XXXIV. Jahrestreffen Deutscher Katalytiker
21. 3. –23. 3. 2001 Weimar

Investigations on selected preparation steps in the formation of Copper-Zinc-Hydroxycarbonates

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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]. One of the reasons for the still ongoing research concerning the chemical and structural identity of these precursors is the presumed conjunction to the activity of the final catalyst [2,3]. The influence of the chemistry of the precursors in its broadest sense including not only the Cu/Zn ratio or phase composition but also microstructural features e.g. compositional and structural disorder or particle sizes on the characteristics of the copper finally obtained is yet scarcely considered.

In spite of the often observed influence of the preparation conditions on the nature of the precipitates comparative studies on the effects of various synthesis procedures often lack control over reaction parameters and the variations of them and in turn reproducibility of the results. Hence, there is an ongoing discussion about the importance of the crystalline phases rosasite ($(Cu_xZn_{1-x})_2(OH)_2CO_3$) and aurichalcite ($(Cu_xZn_{x-1})_5(OH)_6(CO_3)_2$) on activity of the final catalyst.

We have investigated selected preparation steps during and after the precipitation and the transformations of the phases thereby. Especially, we focused on the effects of the post precipitation procedures of aging and washing on the thermal decomposition properties.

Experimental and Results

The hydroxycarbonates were prepared according to the coprecipitation method with computerized control and monitoring of the precipitation parameters such as pH and rate.

The effects of aging and washing on the characteristics of the solids were studied in detail on samples of nominal composition of Cu:Zn = 70:30 mol%. At the 70:30 sample both rosasite and aurichalcite crystallize simultaneously followed by a long

term decrease of the amount of aurichalcite. Thermogravimetric measurements coupled to mass spectrometer (evolved gas analyses) show drastic changes of the patterns synchronous with the aging. In particular, the pattern obtained at the time of the crystallization is exceedingly broadened with multiple events and a noticeable exclusive high temperature evolution of CO_2. Upon prolonged aging a high temperature shift of the decomposition temperature is found. A similar pattern to that found at the peak of the crystallization was obtained after repeated washing of a 70:30 sample, although no significant changes could be detected by XRD and IR after each washing step. These results indicate microstructural alterations of the precipitates presumably with contributions of X-ray amorphous hydroxy-rich materials.

For a better understanding and the evaluation of the rates of the transformations in the course of the precipitation and aging processes titration curves were recorded. The titrations were performed in both ways increasing and decreasing and at two different speeds. Different pathways of the precipitate formation were readily observed and self-evident by visible changes of the precipitates. Particularly, the phase transformation within the increasing titration at slow speed has been investigated by XRD. The initial precipitate consists of pure gerhardtite ($Cu_2(OH)_2NO_3$) that rapidly transforms into malachite at higher pH. The rate of transformation was determined at different temperatures and metal to carbonate ratios.

In summary, we confirm the strong influence of the conditions of the precipitation especially the aging and washing on the characteristics of the materials obtained.

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[3] M.S.Spencer, Catal. Lett. 66 (2000) 255.