



	<b>Experiment title:</b> XAFS studies of the effect of water on rhenium promoted cobalt Fischer-Tropsch catalysts	<b>Experiment number:</b> CH-1632
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 08.06.04 to: 14.06.04	<b>Date of report:</b> 14.06.2004
<b>Shifts:</b> 18	<b>Local contact(s):</b> Wouter van Beek	<i>Received at ESRF:</i>
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## Report:

The Fischer-Tropsch synthesis is currently being widely studied as a step in the gas-to-liquids (GTL) technology. Supported cobalt catalysts continue to be the preferred catalyst system in Fischer-Tropsch synthesis (FTS).

Our previous studies [1,2], using a variety of methods, have shown that Al<sub>2</sub>O<sub>3</sub>-supported cobalt catalysts, and especially those promoted with reduction promoters such as Re, deactivate faster with addition of water, and that the effect of water is likely due to oxidation of cobalt. The catalysts were apparently oxidised in H<sub>2</sub>O/H<sub>2</sub> mixtures with a ratio much lower than anticipated for oxidation of bulk Co<sup>0</sup>. It was suggested that, because the promoter allows reduction of clusters interacting more strongly with the support, these cobalt clusters are more sensitive to deactivation by oxidation. Jacobs *et al.* have found that there are apparently two regimes in which water influences activity, a low partial pressure regime ( $P_{\text{H}_2\text{O}}/P_{\text{H}_2} < 0.6$ ) where the effect of water is reversible and a higher pressure regime ( $P_{\text{H}_2\text{O}}/P_{\text{H}_2} > 0.6$ ) whereby irreversible impacts on the activity are observed [3]. The effect of water on Pt-promoted Co catalysts has also been studied with XAFS [4]. The conclusion from this work is that at low H<sub>2</sub>O partial pressures the effect of water is due to adsorption inhibition, while for high water partial pressures, changes

in cobalt structure were observed. In addition, the effect of water apparently depends on the choice of support material [5]. For supports where there is a weak interaction with cobalt, such as silica, cobalt oxides produce highly reducible, large cobalt clusters after standard reduction (623 K, H<sub>2</sub>), whereas supports such as Al<sub>2</sub>O<sub>3</sub>, yielded much smaller clusters with a smaller fraction of cobalt being reduced.

In this study we have extended this work to include the study of Fischer-Tropsch catalysts used in reaction. The study involves catalysts used in FTS reaction on different supports with high and low surface area.

### **Experimental method:**

XAFS were collected for the Co-K absorption edge (7709 eV). We have used a Lytle type catalyst cell for reduction and water treatment. The water-cooled furnace consists of a sample cell with Kapton windows that can withstand temperatures up to 450°C. The gas flow and the cell temperature can be controlled and monitored from outside the X-ray hut. The catalysts were reduced in flowing 5%H<sub>2</sub>/He and H<sub>2</sub>O/H<sub>2</sub>/He at temperatures up to 450°C. The H<sub>2</sub>O:H<sub>2</sub> ratio was 10.

Short scans of the edge profiles of the Co K edge were collected while the catalyst samples were heated in the reducing gas mixture in order to follow the structural changes as a function of temperature. After reduction, the samples were cooled to room temperature before full scans of the whole EXAFS region were collected. The samples were subsequently heated to 250°C and exposed to the H<sub>2</sub>O/H<sub>2</sub> mixture for 1 hour.

