

Experimental report: 31-01-46

Understanding of CO₂ hydrogenation mechanism and deactivation by H₂O on Cu-Zn based catalysts

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We performed the experiment 31-01-46 at the Swiss-Norwegian beamline BM31 in the period from 24 to 29 January 2018 (15 shifts). Cu and Zn K-edge XANES and EXAFS spectra were measured on a set of Cu/ZnO/zeolite based catalysts, with different loadings of Cu in the range of 2 to 6 %. The catalysts were filled between two beds of quartz wool in the quartz capillary of 1 mm diameter and 20 μ m wall thickness. In situ XAS and XRD measurements were performed in transmission mode at temperature range between 30 and 260 C and pressure range between 1 and 15 bar.

Firstly, samples was activated with a flow of diluted hydrogen (5 vol. %) and heated at a rate of 1°C min⁻¹ to 260 °C (P=15 bar). We observed stepwise reduction of CuO to metallic Cu (Fig. 1) however oxidation state of Zn remained unchanged. After 2 hours of activation in hydrogen, gas composition was switched to the reactive CO₂/H₂ mixture (10 ml/min) containing 25 vol. % of CO₂ and 75 vol. % of H₂, while measuring the Cu and Zn K edges XANES and EXAFS (waiting until steady stay mode).

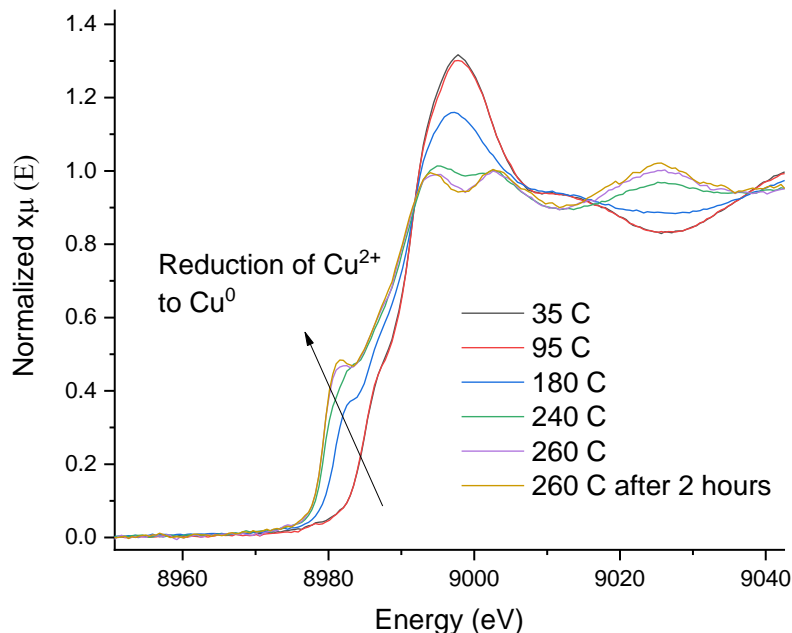


Fig. 1. Cu K-edge during 2 wt. % Cu/ 2 wt. % Zn/ Zeolite Y (Si/Al=12) catalyst activation in 5 vol. % H₂.

After that, it was performed experiment at transient conditions upon cycling dry and wet atmospheres (by addition of 5 vol. % of H₂O vapor to the feed gas mixture by using saturator). A mass spectrometer was used to evaluate online the CO₂ conversion as well as formation of methanol. Despite of decreasing of CO₂ conversion in the presence of H₂O, any significant

changes in Cu K-edge (Fig. 2a) and Zn K-edge (Fig. 2b) was not observed. We have repeated this transient experiment ($\text{CO}_2+\text{H}_2/ \text{CO}_2+\text{H}_2+\text{H}_2\text{O}/ \text{CO}_2+\text{H}_2/ \text{CO}_2+\text{H}_2+\text{H}_2\text{O}$) several times, however Cu and Zn XANES spectra remained stable. Abovementioned result was attributed to surface changes on metallic Cu and/or ZnO nanoparticles during inhibiting with water vapor, while bulk Cu/ZnO (which account to 95-98 % of total Cu and Zn) remain in unchanged state.

