 15 h and the experimental approach is summarized in Figure 3.

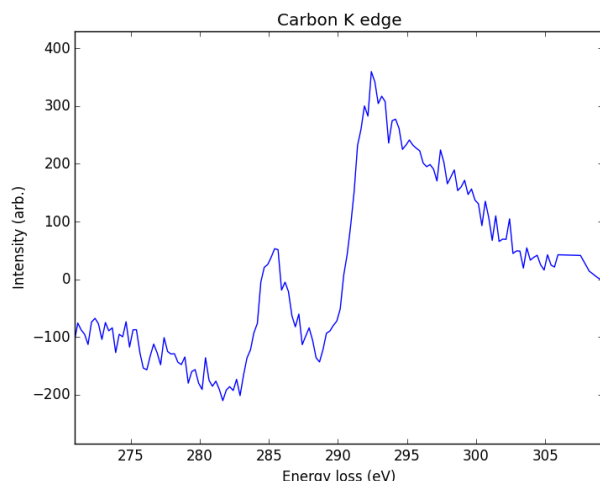


Figure 1: XPS C 1s-edge of Co/TiO₂ FTS catalyst after 15 h of *in-situ* carburization reaction.

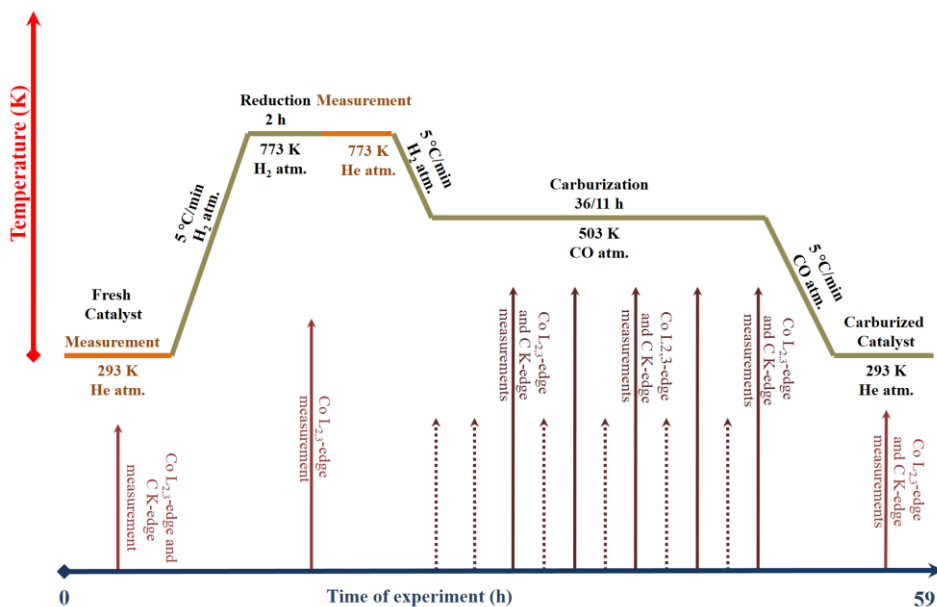


Figure 2: Profile for carburization reaction of Co/TiO₂ FTS catalyst.

