



	Experiment title: Combined XAS-XRD study of the deactivation of Co-based Fischer-Tropsch catalysts under realistic working conditions	Experiment number: 01-01-724
Beamline: BM01B	Date of experiment: from: 02.11.06 to: 07.11.06	Date of report: 12.11.2006
Shifts: 15	Local contact(s): Wouter van Beek	<i>Received at ESRF:</i>
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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. Supported cobalt is the favourable catalytic material for synthesis of long-chain hydrocarbons 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, 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].

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 17 keV.

The sample cell consists of Al windows and is heated by 2 cartridge heaters. The cell can withstand temperatures up to 600 °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.

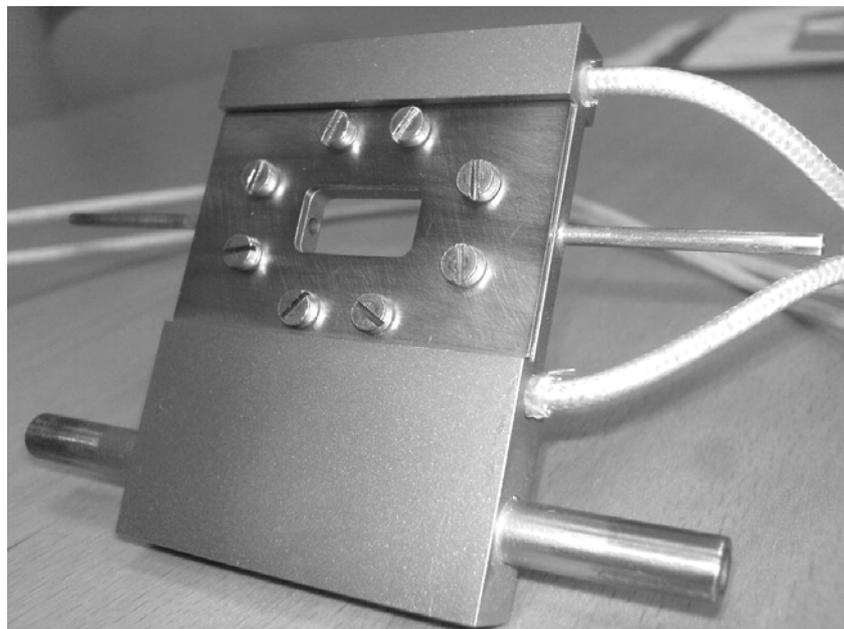


Figure 1: Cell set-up for combined in situ XAS-XRD

The experiments were performed in two steps. The first step was the reduction of the Co_3O_4 to obtain the metallic phase prior to the reaction. The reduction feed was 5% H_2 /He (20 ml/min) and the temperature and time was varied for the different samples to obtain a sufficient fraction of metallic Co. The Fischer Tropsch reaction was carried out at 210°C with a gas composition of 5%(CO+ H_2)/He (20 ml/min). The stoichiometric ratio between H_2 and CO was 2.1. The gas lines to and from the cell were heated for preheating the gas and 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 and diffraction spectra were collected during the reduction and the reaction. After four hours of 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 K-edge XAS of certain valence states of transition metal compounds often contain a pre-edge feature a few eV before the edge. This feature is useful because it yields structural and electronic information. The phase transformation of Co_3O_4 to CoO takes place at the same temperature for both the Re promoted and the unpromoted Co/ Al_2O_3 catalysts. The second reduction step transforming CoO to the metallic phase occurs more rapidly and at a lower temperature for Co-based catalysts promoted with Re. Linear combination of the spectra at 350 °C for this sample show that 70 % of the oxide is reduced to the metallic phase compared to 15

% for Co/Al₂O₄. A fraction of 50% reduction is obtained for the Co/Al₂O₄ by further increasing the temperature to 450 °C.

Linear combination of XANES profiles show that the cobalt is present as Co(0) and CoO before the reaction. When the catalysts are exposed to the reaction gases the fraction of metallic Co and CoO is unchanged. This indicates that re-oxidation of the cobalt metallic phase is not the reason for deactivation of the catalysts at the present reaction conditions.

The diffraction spectra obtained from XRD will give valuable information about the particle size of the Co₃O₄ prior to the reaction compared to the reduced Co metallic particles. Calculation of the Co particle sizes before and after the Fischer-Tropsch reaction will give useful information to clarify if sintering of the Co is responsible for the deactivation. Further analysis of the XAS and the XRD profiles are in progress.

References

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