JOURNAL OF MATERIALS SCIENCE 20 (1985) 1211–1214

Preparation of copper–cobalt oxide spinels by thermal decomposition of copper–cobalt basic nitrate mixed crystals

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Copper–cobalt oxide spinels with a common formula $Cu_xCo_{3-x}O_4$ $(0 \leqslant x \leqslant 1.0)$ have been prepared by thermal decomposition at 350° C in air of single-phase mixed basic nitrate precursors $(Cu, Co)_2(OH)_3NO_3$. The formation of the oxide phase during the thermal treatment has been associated with a diffusionless mode of transformation, established for some hydroxides and hydroxysalts with a layer-type structure.

1. Introduction

The introduction in preparation of copper–cobalt oxide spinels ($Cu_xCo_{3-x}O_4$) goes quite a long way back. The first papers reporting the existence of these compounds have been published more than 50 years ago. Since that time, a large variety of precursors and experimental conditions have been unsuccessfully tested in order to prepare the compound with $x = 1.0$. The results obtained till 1972 have been reviewed by Rasines [1]. Recent investigations [2–5] carried out in our laboratory have also contributed to elucidating the problems of preparation and the cationic distribution in spinels with x values as large as 0.7.

Analysis of the cumulative data available allows specification of some typical drawbacks of the preparative methods used up to now and indicates what kind of precursors and experimental conditions are to be chosen in order to obtain spinels with high x values. These compounds are interesting due to their valuable catalytic properties [6].

The main, and obviously the most recently realized difficulty in the preparation of spinels with high x values, is related to their low thermal stability. When heated in air above temperature $t_k = 400$ to 450° C they decompose to oxygen, copper oxide and a spinel with a low copper content [3, 7]. For this reason, it has been impossible to prepare these compounds either by a reaction between the solid oxide components or by thermal decomposition of various precursors at temperatures higher than t_k [8–11].

Thermal treatment of some polyphase precursors decomposing below t_k is also not appropriate, since this temperature is too low to activate transport processes between the solid decomposition products [12]. Syntheses using thermal decomposition of mixtures of Co(II) and Cu(II) nitrates are also worth noting. They allow preparations of spinels with $x \leqslant 0.9$ [2]. Due to the complicated chemical and phase transformations proceeding in the system during the thermal treatment, these methods actually lead to the formation of a mixture of spinels with different x values [5].

Two more methods of $Cu_xCo_{3-x}O_4$ preparation are of particular interest. By the first one, natural minerals with the formula $(CuO{\cdot}Co_2O_3){\cdot}H_2O$ decomposing at 200° C are used [13]. The lattice parameters of the spinels obtained by the authors indicate high x values. With the second method, a precursor representing mixed $(Cu_yCo_{1-y}){\cdot}(OH)_2$ crystals is decomposed at low temperatures [7].

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The applicability of this method is restricted by the upper limit of y ($y = 0.2$ [14]), owing to which spinels with $x \leqslant 0.6$ may be prepared.

Irrespective of their shortcomings, the above two methods reveal the most important properties which an ideal precursor for the preparation of copper–cobalt oxide spinels should possess. We are of the opinion that it should be a chemically homogeneous system having an atomic copper-to-cobalt ratio (Cu/Co) within the range $0 \leqslant \text{Cu/Co} \leqslant 0.5$ and decomposing at temperatures below t_k. In addition, the thermal decomposition of the precursor should proceed without formation of separate phases with various Cu/Co ratios. This would ensure chemical homogeneity of the spinel obtained.

The data on the existence of copper–cobalt compounds possessing the above properties are rather scarce. Our attention was attracted by the basic nitrate system $Cu_2(OH)_3NO_3$–$Co_2(OH)_3NO_3$ which is supposed to form a continuous row of mixed crystals [15]. All the properties of these mixed crystals such as homogeneity, possibility of formation of each composition within the range of spinel stoichiometry and appropriate decomposition temperature correspond to our concept about the ideal precursor. In the present paper we report the results of our experiments on the preparation of copper–cobalt oxide spinels with x up to 1.0 using several precursors precipitated from Cu(II) and Co(II) solution of nitrates with sodium hydroxide.

2. Experimental details

To verify the assumptions concerning the effect of the precursors phase composition and homogeneity on the properties of the products obtained, we prepared three types of precursor: (a) a two-phase mixture of $Co(OH)_2$ crystals and $(Cu_{2-z}Co_z)\cdot(OH)_3NO_3$ mixed crystals, (b) a mixture of $Co_2(OH)_3NO_3$ and $Cu_2(OH)_3NO_3$ crystals, and (c) single-phase mixed $(Cu_tCo_{2-t})\cdot(OH)_3NO_3$ crystals. A series of samples of each type were used. The Cu/Co ratio monotonically increased over the range $0.03 \leqslant \text{Cu/Co} \leqslant 0.5$.

