

Controlling the Microstructure of CuO/ZnO Systems by Preparation and Thermal Processing from Hydroxycarbonate Precursors

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Introduction

Mixed copper-zinc hydroxycarbonates are well known precursors for the preparation of ZnO supported Cu catalyst widely used for methanol synthesis or reforming [1]. The high performance of this system is in the first place due to the high dispersion and thermal stability of the copper particles produced. In addition, evidence was found recently that the microstructure, in particular microstrain of the copper particles, resulting from the strong interaction of the two components ZnO and Cu is correlated to catalytic activity [2]. These features are presumed to depend critically on both the characteristics of the precursors including not only the phases present but also their microstructural features such as compositional and structural disorder or particle sizes which in turn result from the conditions under which they were prepared and the conditions under which they are further processed.

Samples with different preparation histories were subjected to thermal decomposition under various conditions and monitored in situ by TG-MS and microscopy. We focused especially on the effects the post-precipitation treatments induce on the precursors and their implications on the decomposition process and the structural properties of the resulting materials.

Experimental and Results

The precursors of varying Cu/Zn ratios prepared via the coprecipitation method according to the constant-pH or decreasing-pH method respectively with computerized control of pH and precipitation times comprise the crystalline phases rosasite, $(\text{Cu}_x\text{Zn}_{1-x})_2(\text{OH})_2\text{CO}_3$, aurichalcite and hydrozincite, $(\text{Cu}_x\text{Zn}_{1-x})_5(\text{OH})_6(\text{CO}_3)_2$. In addition, the presence of amorphous phases of similar stoichiometry as for the crystalline phases is considered.



Calcination in air of samples shows a carbonate species decomposing separately at considerably elevated temperatures which magnitude correlates roughly to the amount of aurichalcite of the precursors. Its amount strongly decreases along with the initial period of ageing where transformation and crystallization takes place via hydroxy-rich intermediates. In addition, a concomitant decrease of the amount of nitrate remaining from the preparation is observed. The presence of this anion exerts an extremely adverse effect on the formation of the high temperature carbonate species. Both processes ageing and washing shift the decomposition temperatures to higher values. However, the absence of this specific feature in well crystalline reference material finally indicates that the origin is that of a microstructural interaction. It is assumed that an amorphous aurichalcite-like material forms a coating of the particles which decomposes at lower temperatures thus trapping the residual carbonate.



Conditions during thermal decomposition leading to elevated water partial pressures sensitively reduce the amount of the high temperature carbonate. On the other hand, the growth of the resulting copper-oxide crystallites is promoted. This effect is provoked by both sample masses or heating rates and the anionic composition, i.e. the amount of hydroxide of the precursors. Finally, the structural implications of the calcination conditions, accompanying the evolution of the stable carbonate species were investigated.

No significant influence of the phase composition or the crystallite sizes of samples containing aurichalcite and hydrozincite on the crystallite sizes of the resulting CuO and ZnO are observed. However, the proportion of (cupro)-hydrozincite correlates to the amount of microstrain found for the final copper crystallites. In contrast, a strong decrease of the crystallite sizes of copper with increasing amounts of zinc of the copper-rich precursors is found. This decrease correlates to the copper/zinc ratio for rosasite which again depends on the method of preparation.

[1] T. Matsuhisa, in *Catalysis Vol. 12- A specialist periodical report*, The Royal Society of Chemistry, Cambridge, (1996) p. 20
 [2] M.M. Günter, T. Ressler, B. Bems, C. Büscher, T. Genger, O. Hinrichsen, M. Muhler, R. Schlögl. *Catal. Lett.* 71, 37-44 (2001).