	<b>Experiment title:</b> Combined XAS-XRD study of the deactivation of Co-based Fischer-Tropsch catalysts under realistic working conditions	<b>Experiment number:</b> 01-01-815
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 17.09.09 to: 22.09.09	<b>Date of report:</b> 02.03.2010
<b>Shifts:</b> 15	<b>Local contact(s):</b> Hermann Emerich	<i>Received at ESRF:</i>
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### Report:

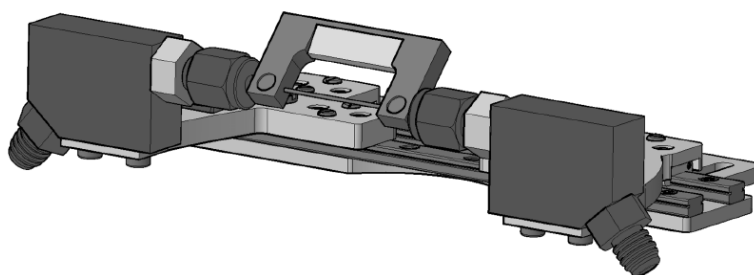
Fischer – Tropsch synthesis (FTS) is a major research topic, being under investigation for many years and the complexity of the catalysis behind it is still a challenge for the scientific community. The main purpose of this process is to produce synthetic petroleum substance having synthesis gas as feed. During the last years increasing attention has been given to the cobalt based FT catalysts due to their favourable properties in terms of per pass activity, selectivity, stability and low water gas shift activity [1]. Despite the advantages of Co – based FTS, which are corresponding well with natural gas derived feedstocks, the relatively high price of the metal comparing to Iron inhibits its viability in commercial scale. Thus, understanding of deactivation mechanisms that occur during reaction can play a key role in systems exploitation [2].

The main causes of catalyst deactivation in cobalt based FTS as they appear in the literature are: (i) poisoning (ii) re-oxidation of cobalt active sites (iii) formation of stable surface carbon species (iv) carburization (v) surface reconstruction (vi) sintering of cobalt crystallites (vii) metal-support solid state reactions (viii) attrition [2]. At present, there are not sufficient chemical knowledge to explain or to distinguish between the proposed deactivation mechanisms. Since the study of catalyst deactivation is a

characterization oriented problem, spent catalyst has to accurately characterized and compared with the fresh one. In FTS two main problems exist and hinder this procedure, the surface coverage of the spent catalyst with hydrocarbon waxes and the pyrophoric character of cobalt in metallic state. Additionally, The partial pressures of steam,  $H_2$  and CO in the reactor are crucial for the selectivity and deactivation behaviour of the catalysts. Hence, the *in situ* studies performed at realistic conditions ( $473K < T < 523K$ ,  $T > 10\text{bar}$  and CO conversion  $> 50\%$ ) closely resembling an industrial reactor [3], are fundamental for understanding, modelling and minimizing the phenomenon. With the established equipment at SNBL, our dedicated gas distribution sytem and the capillary reactor we are now routinely able to achieve these conditions.

### Experimental method:

XAFS were collected at the Co-K edge and harmonic rejection was done by detuning the Si(111) monochromator crystals. The XRD measurements were carried out at  $\lambda = 0.80074$ . A modified *in situ* cell similar to that proposed by Clausen and Grunwaldt [4] was used in order to combine the X-ray techniques and FT reaction at realistic reaction conditions. The cell consists of a stainless steel base and two linear motion guides (see Fig. 1). The standard Swagelok 1/8 inch unions are fixed at a  $45^\circ$  angle in order to prevent liquid products accumulation inside the cell. A quartz capillary tube was used as a microscale reactor for the *in situ* studies of the FTS. The capillary dimensions are the following: length = 60 mm, outer diameter = 1 mm, wall thickness = 0.02 mm. The catalyst bed length was limited to 10 mm and kept in place inside the quartz tube by quartz wool plugs. The sample was heated by a vertical hot air blower. The heat blower nozzle diameter was 12 mm. Blower calibration has been done with the use of thermal expansion of silver in a AgSi reference sample. The XAS data were collected in transmission mode.



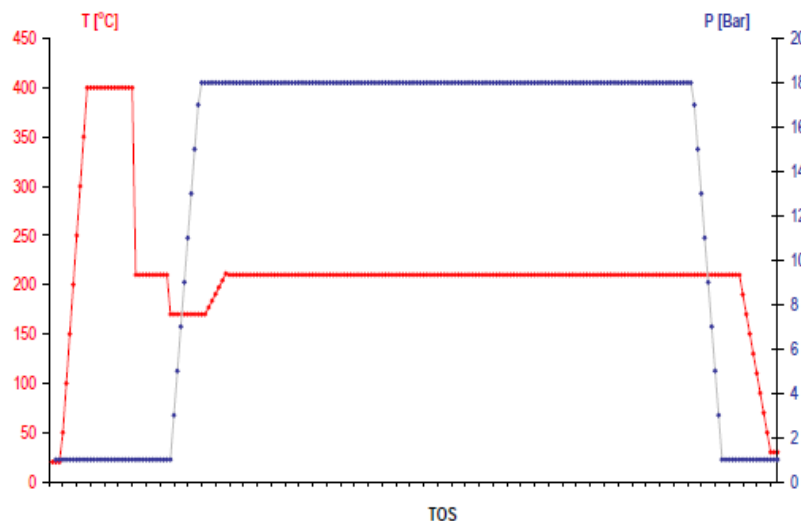
**Figure 1:** Cell set-up for combined *in situ* XAS-XRD