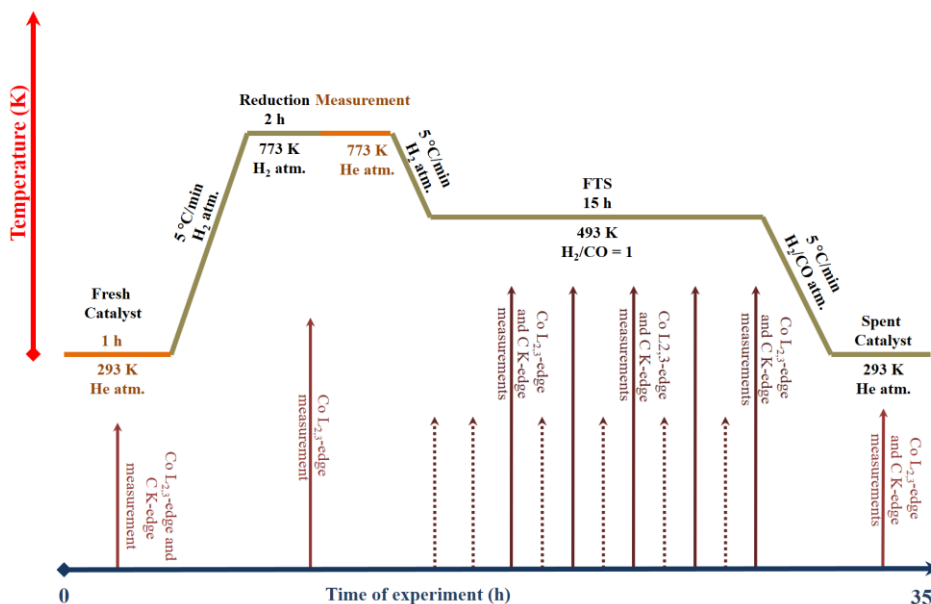


Figure 3: Profile for FTS reaction of Co/TiO₂ FTS catalyst.

Problems identified during the experiments

It was noted that unfortunately in the 10 bar *in-situ* experiments Ni was deposited and subsequently poisoned the catalyst sample. As noted in Figures 4 and 5 the Co signal intensity decreases during the *in-situ* experiment, a process which is accompanied by the appearance of Ni on the catalyst sample. The presence of Ni on the catalyst material is explained by the formation of nickel carbonyl compounds, which were produced by the corrosion of stainless steel from the gas regulator by CO at high pressure (Figure 6). The nickel carbonyls were decomposed by the X-ray beam and Ni was deposited at the beam spot, as noted in Figure 7. The poisoning effect was more evident during the *in-situ* FTS reaction due the effect of the pressure (10 bar), but the poisoning affected in an equivalent manner the *in-situ* carburization reaction, as evidenced by XRD measurements. These experiments are shown in Figure 8. The team members warned that instead of stainless steel gas regulator, a brass one should be used, but the safety department at ESRF did unfortunately not allow the usage of this type of regulator. The local contact did a great effort to optimize the experiment and obtain the XRS measurements, but they cannot be used quantitatively for the purpose of our research.

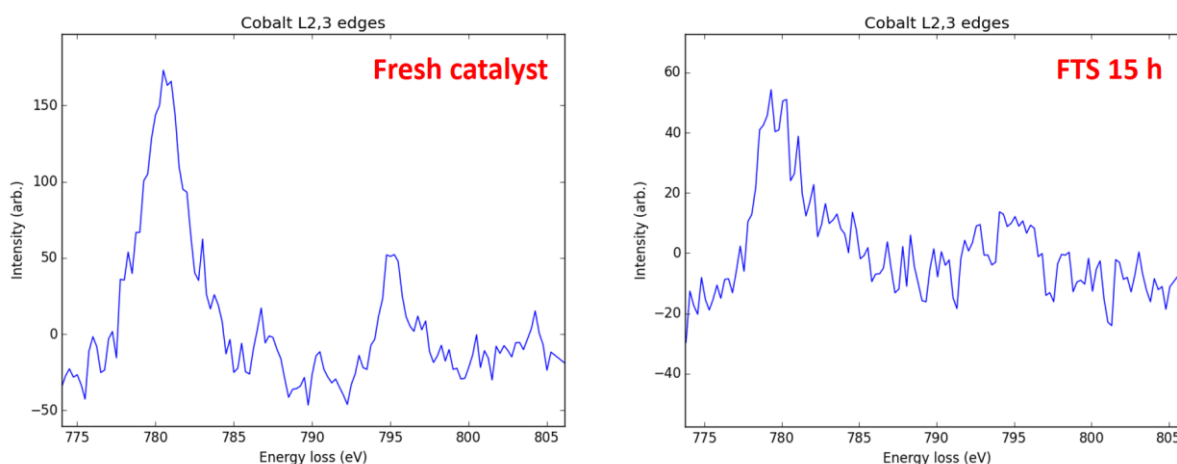


Figure 4: XRS Co L-edges before (left) and after (right) 15 h of *in-situ* FTS reaction of Co/TiO₂ FTS catalyst.

