



	<b>Experiment title:</b> The state of rhenium in cobalt-rhenium Fischer-Tropsch catalysts	<b>Experiment number:</b> 01-01-810
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 10.11.09 to: 16.11.09	<b>Date of report:</b> 01.03.2010
<b>Shifts:</b> 15	<b>Local contact(s):</b> Wouter van Beek	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): *Magnus Rønning *Nikolaos Tsakoumis *Alexey Voronov *Asmira Delic Department of Chemical Engineering, NTNU, N-7491 Trondheim, Norway		

## 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. In order to increase the amount of reduced cobalt in cobalt-based Fischer-Tropsch catalysts, a small amount of a second metal can be introduced into the catalyst system. Rhenium is a frequent choice as reduction promoter [1]. It is generally accepted that rhenium mainly catalyses the reduction of cobalt species interacting with the support [2]. Re promotion hardly affects the first step of reduction, but significantly reduces the reduction temperature for the second step [2-3]. This is because Re reduction occurs at about the same temperature as the first step of cobalt oxide reduction ( $\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$ ).

### Experimental method:

XAS were collected at the ReL<sub>III</sub> edge. Due to technical problems with the monochromator XRD was not available.

A quartz capillary *in situ* cell 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 Figure 1). The standard Swagelok 1/8 inch unions are fixed at a 45° angle in order to prevent liquid products accumulation inside the cell. A condenser tank was installed to collect the liquid products. All the cell parts were made from stainless steel. 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.

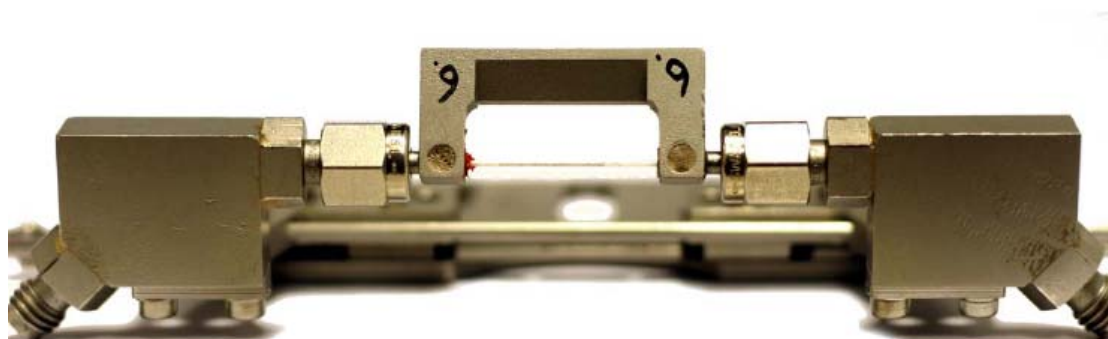


Figure 1. Setup for combined in situ XAS-XRD.

Two samples have been studied. The model sample contained Re only (1% wt.), and was treated by the standard reduction procedure given below. The Co-Re on  $\gamma$ -alumina FT catalyst with mean Co particle size of 10 nm was reduced to obtain the active metallic phase prior to the reaction. The reduction was performed at 673 K for 4 hours using a feed of H<sub>2</sub>/He mixture with ratio 1 (2.5 ml/min) to obtain a sufficient fraction of metallic phase. The second step was pressurisation at 170°C to 18 bar before Fischer-Tropsch reaction at 210°C. The reaction was carried out at 493 K with a gas flows CO: 0.7 ml/min, H<sub>2</sub>: 1.47 ml/min, He: 0.43 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. Full EXAFS scans were collected at room temperature before exposing the catalysts to the reaction gases. Quick EXAFS spectra were collected in continuous mode during both reduction and reaction steps and only during reduction step for the model Re catalyst.

## Results:

The overall data analysis of the spectra is in progress. The successful reduction of the catalyst which was monitored by continuous XAS measurements should give us valuable information about the phase transformations from  $[ReO_4]_{ads}$  in the fresh catalyst to rhenium oxides in lower oxidation states and metallic rhenium. There is a significant difference in the reduction behaviour of rhenium in the bimetallic catalyst and in the model sample. The model with 1% wt. Re reduces in the temperature range 513-553 K, while the bimetallic sample shows rhenium phase transformations up to 638 K. This temperature is close to the maximum temperature during reduction. XANES profiles of the two sequences are shown in fig. 1 and fig. 2.

