



	Experiment title: In situ XAS study of Cu, Pt and Au containing low-temperature water-gas shift catalysts	Experiment number: 01-01-685
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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 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]. 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-Al₂O₃ system. We have previously collected XAS data on a series of Cu- and Au-based WGS catalysts (exp. CH 1531 and CH 1842) where we followed the structural changes in the catalyst particles during reduction in H₂ and CO, respectively [2]. 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 [3] and in oxidation reactions such as CO oxidation [4]. Recently, it has been reported that small, ionic gold particles on doped ceria show superior WGS activity at low temperatures compared to Cu-based systems [5]. The nature of the active site of Au-based catalysts is not known. Despite much debate, there are still contradictory results on the nature of the gold oxidation state and active site.

Experimental method:

XAFS were collected at the Au-L₃ edge and Cr-mirrors were used for harmonic rejection.

The Lytle type 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. Since the metal loadings are relatively low, data were collected in fluorescence mode using a Lytle fluorescence detector with an appropriate filter (Ga, 3μ).

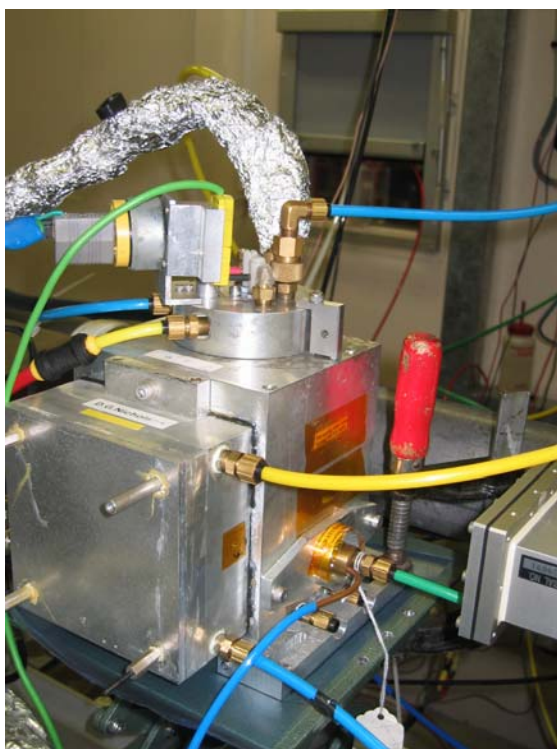


Figure 1: Lytle cell set-up for WGS

The feed consisted of 5%CO/He (30 ml) bubbled through a sparger with H₂O to give a relevant WGS feed composition. The stoichiometric relationship between H₂O 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/H₂O/He and held at that temperature for 1 hour. Short scans of the edge profiles of the Au edge were collected under reaction conditions. The sample was cooled to room temperature in He before additional EXAFS scans were collected.

Results:

The EXAFS at the Au-edge gives information on particle size and composition. The Fourier transformation of the EXAFS of gold deposited on TiO₂ supported on CNF before and after the reaction is shown in figure 2. The structural parameters are presented in table 1. The results from the data-analyses of the spectra indicates that the structural parameters does not change significantly after the reaction.

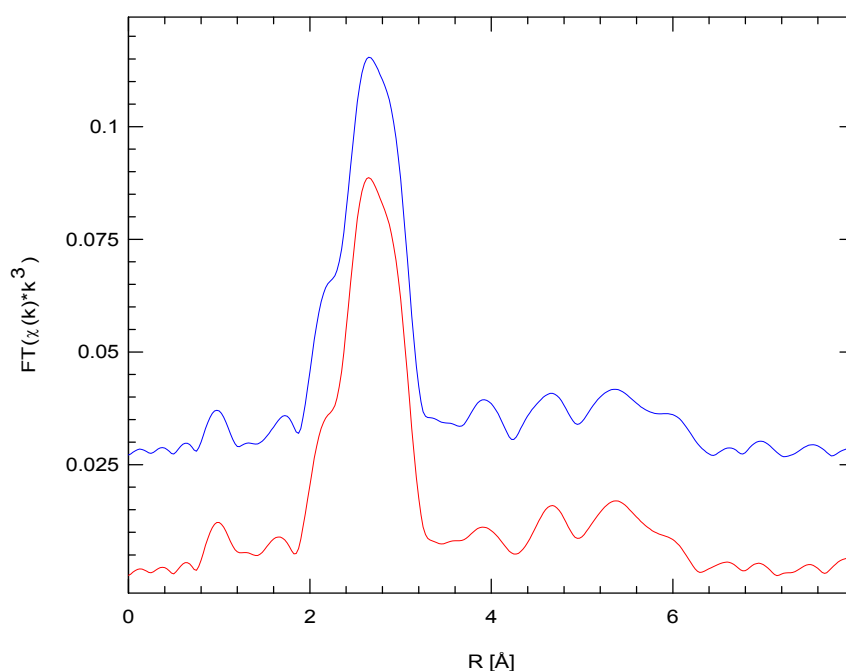


Figure 2: The Fourier transformation of the EXAFS before (red) and after (blue) the WGS reaction

Table 1: EXAFS results at the Au L_{III} edge before and after the reaction

Shell	Before reaction			After reaction		
	N	R(Å)	$\Delta\sigma^2$ (Å ²)	N	R(Å)	$\Delta\sigma^2$ (Å ²)
Au-Au	11,310	2.86	0.016	11.03	2.86	0.015
Au-Au 2.nd	3,010	4.04	0.022	2.12	4.06	0.014

XANES provides information about the oxidation states of the gold species. The XANES analyses show that the composition of oxidation states of gold changes after exposure to the reaction mixture of CO/H₂O/He. This can be seen from the increased amount of Au(III). Further analysis of the XANES profile and EXAFS profile is in progress. Approximately 4 shifts of beamtime were lost due to technical problems and thunderstorms.

References

1. C. Song, Catal. Today, 77 (2002) 17
2. M. Rønning, F. Huber, H. Meland, H. Venvik, D. Chen, A. Holmen, *Catalysis Today*, 100 (2005) 249-254

3. Q. Fu, S. Kudriavtseva, H. Saltsburg, M. Flytzani-Stephanopoulos, Chemical Engineering Journal, 93 (2003) 41
4. M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, J. Catal. 144 (1993) 175
5. Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, Science 301 (2003) 935