	Experiment title: <b>In situ EXAFS and XANES study of the active surface formation in highly active silica supported Zn promoted Cu catalysts</b>	<b>Experiment number:</b> <b>26-01-192</b>
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<b>Shifts:</b> 21	<b>Local contact(s):</b> Serge Nikitenko	
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Dr. Didier Grandjean* <sup>1</sup> , Prof. A. Bliek <sup>2</sup> , Dr. J.C. van den Heuvel* <sup>2</sup> , Prof. B.M. Weckhuysen <sup>1</sup> <sup>1</sup> Department of Inorganic Chemistry and Catalysis, Utrecht University <sup>2</sup> Universiteit van Amsterdam - Instituut voor Technische Scheikunde		

## Report:

Although Zn promoted Cu catalysts, extensively used in the water gas shift reaction, ester hydrogenolysis, methanol synthesis and decomposition have been investigated for some decades, the nature of the active sites as well as the role of promoters are still debated and as a consequence, catalyst design and optimisation is rather empirical. Three different models of the active surface have been proposed in the literature that have all in common the major role played by the reduction temperature both on the nature of the active site and the catalytic activity of these systems.

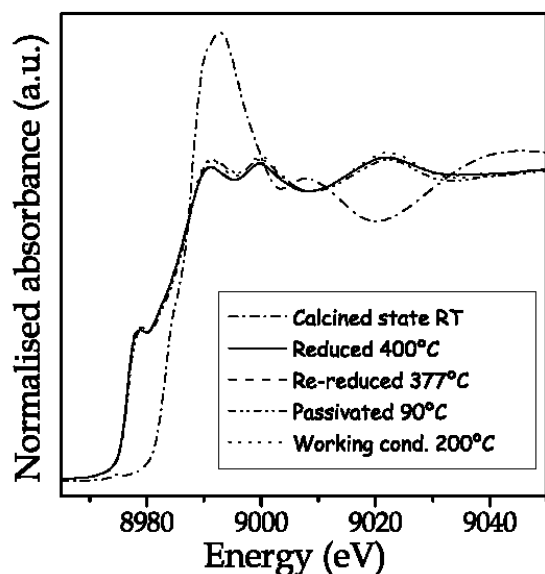
We have recently prepared a new series of highly active Zn promoted silica supported Cu catalysts by homogeneous deposition. LEIS investigations that we carried out on these samples showed that the most active catalyst, i.e. the one reduced at high temperature (673 K), was strongly enriched with ZnO at the surface. In order to address the central question concerning the nature and the formation of the active surface in these Cu/ZnO/SiO<sub>2</sub> catalysts it was essential to fully characterise the oxidation state and the local order around the Cu and Zn species under different gas atmospheres or reaction conditions with a local probe technique such as X-ray absorption spectroscopy.

The main objective of this experiment was to use *in situ* EXAFS and XANES at the Cu and Zn K-edges in two different highly dispersed silica supported Cu-based catalysts i.e. non promoted Cu/SiO<sub>2</sub> binary system and Zn promoted Cu/ZnO/SiO<sub>2</sub> ternary system. These two catalysts were measured already calcined before, during and after reduction in H<sub>2</sub>/He flow at 3 different temperatures 473, 573 and 673 K corresponding to 3 different catalytic activities (673 K has the highest activity). In the Zn promoted system that is the most active catalyst, the reduction treatment was followed by a passivation in N<sub>2</sub>O/Ar flow and a re-reduction to test the effect the N<sub>2</sub>O gas used in the chemisorption method has on the active site. Finally, this catalyst was tested in working condition (methanol synthesis) in H<sub>2</sub>/CO<sub>2</sub> flow.

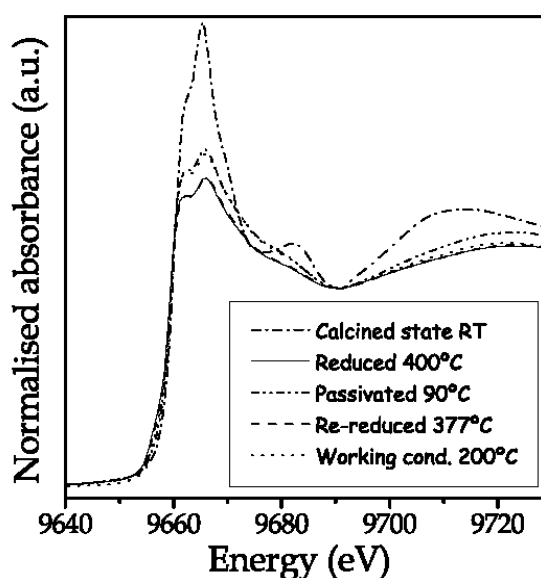
The samples have been studied as self-supporting wafer placed in our in-house controlled atmosphere cell operating at 1 atm that allows full *in situ* treatment. The corresponding gas mixtures used in these reactions were prepared in the experimental hutch from pure gases. In general, EXAFS was recorded before and after the treatments whilst short XANES measurements were made during the same treatments. Both Cu and Zn K-edges were measure in a single scan that was repeated 2 or 3 times to improve the signal to noise ratio. All the prepared catalysts could be measure successfully and the data obtained were in general of good quality.

EXAFS data are being currently analysed in order to elucidate the structures of both Cu and Zn phases present in the catalysts. However, XANES measurements carried out in the Zn promoted Cu/ZnO/SiO<sub>2</sub> ternary system can already point out that large changes are occurring in the local structure and electronic properties of Cu and Zn atoms during the different treatments.

Figure 1 and 2 that present the normalised XANES spectra respectively measured at the Cu and the Zn K-edge in the Cu/ZnO/SiO<sub>2</sub> catalyst is a good example of the quality of the data we obtained in this run and clearly shows the changes of the XANES spectra at the Cu and Zn-K-edges during the different treatments.



**Fig 1:** Normalised XANES spectra at the Cu K-edge in Zn promoted silica supported catalyst during the different treatments.



**Fig 2:** Normalised XANES spectra at the Zn K-edge in Zn promoted silica supported catalyst during the different treatments.

Figure 1 clearly shows that copper oxide is transformed into pure Cu metal during the reduction process. Moreover, the smeared-out wiggles that can be seen in this spectrum indicate that Cu is forming very small particles certainly in the nanometre range. The following treatments on the other hand, have only a very moderate effect on the state of the Cu once this one has been reduced. Cu remains indeed always in a metallic state during all the subsequent treatments. However, a small increase in the intensity of the wiggles of the XANES spectrum could point out a small increase in the particle size. XANES spectra at the Zn K-edge, presented in Figure 2, indicate that the Zn local order is also undergoing large changes during the different treatments. The very strong attenuation of the wiggles of the XANES spectra during the reduction process is certainly the sign of a strong amorphisation and dispersion of the Zn phase during the reduction process. The passivation, on the other hand, seems to produce the opposite effect but to a much smaller extent. The formation of an amorphous mixed Zn/Si oxide phase could be a possible interpretation of these data.

These preliminary results already show that very valuable information on the Cu/Zn silica supported catalysts will be gain from these measurements when the full analysis of the data will be completed.