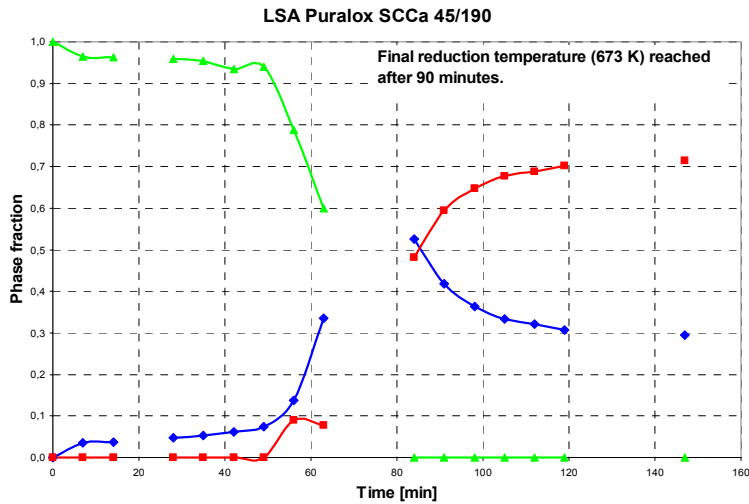
### **Results:**

XANES has been used as a phase-specific TPR in order to identify the different transition phases in the reduction of cobalt. Co K-edge XANES profiles in Figure 1 and 2 recorded during reduction show a 2-step reduction after the following scheme:

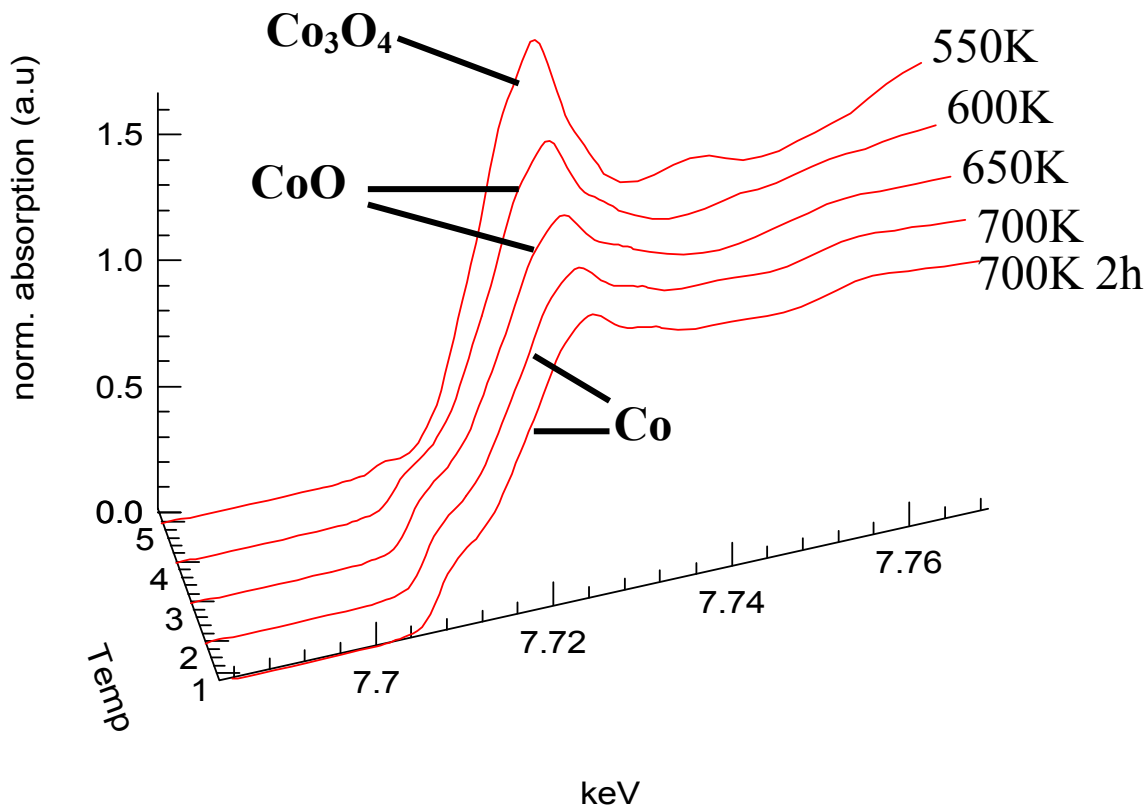


The results will be correlated with conventional TPR measurements to identify the extent of reduction and reduction temperatures.

The XANES TPR is clearly capable of identifying the different reduction steps and thus provide additional information to the TPR results. Linear combination of XANES profiles with those of selected reference compounds give a relatively precise estimate of the extent of reduction of the Co particles.



**Figure 1:** Fraction of Co phases during temperature programmed reduction. Co metal (red), Co<sub>3</sub>O<sub>4</sub> (green) and CoO (blue).



**Figure 2.** XANES profiles at different reduction stages

## References

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