ESRF	**Experiment title:** **Au/TiO_2 and Au/Ce-La-O_x catalysts on carbon nanofibres**	**Experiment number**: 01-01-705
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Report:

The water-gas shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is an important step for production of hydrogen 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]. Highly dispersed gold nanoparticles in association with a partially reducible oxide (ceria, titania) have been shown to exhibit high catalytic activity in the water-gas shift (WGS) reaction [2] and in oxidation reactions such as CO oxidation [3]. The catalytic performance of Au can be defined by three major factors: contact structure, support and particle size. High catalytic activity is achieved by keeping the particle sizes of both Au and oxide particles below 10 nm. The structure and morphology of the oxide support material seems to be very important for the catalytic activity [4]. Fu *et al.* [4,5] demonstrated that gold cations on a ceria based support can catalyse the commercially important water-gas shift reaction. The ionic gold catalysts show superior WGS activity at low temperatures compared to traditional Cu-based systems. There is a debate regarding the structure and external form of nanoparticles of gold, arising from the inherent difficulties in trying to physically characterise such small particles.

Experimental method:

XAFS were collected at the Au-L_3 edge and Cr-mirrors were used for harmonic rejection.

The water-cooled furnace consists of a sample cell with Kapton windows that can withstand temperatures up to 400°C. The gas flow and the cell temperature can be controlled and monitored from outside the X-ray hutch. The cell set-up is shown in figure 1.1. Since the metal loadings are relatively low, data were collected in fluorescence mode using a Lytle fluorescence detector with filter (Ga, 3μ).

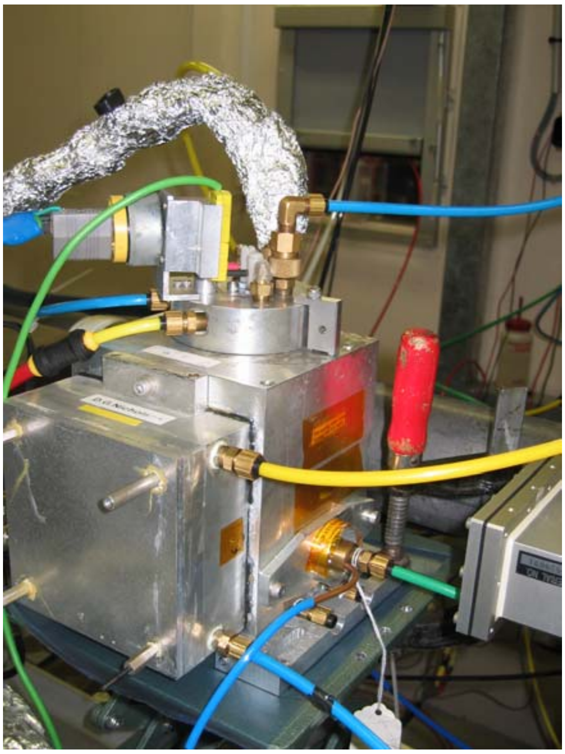

Figure 1:Cell set-up for in situ XAS during WGS reaction

The feed consisted of 5%CO/He (30 ml) bubbled through a sparger with H_2O to give a relevant WGS feed composition. The stoichiometric relationship between H_2O and CO was 1:1. The line from the sparger to the cell was wrapped with heating tape to avoid condensation of the water vapour in the tube. Full EXAFS scans were collected at room temperature before exposing the catalysts to the reaction gases. The catalysts were heated to 300°C in flowing CO/H_2O/He and held at that temperature for 2 hours. Short scans of the edge profiles of the Au edge were collected under reaction conditions. The sample was cooled to room temperature and the gas was changed to pure He before scans of the entire EXAFS region were collected.

Results:

The activity of Au-based catalysts depend strongly on particle size. Comparison of the coordination numbers of Au before and after reaction gives information of particle growth that causes deactivation of the catalysts. The Fourier transformation of gold deposited on TiO_2 supported on CNF before the reaction is shown in figure 1. The structural parameters are given in table 1.

