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Correlations between the nature of mixed Cu/Zn-hydroxycarbonate precipitates, their thermal decompostion behaviour and the crystallinity of the oxides obtained thereby

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Mixed copper / zinc-hydroxycarbonates are well known precursors for the preparation of ZnO supported Cu catalyst [1]. Their manufacture is a deliberate multi-step process starting with the precipitation of the precursors from aqueous solution followed by ageing, calcination and reduction. Structural features such as cristallite sizes or surface areas of the resulting catalysts critically depend on a complex interplay of the characteristics of the precursors corresponding to the method of preparation and the way of further processing. Focusing on the relationship between the nature of precursors and the outcome of the calcination thermogravimetry coupled to mass spectrometry (TG-MS) was used to monitor the decomposition process in situ.

Samples with varying Cu/ Zn ratio were prepared according to different methods with aid of computerized control of precipitation parameters [2]. Different crystalline phases form during the ageing process from initially amorphous materials. Depending on Cu/Zn ratio and method of precipitation various mixtures of hydrozincite / aurichalcite, ($(Cu_xZn_{x-1})_5(OH)_6(CO_3)_2$), rosasite ($(Cu_xZn_{1-x})_2(OH)_2CO_3$) and amorphous constituents result.

Multiple decomposition events reveal the presence of different phases for the amorphous materials due to the distinct precipitation behaviour of Cu and Zn. The TG-MS patterns of the crystallized precipitates may be approximated as superpositions of the single phases. However, samples containing aurichalcite show in addition an exclusive evolution of CO_2 at temperatures beyond 400 °C not observed for pure and highly crystalline material indicating interactions of the decomposing phases. Formation of this species is highly sensitive to the presence of nitrate remaining from the preparation.

Decomposition of the crystalline precipitates result in smaller oxide particles than for the amorphous material due to the presumed greater atomic dispersion of Cu and Zn. Aurichalcite produces larger CuO crystallites than does rosasite. High water partial pressures operative during calcination strongly promote the decomposition process - especially of aurichalcite and the high temperature carbonate phase - and thus affect the crystallinity of the resulting materials. Further details on the decomposition process were gained by in-situ imaging.

Literature:

[1] T. Matsuhisa, Catalysis Vol. 12- A specialist periodical report, The Royal Society of Chemistry, Cambridge, **1996** p. 20. [2]. B.Bems, M.Schur, A. Dassenoy, R.Schlögl, PCCP **2001,** submitted