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Report:

Introduction

Gold catalysts are interesting for the oxidation of CO at low temperatures, which is important both from academic and technical viewpoint [1]. One of the important factors for the activity is that the catalysts are finely dispersed and this can be e.g. achieved by depositing small gold particles on metal oxide supports, i.e. using gold colloids [2,3]. Recently, we have also prepared Au-Ag based catalysts, applying the colloidal method. In order to introduce undesired carbon impurities when high gold concentration (>5 wt%) are necessary [4], we presently prepare gold catalysts also by other methods .

EXAFS is a valuable and appropriate tool to characterize these catalysts in more detail because it can give information on the oxidation state, the particle size of these catalysts, and the extent of alloying in Ag-Au catalysts, all important factors for the catalytic activity [1]. Since at least silver may easily oxidise at room temperature, *in situ* reduction is necessary to obtain information on the extent of alloying in Ag-Au based catalysts. One of the questions is also, how the catalysts behave under CO-oxidation conditions.

In this study, we first tested our newly designed *in situ* EXAFS setups – using on the one hand a small capillary serving as plug-flow reactor and at the same time as X-ray transmittant cell (due to its thin wall); on the other hand a pellet reactor cell. These cells were tested in a first step by investigation of the temperature programmed reduction of some Cu/ZnO catalysts (cooperation with MPI Mülheim).

In a next step we investigated the Au and Au-Ag based catalysts *ex situ* and *in situ*. The catalysts were in a first step completely reduced and then the re-oxidation behaviour was tested. Due to the fact that a gas of 0.25%CO/21%O_2/He was not delivered by the supplying company to ESRF in time, we could only mix a CO containing gas with approximately 800 ppm CO.

Experimental

For the experiment, the samples were diluted with BN and either pressed as pellet (11 mm diameter, for the pellet in situ cell) or used as sieved fraction (capillary cell). The corresponding gas mixture was fed to the *in situ* cell with a gas supply system consisting of mass flow controllers and valves for changing between different gases. The outlet of the cell was connected to a mass spectrometer for gas analysis and the exhaust system at SNBL.

The gold catalysts were investigated *ex* situ, since they were fully reduced. The gold-silver catalysts were treated in 5%H_2/He for reduction and re-oxidation behaviour was studied in 5%O_2/He. The catalysts were hold at a temperature of 100, 200, 300, and 400 °C for ca. 1 hour. Since a crystal change is necessary when studying the catalysts at the Au L3- and Ag K-edge, the experiments were repeated for the second absorption edge.

The reduction of the test catalysts (Cu/ZnO) was also performed in 5% H_2/He using a ramp rate of 1 K/min. The same catalyst was once loaded as pellet and once in the capillary. Both faster absorption spectra (limited to the XANES region) and on-line gas analysis were compared. The content of Cu^{2+},Cu^+, and Cu^0 species was determined by principal component analysis.

Results:

The comparison of the same Cu/ZnO catalyst once in the capillary and once in the pellet cell is shown in Figure 1. The start of the reduction is quite similar in both cases. Also the extent of the different Cu-species is comparable. However, the reduction in the capillary cell proceeds much faster, both found by the XANES spectra and on line gas analysis of hydrogen and water by mass spectrometry in the *in situ* cell.

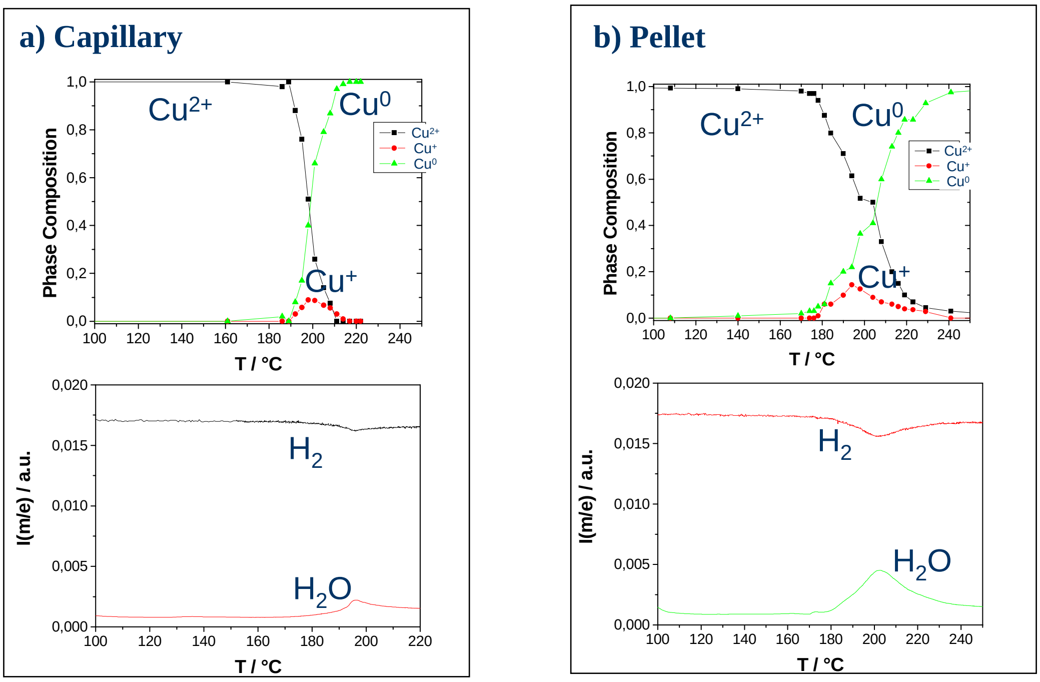

Figure 1: Comparison of the reduction of a Cu/ZnO catalyst in two different types of *in situ* cells.

