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| | Experiment title: Combined XAS-XRD study of the deactivation of Co-based Fischer-Tropsch catalysts under realistic working conditions | Experiment number: 01-01-759 |
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Report:

The Fischer-Tropsch (FT) synthesis is currently being widely studied as a step in the gas-to-liquids (GTL) technology. The main purpose of this process is to produce synthetic petroleum substance. Supported cobalt catalysts are the favourable catalytic materials for synthesis of synthetic crude oil from synthesis gas produced from low-sulphur natural gas. Cobalt is usually chosen as the active component for its high activity, high selectivity to linear paraffins, long life-time and low water-gas shift activity.

Catalyst deactivation is a major challenge in Fischer-Tropsch synthesis. Deactivation effects are observed for catalysts on all commonly used supports. At present, there are not sufficient chemical knowledge to explain or to distinguish between the proposed deactivation mechanisms. The suggested mechanisms include cobalt surface oxidation [1-3], sintering [4,5] and solid state reactions rendering inactive cobalt phases [4,6]. In order to keep high catalytic activity it is essential to avoid activity decline. In case (order) to prevent rapid deactivation catalysts are usually promoted with a noble metals. Introduction of second metal such as rhenium into catalysts structure leads to stability improvement.

The partial pressures of steam, H₂ and CO in the reactor are crucial for the selectivity and deactivation of the catalysts in order to obtain realistic working conditions. Hence, the reaction should be run at high pressure (10-20 bar) and at relatively high conversion (50%) to expose the catalyst to a realistic working environment, closely resembling an industrial reactor [7]. With the established gas distribution system at SNBL and the capillary reactor we are now routinely able to achieve these conditions.

Experimental method:

XAFS were collected at the Co-K edge and Cr-mirrors were used for harmonic rejection. The XRD measurements were carried out at $\lambda=0.5$.

The sample cell consists of a stainless steel support and fitting system. The catalyst introduced to a quartz capillary and been placed between fittings. The capillary cell is heated by a hot air blower. The cell can operate with temperatures up to 500°C. The gas flow and the cell temperature can be controlled and monitored from outside the X-ray hutch. The cell is shown in figure 1. The XAS data were collected in transmission mode.

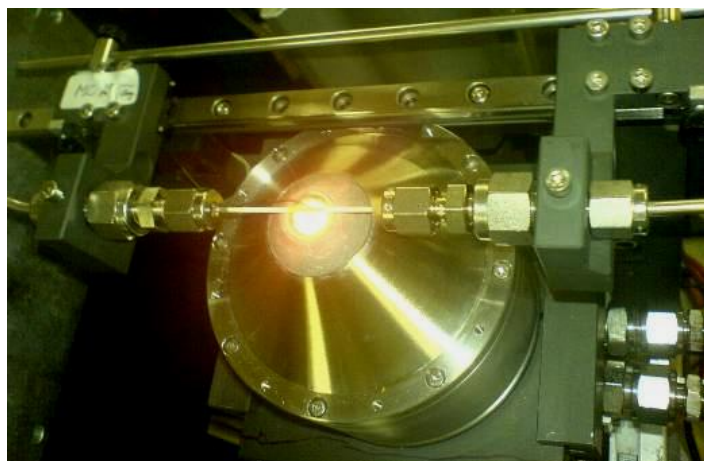


Figure 1: Cell set-up for combined in situ XAS-XRD

The experiments were performed in two steps. The first step was the reduction of the Co₃O₄ to obtain the active metallic phase prior to the reaction. The reduction was performed at 673 K during 4 hours with feed 5% H₂/He (20 ml/min) to obtain a sufficient fraction of metallic Co. The second step was Fischer-Tropsch reaction. The reaction was carried out at 453 K with a gas composition of 5% (CO+H₂)/He (20 ml/min). The stoichiometric ratio between H₂ and CO was 2.1. The gas line from the cell was heated to prevent blocking of the exhaust line. Full EXAFS and XRD scans were collected at room temperature before exposing the catalysts to the reaction gases. Short scans of the edge profiles of the Co edge (XANES) and diffraction spectra were collected during reduction and reaction. After FT-reaction the sample was cooled to room

temperature and scans of the entire EXAFS region were collected, combined with an extended XRD spectrum.

Results:

The overall data analysis of the experimental procedure is in progress. The plan of the experimental procedure is been shown in graph 1.