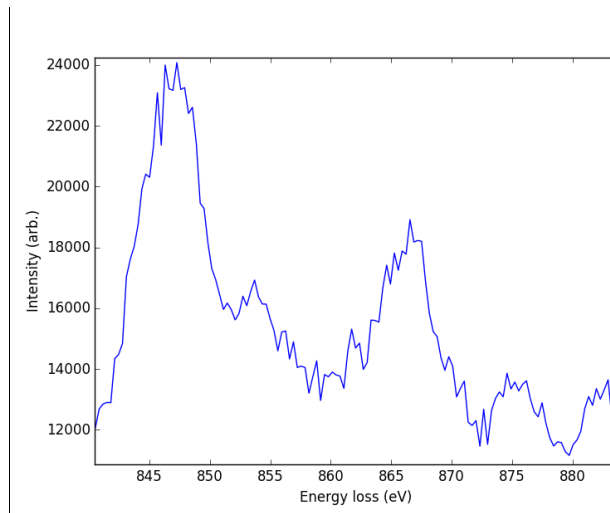


Figure 5: XRS Ni L-edges after 15 h of *in-situ* FTS reaction of Co/TiO₂ FTS catalyst.

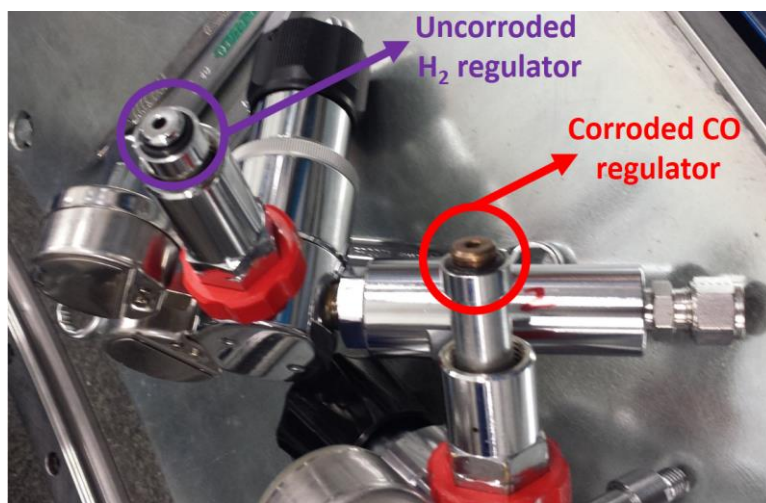


Figure 6: Hydrogen gas regulator (left) and carbon monoxide gas regulator (right).