The experiments were performed in two steps. The first step was the reduction of the  $Co_3O_4$  to obtain the active metallic phase prior to the reaction. The reduction was performed at 673 K during 4 hours with pure  $H_2$  feed (5 ml/min) to obtain a sufficient fraction of metallic Co. The second step was Fischer-Tropsch reaction. The reaction was carried out at 483K with He diluted synthesis gas (2.6 ml/min). The stoichiometric ratio between  $H_2$  and CO was 2.1. The gas line from the cell was heated to prevent

blocking of the exhaust line. EXAFS and XRD scans were collected at 483K (under He flow) before exposing the catalysts to the reaction gases. During the reaction EXAFS and XRD scans were alternated. After FT-reaction the sample was cooled to room temperature, depressurized and extended XRD and EXAFS scans were collected.

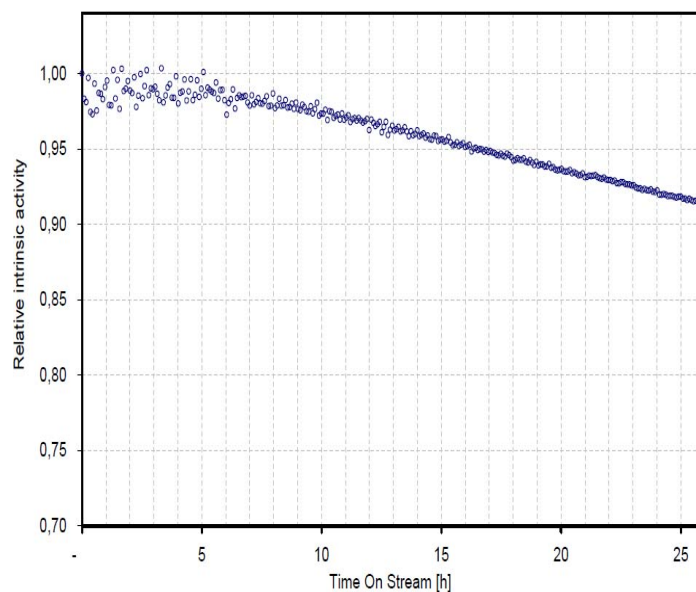
## Results:

The overall data analysis of the experiments is in progress. The plan of the experimental procedure is been shown in Fig. 2.



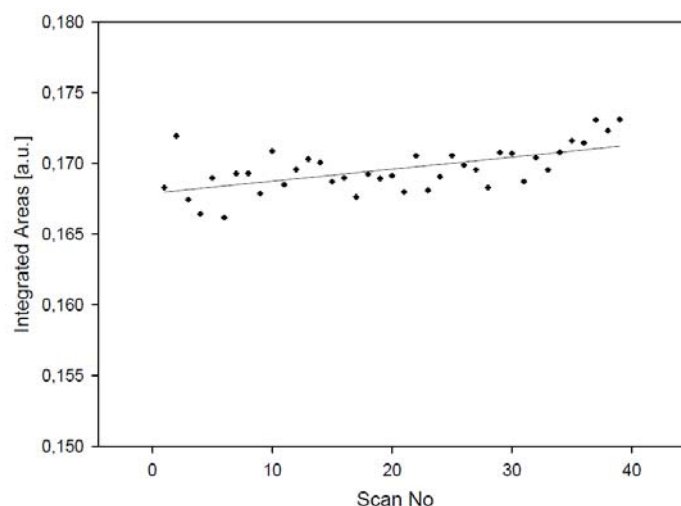
**Figure 2:** Experimental procedure: Pressure and temperature as a function of time.

The reduction of the catalyst was monitored by continuous XANES measurements and will give us valuable information about the phase transformations from  $\text{Co}_3\text{O}_4$ , in the fresh catalyst, to  $\text{CoO}$  and metallic Cobalt. An evaluation of the degree of reduction can be obtained by linear combination of the XANES profiles.



**Figure 3:** Deactivation profile of the FTS run (Normalized MS signal).

The reaction run was approx. 40 h. The MS signal clearly showed the deactivation of the catalyst as a decrease in CO conversion (Fig. 3). Detailed data analysis is in progress. However, preliminary XRD and XANES results show that no significant differences occurred in the bulk of the 10 nm cobalt crystals. XAS results will give us informations about possible reoxidation, carbidization or the formation of mixed metal-support compounds (Co-Al<sub>2</sub>O<sub>4</sub> amorphous structures). The diffraction spectra obtained from XRD will give us an indication of the cobalt cluster growth, the cobalt oxide formation and carbidization at the specific reaction conditions. Line broadening analysis of the Co crystallites will be done and provide information about possible growth during Fischer-Tropsch reaction. Integration of the XRD scattering bump representing the changes in the electron density due to accumulation of higher molecular weight hydrocarbons [5] are showing an increasing trend. However, the data are scattered and (low statistics) does not allow conclusive results. The phenomenon will be better observed by a fast readout detector and higher count rates (Fig. 4). Post mortem analysis of the sample failed due to reoxidation from a leak in the capillary during depressurization.



**Figure 4:** Normalized data of the integrated scattering bump at lower angles connected with the pores being filled by heavier hydrocarbons [5].

In addition to the in situ experiments, model catalysts (Co<sub>2</sub>C, CoO & CoAl<sub>2</sub>O<sub>4</sub>) were analysed to be used as supplementary standard compounds.

## References

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