The precursors were precipitated from solutions of Cu(II) and Co(II) nitrates with diluted sodium hydroxide by continuous titration up to a molar ratio $NaOH/Me(NO_3)_2$ of 1.2. Precursors (a) were prepared by mixing, in preset ratios, of 0.2 M solutions of $Cu(NO_3)_2$ and $Co(NO_3)_2$ and subsequent precipitation with 0.2M NaOH solutions at 75° C. The precipitation conditions were chosen according to [14] with a view to obtaining a two-phase precursor. Precursors (b) were obtained by precipitation of mixed 1.5M solutions of Cu(II) and Co(II) nitrates with 0.5M NaOH at 100° C. Precursors (c) were precipitated by simultaneous addition at 100° C of 0.1M solutions of $Cu(NO_3)_2$ and NaOH to 2.5M solution of $Co(NO_3)_2$ [16]. These conditions were chosen empirically on the basis of the products of solubility values for $Cu_2(OH)_3NO_3$ [17] and $Co_2(OH)_3NO_3$ [18]. All types of precursor precipitates were washed with water and dried in air at 80° C, then subjected to chemical, X-ray diffraction (XRD), thermogravimetric (TG) and differential thermal (DT) analyses.

The copper and cobalt contents in the precipitates were determined with an atomic absorption spectrophotometer. DT and TG analyses were carried out in air, at a heating rate of $5^\circ\,C\,min^{-1}$ and temperatures ranging from 20 to 350° C. The XRD analyses of the precursors and their products after thermal decomposition at 350° C were carried out with a powder diffractometer using Co$K\alpha$ radiation and scintillation registration. The lattice parameters of the spinel phase were determined from the angle position of the (642), (731, 553) and (800) reflections, recorded with a constant speed of $1/8^\circ\,(\theta)\,min^{-1}$, using 99.99% pure silicon as internal standard.

3. Results

The XRD analyses showed that precursors (a) represent a mixture of two phases: β-$Co(OH)_2$ with a brucite-type structure and $Cu_2(OH)_3NO_3$ with a gerhardtite-type structure. The gerhardtite-type phase contained a small amount of cobalt. With increasing copper content, the relative amount of the basic nitrate also increased. Precursors (b) were also two-phase, but contrary to (a), both phases were mixed crystals of copper–cobalt basic nitrates, one of them enriched in cobalt and the other in copper. At Cu/Co ratios below 0.05, the cobalt-rich disordered II-α [19] type of basic nitrate was the main phase. With increasing Cu/Co ratio, lines of the second copper-rich ordered II-β phase appeared in the diffraction pattern. Precursors (c) were single-phase mixed crystals $(Cu_tCo_{2-t})\cdot(OH)_3NO_3$. With low copper contents ($\text{Cu/Co} < 0.03$) their diffraction pattern showed signs of a strong stacking disorder – sharp (001) and broad mixed-index diffraction lines of a pseudohexagonal sublattice. With higher copper contents, a transition to the ordered phase occurred which caused the

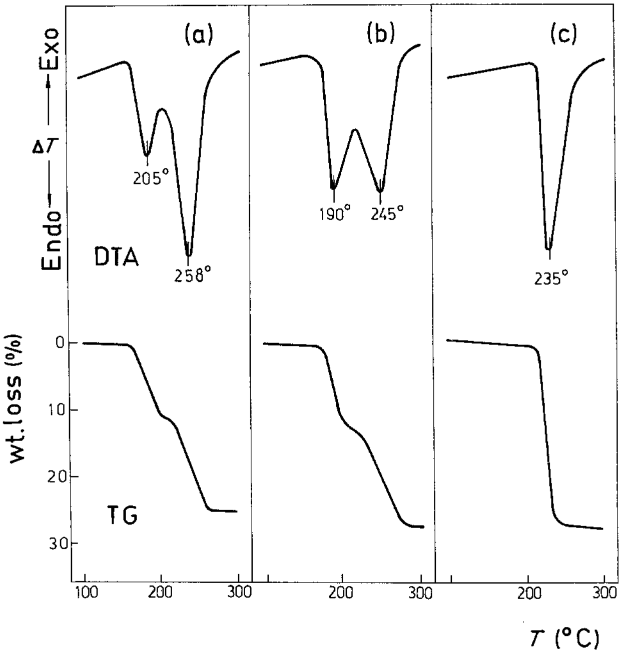

Figure 1 DT and TG decomposition curves of: presursor (a) with Cu/Co = 0.42; precursor (b) with Cu/Co = 0.43; and precursor (c) with Cu/Co = 0.48.

appearance of new weak lines and the line splitting, typical of the monoclinic supercell.

