

Experimental report: CH 5057

In situ XRD and XAS measurements of a highly selective copper zinc catalyst for carbon dioxide hydrogenation to methanol

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We performed the experiment CH 5057 at the Dutch-Belgian beamline BM26A in the period from 12 to 17 July 2017 (15 shifts). Cu and Zn K-edge XANES and EXAFS spectra were measured on a set of fresh and used methanol synthesis catalyst (20 wt. % Cu/ 7 wt. % Zn/zeolite) and commercial CuO/ZnO/Al₂O₃ catalyst. 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 measurements were performed in transmission mode at temperature range between 30 and 260 C and pressure range between 1 and 15 bar. Unfortunately, we were not able to perform in situ XRD measurements, since XRD is done at BM26A on a very limited basis in combined experiments, while EXAFS is the core technique at this beamtime.

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. At the same time we do observed minor reduction of ZnO phase as well (Fig. 1). 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. During catalytic experiment we observed the increasing of methanol selectivity during first 12 hours on stream, therefore it was interesting to correlate XAS changes of fresh and used (“selectivated”) catalysts during in situ XANES and EXAFS measurements.

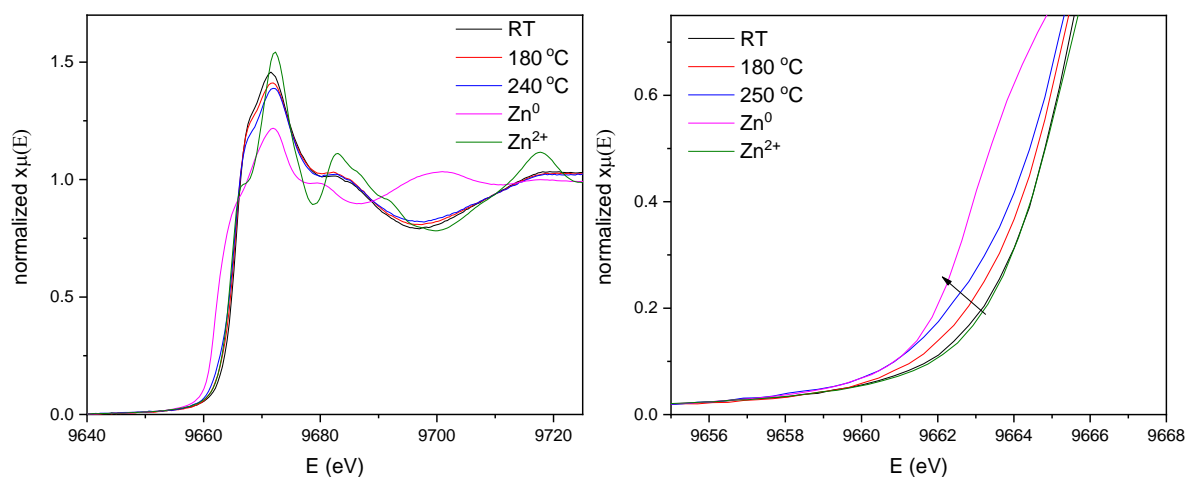


Fig. 1. Zn K-edge during Cu/ZnO/ZSM-5 catalyst reduction in H₂.

At the same time we found that reduction of Zn occurs much easier for the sample which was already “selectivated”. This demonstrates that the reduction of zinc has a higher induction barrier on the fresh catalyst, and, more in general, that the tendency of zinc to reduce is

proportional to the selectivity of the catalyst with respect to the production of methanol. In addition, the initial relatively high content of reduced Zn(0) of “selectivated” catalyst ($\approx 10\%$ accordingly to LCF) suggests that the “selectivated” catalyst maintains the altered structure even after it is removed from the reactor, as also evidenced by the initial high methanol selectivity of the reused catalyst (based on MS data). This signifies the increase of the zinc oxide reducibility during carbon dioxide hydrogenation reaction and incorporation of zinc species onto the surface of the copper particle that lower pure metallic copper sites. This modification of the catalytic sites results in continuous reduction of carbon monoxide production and the enhancement of methanol selectivity, because metallic copper and copper-zinc oxide interface are active sites for rWGS.

Results, obtained during this beamtime allow us to make conclusion regarding participation of reduced Zn species in catalytic CO₂ hydrogenation to methanol. We attributed gradual increasing of methanol selectivity to reduction of ZnO phase and incorporation of zinc species onto the surface of the copper particle. At the same time additional transient experiment as well as in situ XRD measurements should be performed in order to validate this hypothesis. I would like to note the exceptionally kind help of local contacts during this beamtime.