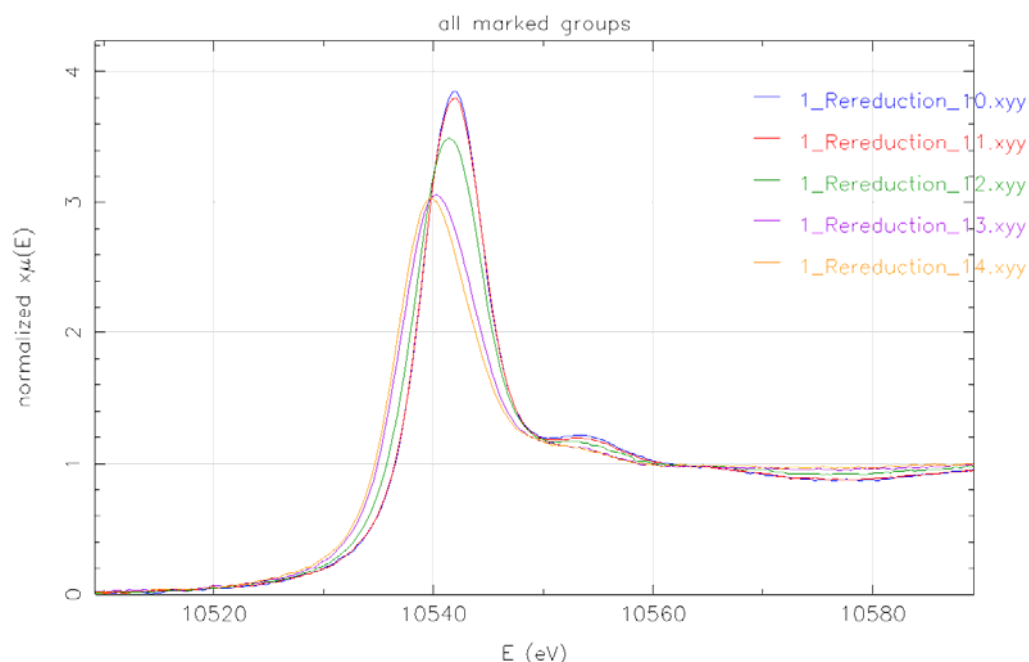


Figure 1. Re edge profiles during reduction of the model sample.

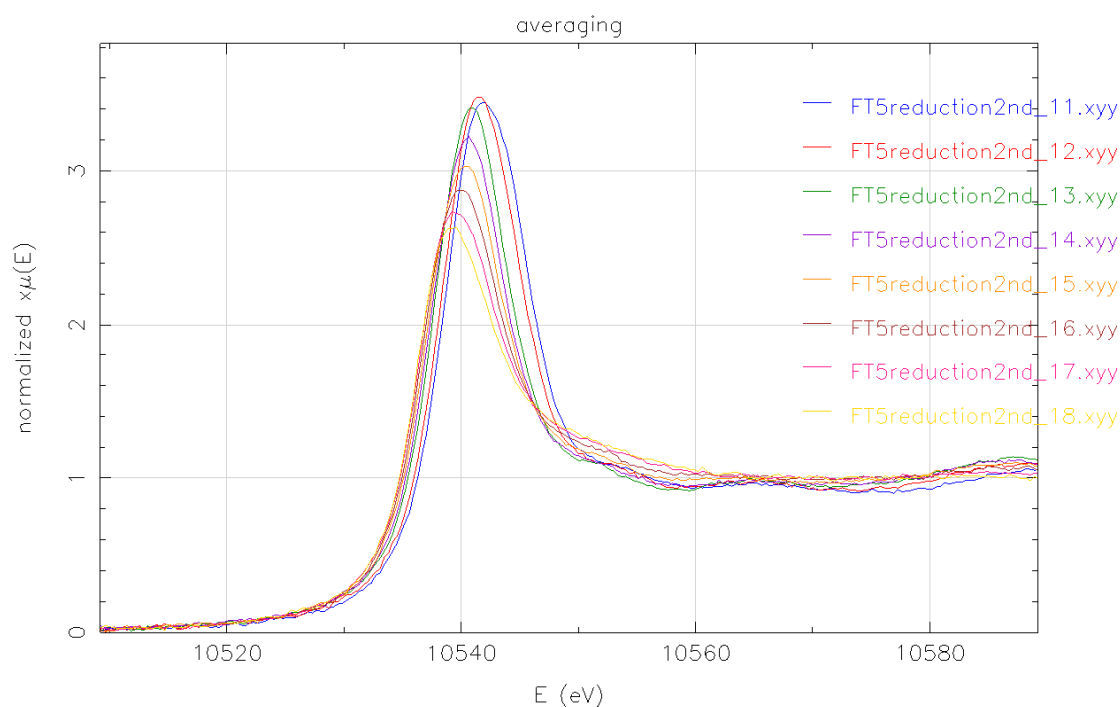


Figure 2. Re edge profiles during reduction of the Co-Re catalyst.

It can be seen from the figures that in both cases the rhenium oxide reduction is going continuously to a lower oxidation state.

Quick EXAFS on  $\text{ReL}_{\text{III}}$  gives nice time resolution, but the spectra are noisy. For data analysis several EXAFS spectra have to be averaged in order to obtain a decent signal to noise ratio. It is difficult to extract structural details about the local geometry of Re from the  $\text{ReL}_{\text{III}}$  edge EXAFS analysis of these samples. This shows that the next phase of this proposal where we want to explore the Re K-edge EXAFS is of high importance.

## References:

1. Mauldin, C.H., United States Patent 4,568,663, 1986.
2. Borg, Ø., et al., *Fischer-Tropsch synthesis over un-promoted and Re-promoted  $[\gamma]\text{-Al}_2\text{O}_3$  supported cobalt catalysts with different pore sizes*. Catalysis Today, 2009. **142**(1-2): p. 70-77.
3. Guzzi, L., et al., *Structure of Pt-Co/ $\text{Al}_2\text{O}_3$  and Pt-Co/ $\text{NaY}$  Bimetallic Catalysts: Characterization by In Situ EXAFS, TPR, XPS and by Activity in Co (Carbon Monoxide) Hydrogenation*. Topics in Catalysis, 2002. **20**(1): p. 129-139.