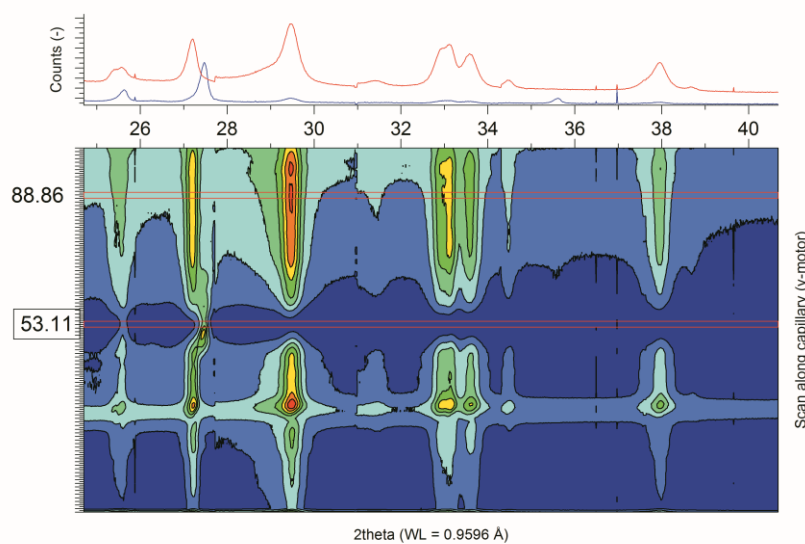


Figure 7: 2D XRD patterns after 15 h of *in-situ* FTS reaction of Co/TiO₂ FTS catalyst.

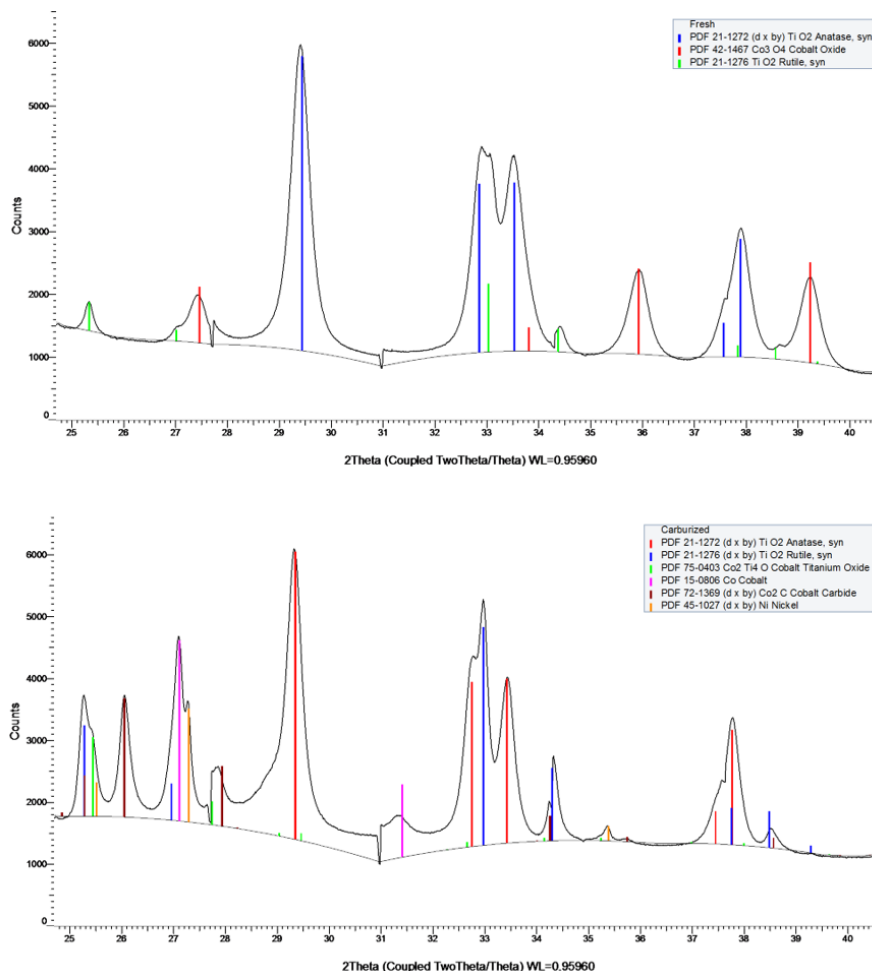


Figure 8: XRD patterns, before (above) and after (below) 15 h of *in-situ* carburization reaction of Co/TiO₂ FTS catalyst.

Observations

In order to complete the research plan proposed for this beamtime, new granted shifts should be needed. Problems as the poisoning of the catalyst by nickel were already identified and they can be corrected in a future beamtime. In addition, during this beamtime, the acquisition of data was optimized, which increases the chances to perform successful measurements in a future granted beamtime.

References

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