The results clearly show that for dynamic changes the capillary cell is more useful than the pellet cell. However, for static experiments, as used in the case of gold catalysts, the pellet cell is also appropriate, giving better signal/noise ratios at SNBL.

Investigation of Au/TiO_2 and Au/ZrO_2 catalysts prepared by the colloidal route showed that gold was in reduced state, in accordance with previous EXAFS measurements [5]. The same was found for catalysts prepared by flame-synthesis, although the flame has oxidizing character. Probably, the high temperature used during this process, cause the reduction of the gold particles.

In our further work, we focussed on the Au-Ag catalyst system, prepared by the colloidal method. An $Au\text{-}Ag/TiO_2$ catalyst was investigated for this purpose in detail in the as prepared state, during reduction in hydrogen at 100, 200, 300, 400 °C, after reduction at room temperature, and then during oxidation at the same temperatures in oxygen. Some of the results are depicted in Figure 2.

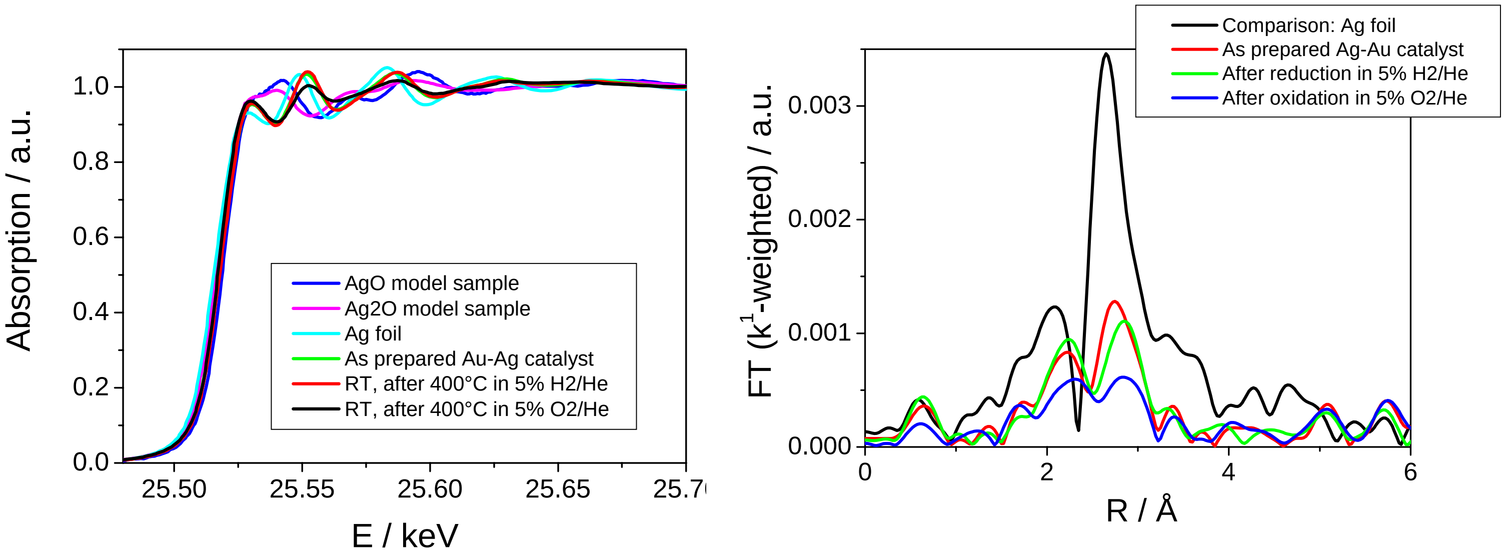

Figure 2: XANES and Fourier transformed EXAFS spectra (Ag,K-edge) at selected treatment steps of the $Ag\text{-}Au/TiO_2$ catalyst, some model samples are shown for comparison.

The XANES spectra at the Ag,K-edge (and also at the Au L3-edge, not shown) reveal that the $Au\text{-}Ag/TiO_2$ catalyst seems to be in reduced state, already after preparation. This can be explained by the use of gold-silver colloids for the impregnation of the catalysts. No change is principally found after reduction in hydrogen at 400 °C. The distinct difference to the metallic silver foil can be traced back to some Au-Ag alloying. This can be also seen in the Fourier transformed spectra.

Some oxidation of silver in $5\%O_2/He$ is found after treatment at 400 °C, but still some silver remains in reduced state, probably due to alloying with gold. The oxidation of silver starts at about 300 °C, according to spectra taken under reaction conditions at these temperatures. Hence, during low temperature CO-oxidation in air both gold and silver should remain in reduced state. Structural analysis under CO-oxidation conditions, however, still has to be undertaken. With 800 ppm CO in 21% O_2/He it was difficult to detect catalytic activity and structure at the same time, as desired.

Conclusions:

The study has shown that alloying of gold-silver based catalysts has been achieved by starting from gold-silver colloids and was proved in this *in situ* EXAFS study. It appears that both gold and silver are in reduced state after the preparation process. Silver is stable in metallic (alloyed) state up to 300 °C. It will be interesting to determine structure and activity at the same time. In the meantime we have also prepared further Au-Ag catalysts by other methods.

Our *in situ* EXAFS setup, using a pellet and a capillary cell has been compared during the reduction of Cu/ZnO catalysts. Both setups give principally the same results, however, the capillary cell is to be preferred, if dynamic studies are performed [6,7].

Several papers have already emerged from this beam time, partially in combination with further EXAFS beamtimes [8-10].

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