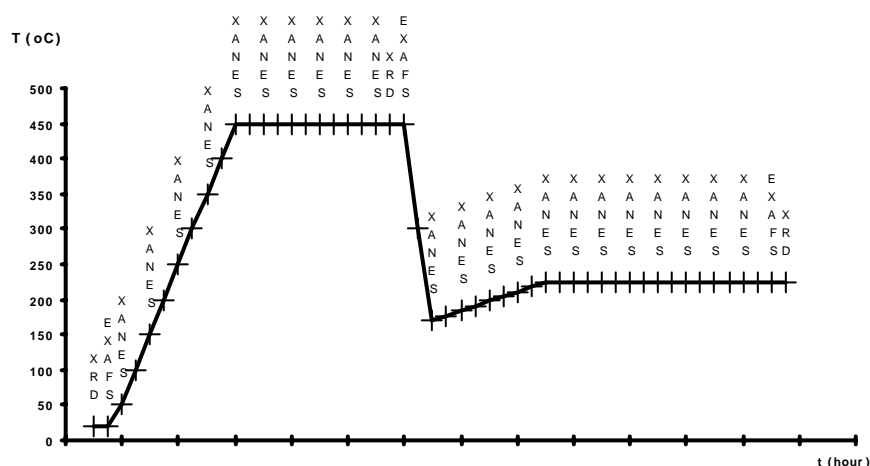


Figure 1: Experimental procedure. Used technique and temperature as a function of time.

The successful reduction of the catalyst witch was monitored by continues XANES measurements will give us valuable information about the phase transformations from Co_3O_4 , in the fresh catalyst, to CoO and metallic Cobalt. An evaluation of the degree of reduction can be obtained by the linear combination of the obtained XANES profiles.

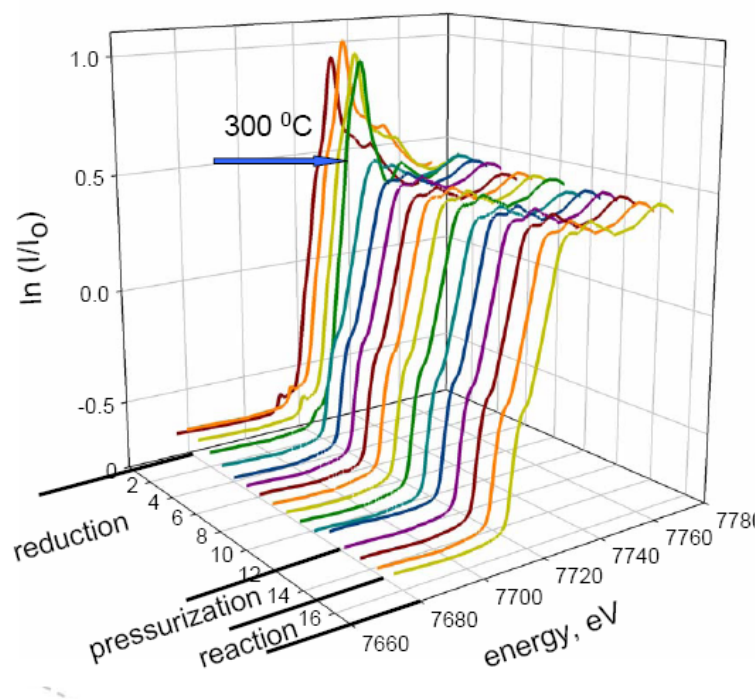


Figure 2: Raw data plot showing the transition for the oxide form of cobalts to the metallic Co during the reduction before subsequent pressurisation and FT reaction.

The diffraction spectra obtained from XRD before and after the reaction will give us an indication of the cobalt cluster size and the cobalt oxide formation, if re-oxidation process occurs under the specific reaction conditions. Calculation of the Co particle sizes before and after the Fischer-Tropsch reaction will be done using the Scherrer equation to reveal if sintering are contributing to catalyst deactivation. However, results in this particular run were hampered by Ni contaminations from the gas feeding system. This needs to be sorted out before next experiment period.

Moreover XANES results will give information about the change in oxidation states of Cobalt in the same way as they did in reduction nevertheless in opposite direction. In contrast with the XRD technique XANES results may also contain information about cobalt – substrate amorphous structures (Co/Al₂O₄) which are candidate inactive species that may result catalyst deactivation.

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