The DT and TG analyses showed two-stage endothermal decomposition of precursors (a) and (b). The first endothermal minimum for precursors (a) corresponds to the decomposition of the hydroxide phases, whereas the second indicates the decomposition of the basic nitrate. The DT and TG curves of precursor (a) with Cu/Co = 0.42 are given in Fig. 1a.

With precursors (b), the first and the second endothermal minima indicate the decomposition of the basic nitrates rich in cobalt and copper, respectively. Fig. 1b presents the DT and TG curves of a precursor (b) with Cu/Co = 0.43.

Precursors (c) decompose in a single stage. With increasing copper content the endothermal minimum in the DT curves is shifted to higher temperatures. The DT and TG curves of this type of precursors with Cu/Co = 0.48 are given in Fig. 1c.

The XRD analyses of the decomposition products of precursors (a) and (b) showed the presence of two phases: a spinel and CuO, i.e. these precursors are not appropriate for the preparation of spinels with high x values. The decomposition products of precursors (c) are single-phase spinels up to Cu/Co = 0.5. With Cu/Co ratios above this value, two phases are obtained: a spinel with $x = 0.1$ and CuO. The dependence of the lattice parameter of the spinel on the Cu/Co ratio of precursors (c) is presented in Fig. 2.

4. Conclusions

The first and the most important conclusion drawn from the experimental data is that $Cu_xCo_{3-x}O_4$ spinel with $x = 1.0$ exists and can be prepared. Its successful synthesis strongly depends on the properties of the precursor and on the mechanism of the oxide phase formation. Obviously, no interaction proceeds between the solid components of polyphase precursors during the decomposition process.

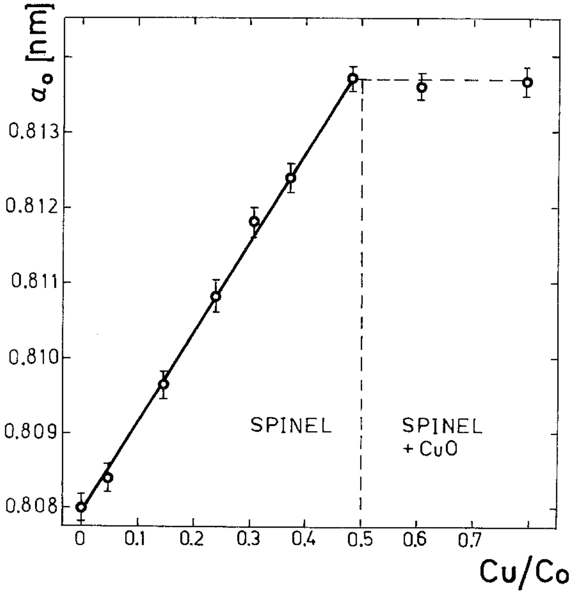

Figure 2 Dependence of the lattice parameter of the spinel on the Cu/Co ratio of precursor (c).

This concerns not only the case in which the initial phases have different crystal structures (precursors (a)), but also the case of isostructural phases and very close lattice parameters (precursors (b)). Each of the phases present in these two types of precursors decompose separately, and the decomposition products do not interact at temperatures below t_k. In other words, there is no diffusion transport between the solid components of the system. Therefore, it can be assumed that the spinel formation from precursors (c) is associated with a special mechanism, regarded as a collective transformation which requires no long range diffusion. An analogous mechanism of formation of oxide products was established for compounds with structures topologically similar to that of the mixed copper–cobalt basic nitrate, namely some bivalent metal hydroxides with a layer brucite-type structure [20, 21]. The structure of the $Me_2(OH)_3NO_3$ basic salts (Me = Cu, Co) can be derived from that of brucite by substituting NO_3 groups for 1/4 of the OH groups [22]. This occurs with no change of either cationic coordination or polyhedra packing in the metal–oxygen layers, i.e. the geometrical conditions needed for the collective transformation are preserved. One should expect in this case the structural similarity to be associated with a similarity in the oxide formation mechanism. In fact, the type of transformation of mixed copper–cobalt basic nitrates during their thermal decomposition seems to be analogous of that estabished for some pure isostructural compounds such as $Cu_2(OH)_3NO_3$ [23] and $Zn_3(OH)_4(NO_3)_2$ [24].

Indeed, the particular case discussed here is much more complicated due to the change of the valency state of Co(II) to Co(III) followed by the formation of two cationic sublattices. More studies, which form an ample field for future investigations, have to be carried out to establish in detail the transformation mode associated with the particular type of mechanism, assumed here. However, even at this stage, the fact that it is possible to prepare a single-phase copper–cobalt oxide spinel with the highest x value at moderate temperatures and oxygen partial pressures holds out opportunities for application of the diffusionless transformations of mixed crystal precursors in the preparation of new oxide materials with interesting catalytic, electric and magnetic properties. In this respect the mixed-crystal precursors of basic nitrates with layer strucutres deserve a special consideration.

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Received 17 February
and accepted 12 April 1984