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Coprecipitation of copper/zinc compounds in metal salt–urea–water system

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Abstract

A study of composite and structural changes of particles prepared by coprecipitation in solutions of Cu^{2+} and Zn^{2+} salts at different starting molar ratios of the corresponding metal nitrates (4:1, 2:1, 1:1, 1:2, 1:4) in the presence of urea is described. The effects of the initial concentration ratios and the ageing time on the final product were discussed in some detail. The final solids were characterized by SEM–EDS, XRD. On ageing at 85 °C, the change from initially amorphous particles to crystalline structure takes place and the results depend on the metal ratio used.

Keywords: Coprecipitation; Spectroscopy; X-ray methods; Grain size; Nanocomposites

1. Introduction

The composite Cu/Zn-oxide particles have been used as catalysts for water-gas shift reaction and methanol synthesis.[1–3] These solids were mostly prepared by precipitation in aqueous solutions of the corresponding metal nitrates in the presence of either sodium or ammonium carbonates that yielded hydroxycarbonate precursors. The later were then converted to mixed oxides by calcination. The importance of identifying phases of the intermediates and products with different Cu/Zn ratios was stressed by Stone and Waller[1]

The homogeneous alkalization of metal salt solutions by hydrolysis of urea was widely explored for the preparation of pure or mixed metal oxides.[4–7] In mixed systems, various phases can form. Such solids composed of spherical particles were always amorphous, while particles of other morphologies were crystalline.[5]

Whittle et al.[2] showed the morphological and composite changes of non calcined precursors of copper zinc oxide (Cu:Zn = 2:1) formed during the coprecipitation from metal nitrate solutions by sodium carbonate, the influence of aging, and its effect on catalyst properties. By reducing the concentration of carbon dioxide with air which was passed through the reaction mixtures, they reported about Cu-rich nanoparticles formation. The number and size of the product particles were strongly dependent on the ageing time.

Two methods of preparation of Cu/Zn-oxide catalyst were compared in the study of Shishido et al.,[3] i.e., coprecipitation with sodium carbonate in aqueous solutions of metal nitrates, and homogeneous precipitation using urea hydrolysis. The latter method yielded a better catalyst for hydrogen production by steam reforming of methanol.

Saler-Illia et al.[6] also explore a homogeneous precipitation method for the mixed copper–zinc basic carbonate in order to prepare precursors of binary Cu/ZnO catalyst. The composition of the obtained solids depended on the initial reactant concentration and ageing time. At low zinc concentration, a mixture of zincian–malachite and Zn doped tenorite were obtained. With prolonged ageing zincian–malachite dissolves and zinc-doped tenorite was formed. Depending on the quantity of each metal ion aurichalcite (A), zinc–malahite and Zn-doped tenorite were formed.

This work describes the preparation of mixed Cu/Zn basic carbonates prepared from different molar copper to zinc ratios in the starting solutions (4:1, 2:1, 1:1, 1:2 and 1:4) by ageing aqueous solutions of zinc and copper nitrates in the presence of urea at temperatures up to 85 °C. These materials have been characterized by various techniques.

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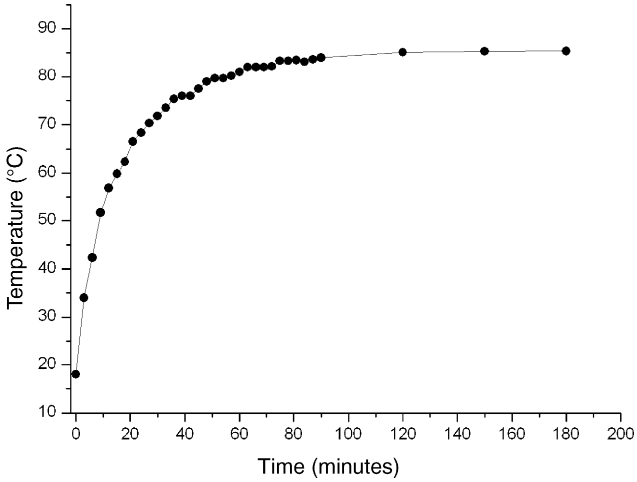

Fig. 1. Temperature profile in the test tube as a function of time.

2. Experimental

All reagents were analytical grade. To avoid hydrolysis on storage, fresh stock solutions were prepared from $Cu(NO_3)_2{\cdot}2.5H_2O$ (Aldrich) and $Zn(NO_3)_2{\cdot}2H_2O$ (Aldrich) and urea (Aldrich). All precipitation experiments were carried out in 14 cm^3 tightly sealed screw-capped borosilicate test tubes.

