



	Experiment title: Effect of catalyst structure and composition on the water-gas shift activity for Cu-based hydrotalcite catalysts	Experiment number: CH-1531
Beamline: BM01B	Date of experiment: from: 28.10.2003 to: 01.11.2003	Date of report: 02.11.2003
Shifts: 12	Local contact(s): Hermann Emerich, Wouter Van Beek	<i>Received at ESRF:</i>
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Report:

The water-gas shift (WGS) reaction is attracting renewed attention because of its importance in hydrogen production for use in PEM fuel cells [1]. The WGS reaction can be used to reduce the CO level in the reformed fuel: $\text{CO} + \text{H}_2 \rightarrow \text{CO}_2 + \text{H}_2$. Cu is usually preferred as the active component in such WGS catalysts because of its high activity at low temperatures. Since Cu is prone to deactivation, there is a need for catalysts with high activity and stability compared to the traditional CuO-ZnO-Al₂O₃ system. The stability of the catalyst can be improved by introducing other components such as Ce [2] and by using novel preparation methods. We have synthesised a series of Cu-based catalysts derived from hydrotalcite structures. It is known that catalysts of hydrotalcite-like compounds possess high activity and thermal stability and high metal dispersion. We also wanted to compare the reduction behaviour of the catalysts in H₂ and CO, since CO is one of the main components in the feed from the reformer.

The present study is an *in situ* XAFS study of the reduction of Cu-Zn-Ce-containing WGS catalysts using a Lytle catalyst cell (Figure 1) and 5% CO/He and 5% H₂/He as reduction gases. The influence of Ce promotion on Cu dispersion and Cu crystal size will also be addressed in the detailed data analysis.

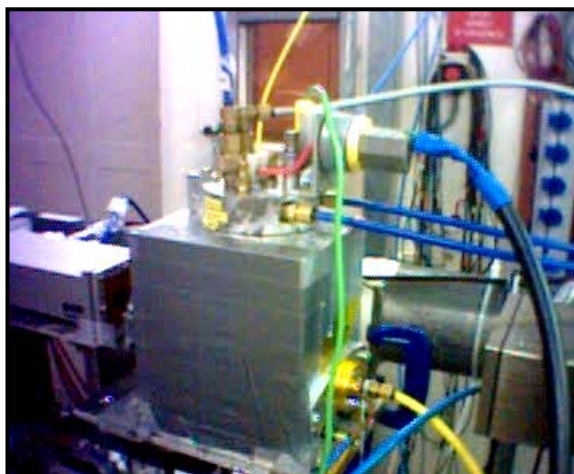


Figure 1: The Lytle cell at work in transmission mode at the SNBL

Experimental method

XAFS were collected for the Cu-K and Zn-K absorption edges and for some samples the Ce-K edge. This was the first measurements using the new monochromator crystals at the Swiss-Norwegian beamline BM01B. The Si(111) reflection was used for the Cu and Zn K-edge data, whereas for the Ce K-edge the Si(311) reflection was preferred. The Si(311) monochromator crystal was at the time not tested and tuned, and was hence not yet giving optimal data quality. The Ce K-edge data still seem adequate for a qualitative comparison of the samples.

The water-cooled furnace consist 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 hut.

The catalysts were reduced in flowing 5%CO/He or 5%H₂/He at temperatures up to 400°C.

Short scans of the edge profiles of the Cu and Zn edges 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. After reduction, the samples were cooled to room temperature before full scans of the whole EXAFS region were collected. This was done for both the Cu and the Zn K-edges, and also for the Ce K-edge for the samples containing Ce.

Results

The aim of the study is to find the effect of Ce promotion on the catalysts and correlate these findings with activity and stability tests. It is very likely that catalyst activity and stability can be correlated to structural properties of the active materials in the catalysts such as particle size and composition. Preliminary XAFS analysis indicate that the data are able to give information about the local environment of the different elements in the catalysts. The results show that Cu is more easily reduced in CO than in H₂. As shown in Figure 2, Cu is starting to be reduced at temperatures below 150° C in 5% CO whilst by using 5%H₂ the reduction starts at approximately 200° C. As expected, ZnO is not reduced even by raising the temperature to 400° C.

In the more detailed structural analysis we want to investigate the influence of Ce promotion on Cu dispersion and Cu crystal size. Bimetallic interactions and structure-activity correlations will also be addressed.

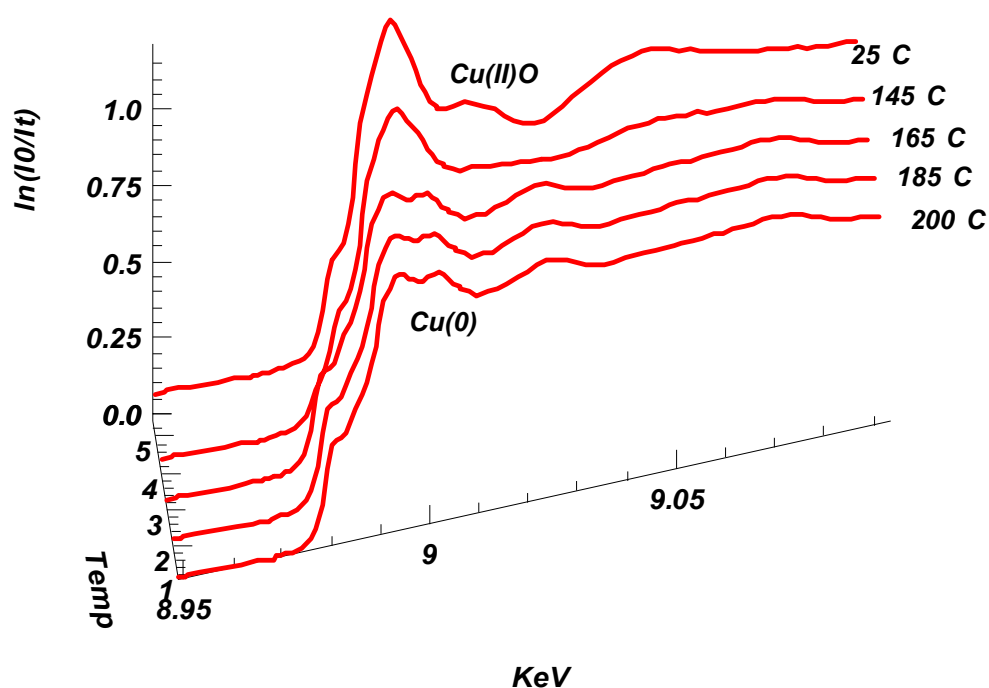


Figure 2: The Cu K-edge profiles of a Cu-Zn-based WGS catalyst showing the transition from CuO to Cu metal during heating in 5% CO/He

References

- [1] C. Song, Catal. Today, 77 (2002) 17-49
- [2] Y. Li, Q. Fu, M. Flytzani-Stephanopoulos, Applied Catalysis B 27 (2000) 179–191