Thermal analysis as a guide for preparation of supported Cu-catalysts

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Cu/Zn based catalysts are of industrial importance for the methanol synthesis. The combination of thermogravimetric analysis (TG), differential scanning calorimetry (DSC) coupled to mass-spectrometry has been applied to study the thermal decomposition of Cu/Zn hydroxycarbonates, which are used as precursors for the active catalyst. The Temperature Programmed Reduction (TPR) and Mass spectrometry (MS) methods were used to study the reduction kinetics of the oxide precursor transforming into the active catalyst. Original TG, TPR, MS and DSC profiles as well as the results of a formal kinetic analysis of the calcination and activation processes are compared with transformations taking place in the solid phase, which has been studied by means of in-situ XRD and NEXAFS spectroscopy.

 A series of hydroxycarbonate precursors with different Cu/Zn molar ratios (40/60, 60/40, 80/20) was synthesized under conditions reported as an optimum for the catalytic performance. The samples contain primarily two crystalline phases *Aurichalcite*, $(Cu,Zn)_5(OH)_6(CO_3)_2$, and *Zincian malachite*, $(Cu,Zn)_2(OH)_2CO_3$.

At least four formal decomposition stages of CO_2 and H_2O evolution cause the main weight loss in the TG experiments. Kinetic parameters of each stage were estimated using a well-described procedure [1]. The best fit quality for all studied samples was obtained for a four-step competitive reaction model. The experimental TG dependences are adequately described by an *n*-th order equation and a 3D *Jander* diffusion equation. Based on the determined kinetic parameters, constant weight loss experiments were performed and the effect on porosity of the calcined material was investigated. The influences of gas flow, sample weight, and water transfer conditions on the reaction pathway were studied. The presence of H_2O vapour in the reaction feed accelerates the decomposition and dramatically changes both the TG reaction profile and the catalytic performance of the resulting catalyst (Fig. 1).
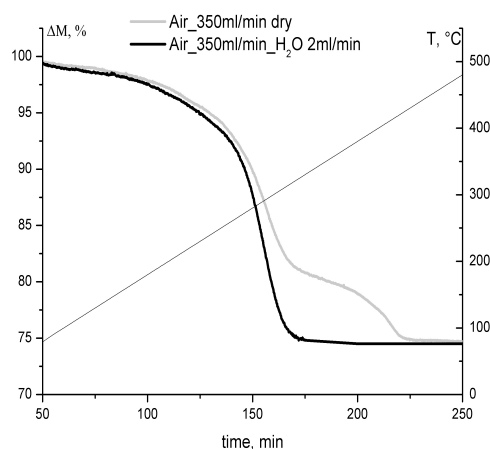

Figure 1. Effect of water vapour on the TG decomposition profile [2]

The thermokinetic analysis of the catalyst reduction revealed that the process proceeds via two consecutive stages formally described by the Prout-Tompkins autocatalytic equation [3]. The last step of reduction yielding the active metallic Cu phase was found to be limited most likely by the residual carbonate decomposition [4]. Based on these findings the calcination and activation protocols were optimized with respect to the desired catalyst composition.

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