Predetermined volumes of Cu(II)-, Zn(II)-nitrate, and urea stock solutions, and water were used to obtain desired metal ion ratios and reactants concentrations. In all experiments, 10 cm^3 of these solutions were poured into 14 cm^3 screw-capped borosilicate test tubes which were placed into a preheated oven (90 °C) and kept for various time intervals. After 90, 120 and 180 min, the tubes were quenched to room temperature in cold water. During these experiments, the temperature was measured in the center of test tubes with a Fluke 54 II thermocouple type K with thickness of 1 mm. The resulting temperature profile in the test tube is reproduced in Fig. 1.

In all experiments, the total concentration of urea and metal ions were kept constant at 0.5 and 5×10^{-3} mol dm^{-3}, respectively. Five different molar ratios of Cu/Zn were prepared, e.g., 4:1, 2:1, 1:1, 1:2 and 1:4. The resulting solids were characterized by scanning field emission electron microscopy (SEM, Zeiss Supra 35 VP with EDS analyzer), while X-ray diffraction analyses (XRD) were carried out on a Siemens D-5000 X-ray diffractometer.

3. Results and discussion

Scanning electron micrographs in Figs. 2–4 illustrate the effect of the reaction time on the formation of particles at different Cu/Zn ratios. In all three systems, at first somewhat polydisperse spheres are formed which eventually change into much larger spheres of composite structure (formation of dandelions). In addition to these three systems, experiments were carried out with two other metal ion ratios and some general observations during the formation of particles in all five cases, together with the results of the EDS analyses are summarized in Table 1.

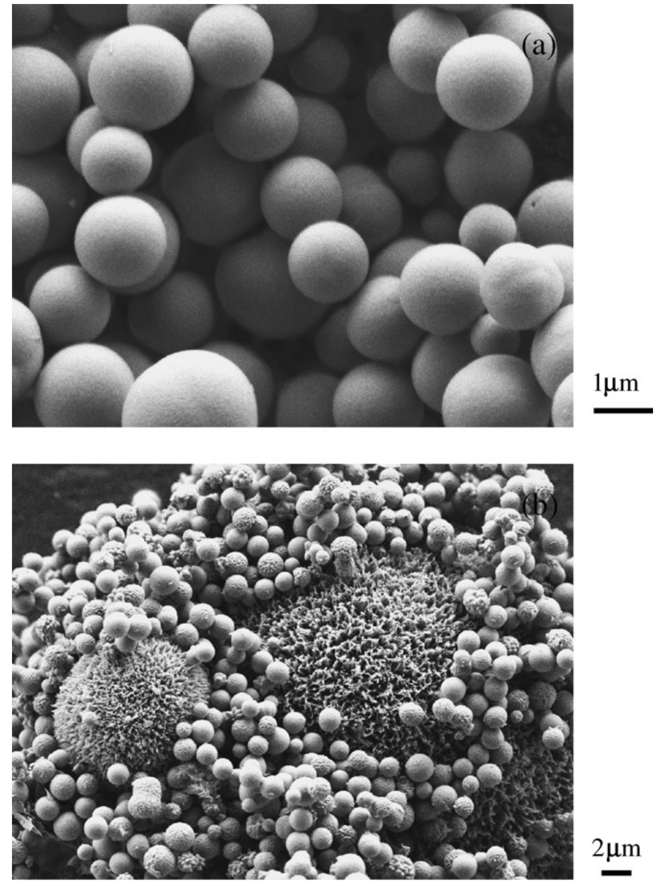

Fig. 2. SEM images of samples prepared at Cu:Zn 2:1: (a) aged 90 min, (b) aged 180 min.

The XRD (Fig. 5) of all studied systems confirmed that these solids are basic carbonates as listed in Table 1.

The electron micrographs show rather dramatic changes of the originally precipitated solids, with time both in terms of particle structure and size. The conversion from amorphous to crystalline solids seems to proceed through a solution/reprecipitation process with the formation of uniform large composite dispersed solids. This mechanism is further corroborated by XRD (Fig. 5). The XRD analysis of the prepared coprecipitates has shown that the initial spherical particles, generated at 90 min are amorphous with a modal size of 1 μm. The chemical composition of these original particles was essentially the same regardless of the ratio of $Cu(NO_3)$ and $Zn(NO_3)$ in the starting solution. Thus, the EDS spot analysis showed that the solids are always Cu-rich consisting of 81–99 at.% Cu and 19–1 at.% of Zn (Table 1). Only at four times excited Zn^{2+} concentration in reacting solutions (Cu^{2+}/Zn^{2+} = 1:4) XRD spectra reviled weak bands, most likely copper zinc carbonate hydroxide even at ageing times of 90 min. High Cu/Zn molar ratio in particles formed during early stages of ageing is in general agreement with the results obtained by Soler-Illia et al.[6] According to their work amorphous Cu phase, due to lower solubility constant, precipitates first, adsorbs Zn(II) but does not trigger the heterogeneous nucleation of mixed coprecipitate such as aurihalcite which takes place at the expense of hydroxylated Zn(II) aqueous species and already formed amorphous Cu phase. Further crystal growth