



	Experiment title: XAFS studies of the effect of water on rhenium promoted cobalt Fischer-Tropsch catalysts	Experiment number: CH-1842
Beamline: BM01B	Date of experiment: from: 10.02.05 to: 17.02.05	Date of report: 21.02.2005
Shifts: 18	Local contact(s): Wouter van Beek	<i>Received at ESRF:</i>
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Report:

The water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is an important step in the production of H_2 by steam reforming of hydrocarbons. Recently, the WGS reaction has received renewed interest as a key step in fuel processing to reduce the CO level in hydrogen produced for PEM fuel cell applications [1]. Cu is usually preferred as the active component in such WGS catalysts because of its proven activity at low temperatures. However, since Cu is prone to deactivation, there is a need for catalysts with improved activity and stability compared to the traditional CuO-ZnO- Al_2O_3 system. We have previously collected XAS data on a series of Cu-based WGS catalysts (exp. CH 1531) where we followed the structural changes in the catalyst particles during reduction in H_2 and CO, respectively. The characterisation of the Cu-based catalysts is coming towards the end and will be published in a special issue of Catalysis Today. We want to extend the XAFS characterisation of selected samples by studying the catalyst under WGS reaction conditions. We also want to compare the Cu-based catalyst with Au containing catalysts. Recently, it has been reported that small, ionic gold particles on $\text{CeO}_2/\text{La}_2\text{O}_3$ supports show superior WGS activity at low temperatures compared to Cu-based systems [2]. We have prepared Au-containing samples where we have used our knowledge from the Cu-based system to improve metal dispersion and oxygen storage capability of the catalysts. The water-gas shift activity for these catalysts has been tested in a fixed-bed reactor over a wide temperature range and

show promising WGS activity. We want to use information obtained from EXAFS analysis in combination with complementary techniques such as chemisorption, TEM, XRD and TPR to increase the understanding of the catalyst properties.

Experimental method:

XAFS were collected for the Cu-K and Au-L₃ edges.

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 hutch.

The catalysts containing were reduced in flowing 5% H₂/He at 260°C and hold for 2 hours and short scans of the edge profiles of the Cu 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. Full scans of the whole EXAFS region were collected at room temperature before and after the reduction of the samples. The catalysts were passivated in 2% O₂/He for 1 hour at room temperature and full EXAFS scans were collected.

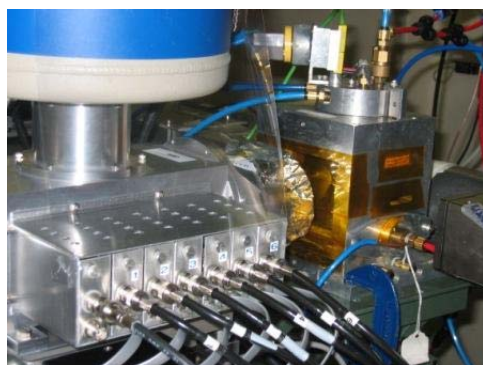


Figure 1. In situ EXAFS cell

The same cell was used for in-situ treatment (He, O₂ or H₂) of the Au-catalysts. Full scans of the whole EXAFS region were collected at room temperature and after the treatments. An Au-TiO₂ catalyst supported on carbon nanofibres was reduced for 1 hour in flowing 5% H₂/He at 300°C. Calcination was performed at 300°C in 5% O₂/He and the temperature was hold for 2 hours. The same temperature was used for thermal treatment in pure He for 2 hours. Short XANES scans were collected during the heating. Data were collected in fluorescence mode using a 13 element solid state detector. EXAFS scans have been performed for identification of different phases in the catalysts to compare various preparation methods. The EXAFS analyses have also been used to find the particle size of Au.

Results:

The EXAFS at the Au-edge gives information on particle size and composition. The results from the in situ experiment show that the particle size of gold increases after thermal treatment in different gases, shown in figure 2. The EXAFS scans show that gold is present as Au(0) after preparation of the catalyst. After oxidation in flowing 5%O₂/He at 300°C for 2 hours, 15% of the Au is present as Au(III). The Au(III) can be fully reduced again in 5%H₂/He at 300°C for 1 hour. The data are currently being correlated with other physiochemical data.

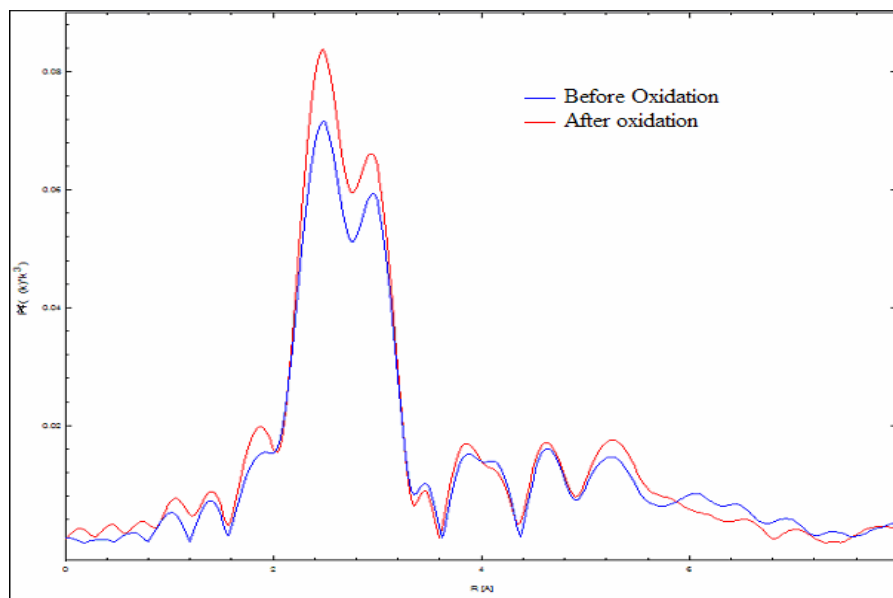


Figure 2: The Fourier transformation of the Au EXAFS spectra before and after in-situ oxidation for gold deposited on titanium oxide on carbon nanofibres.

EXAFS scans of powder samples indicates that preparation of Au-catalysts from colloid-solution gives metallic gold deposited on the support without any thermal treatment.

Because of problems with the beamline vacuum system we lost about 24 hours of beam time, restricting the number of samples compared to the original plan.

References

- [1] C. Song, *Catal. Today*, **77** (2002) 17-49
- [2] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science*, **301**, Issue 5635 (2003) 935-938