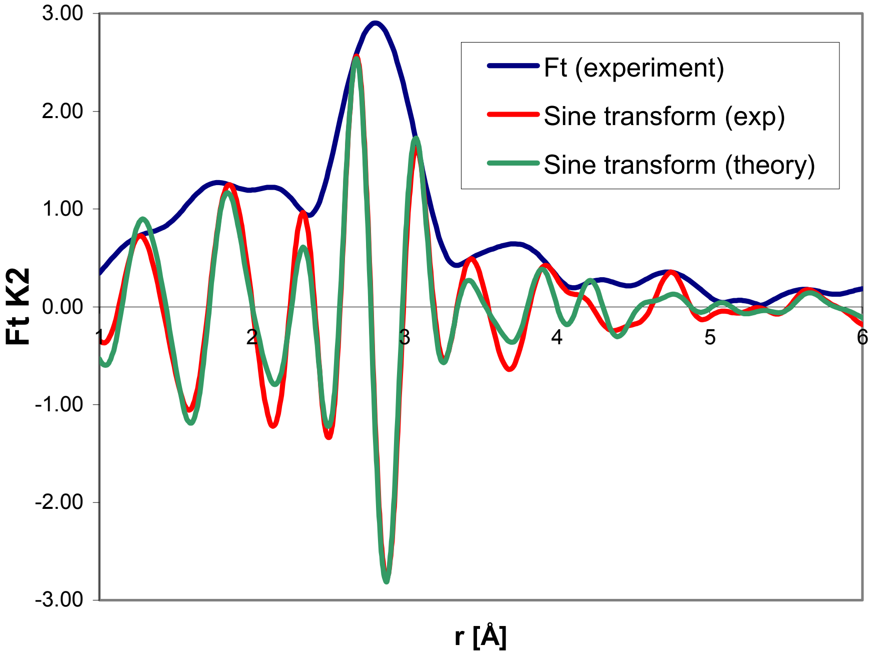

Figure 2: The Fourier transformation of the EXAFS before the WGS reaction

Table 1: EXAFS results at the Au L_{III} edge

Shell	N	R(Å)	$\Delta\sigma^2$ (Å^2)
Au-Au	6.8	2.82	0.019
Au-Au 2.nd	2.3	4.01	0.021
Au-O	0.2	2.14	0.006

The results obtained from the EXAFS analysis shows that with decreasing coordination numbers the interatomic distance of the first (R_1) and second (R_2) coordination shell decreases. This clearly shows the presence of a contraction in the interatomic distances that amounts to approx. 2 % for the first coordination shell. EXAFS analysis of samples after the reaction show that the coordination number increases after the treatment which indicate larger gold particles on the surface.

XANES provides information about the oxidation states of the gold species. Linear combination of XANES profiles show that the gold is present as Au(0) and Au(I) before the reaction. When the catalysts are exposed for the reaction gases the fraction of metallic and ionic gold are changing. XANES spectrums obtained after the reaction in flowing He show that the metallic fraction has increased compared to the results obtained before the reaction. This can indicate atom migration of Au during the reaction that leads to a smaller fraction of Au interacting with the support. The fraction of Au(0) and Au(I) for gold deposited on titanium oxide supported on CNF is given in figure 3.

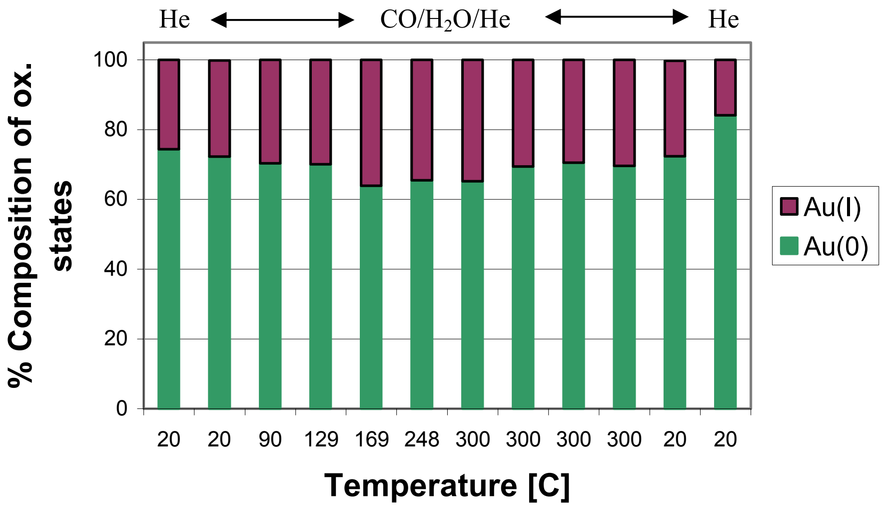

Figure 3: Percentage distribution of oxidation states of Au

Further analysis of the XANES profiles and EXAFS profiles is ongoing.

References

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