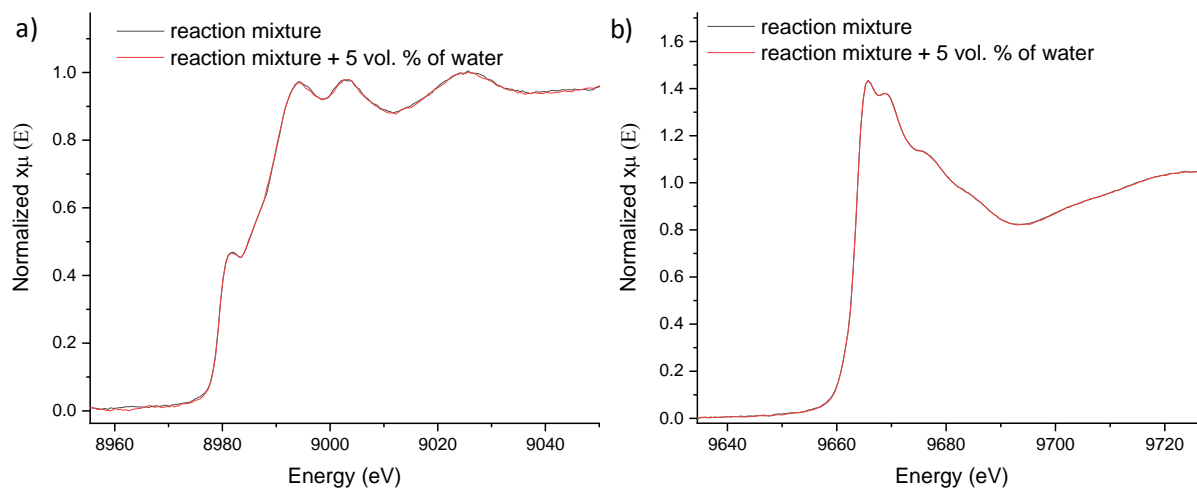


Fig. 2. Cu K-edge (a) and Zn K-edge (b) before and after addition of 5 vol. % of water vapour to reaction mixture containing 25 vol. % of CO_2 and 75 vol. % of H_2 .

We have performed the same experiment for samples containing 6 wt. % of Cu and sample containing 2 wt. % of Cu supported on zeolite Y with Si/Al ratio of 30.

At the time of writing, only partially processing of the PXRD data has been performed. We observed significant sintering of Cu phase during reduction and activation in H_2 and formation of FCC metallic Cu phase. At the same time we didn't observe formation of Cu/Zn alloy.

In addition during the last 1 shift we were able to perform test measurement concerning other catalytic system (Pd/ZnO catalyst which shows very promising activity and selectivity in CO_2 hydrogenation to methanol) to assess the feasibility of XAS for this type of catalyst. Due to the lack of time we have performed in situ reduction only (Fig. 3), however obtained results make allow shedding the light on high reactivity of this material.

Unlike to Cu/ZnO based system, we do observed reduction of ZnO and formation of Zn^0 . However we still cannot make conclusion regarding participation of reduced Zn species in

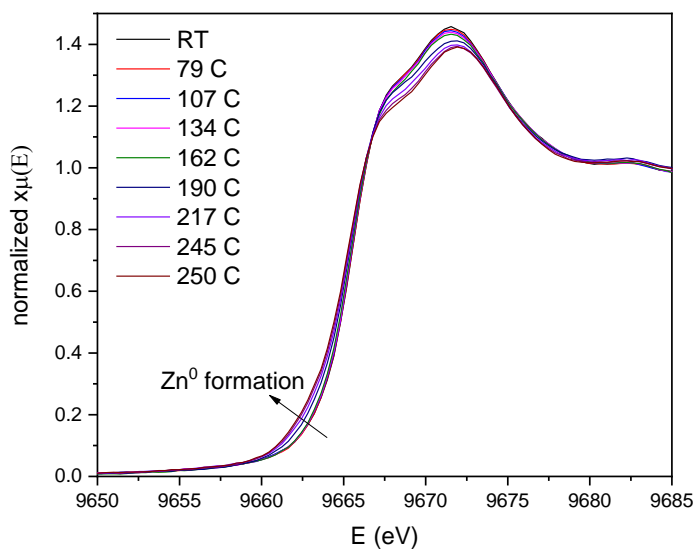


Fig. 3. *In situ* Zn K-edge spectra during Pd/ZnO catalyst reduction in H_2 .

catalytic mechanism based on this finding alone. To reach definite and trustworthy conclusions about the oxidation state and structure of actual active sites in the methanol synthesis reaction additional time resolved experiments should be performed.

Results, obtained during this beamtime allow us to make one step closer to understanding mechanism of CO₂ hydrogenation to methanol. Based on preliminary data processing we can conclude that activation and dissociation of H₂ takes place on metallic Cu nanoparticle surface, but not on Cu/Zn alloy like as it was thought before. Based on these XAS and XRD data we are preparing the manuscript for further publication.

I would like to note the exceptionally kind help of local contacts during this beamtime, which allowed us to continue the experiment even when we were faced with heat-gun problem during the weekend.