JOURNAL OF MATERIALS SCIENCE 23 (1988) 181–184

Zinc–cobalt oxide spinels with precursor-controlled degree of inversion

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Zinc–cobalt oxide spinels, $ZnCo_2O_4$, have been prepared by thermal decomposition of three different precursors: (I) coprecipitated zinc–cobalt hydroxide nitrate; (II) coprecipitated zinc–cobalt hydroxide, and (III) zinc–cobalt hydroxide nitrate prepared by isomorphous replacement of the tetrahedrally coordinated Co^{2+} ions in the double-layered parent cobalt hydroxide nitrate by Zn^{2+} ions. It has been shown that the cationic distribution in the oxide product is predetermined by the cationic distribution of the precursor. The coprecipitated precursors (I) and (II) decompose to statistical spinels, whereas precursor (III) decomposes to a normal $Zn[Co_2]O_4$ spinel.

1. Introduction

The oxide spinels $M_xCo_{3-x}O_4$ ($0 < x \leqslant 1$; M = divalent metal) show a significant catalytic activity in processes of low-temperature oxidation and hydrogenization of hydrocarbons [1]. They are used in practice for the neutralization of harmful components of waste motor gases [2–4].

The catalytic properties of the oxide phases depend not only on their chemical composition but also, to a considerable extent, on their morphology, texture and structural perfection [5]. That is why methods allowing simultaneous control of several important structural and morphological characteristics are preferred for the preparation of these oxides.

A series of achievements of the so-called "soft chemistry" demonstrated that polycrystalline complex oxide materials with definite characteristics can be obtained using initial compounds with preset composition, structure and mechanism of the final crystalline phase formation [5, 6]. A number of investigations carried out recently on the preparation of $M_xCo_{3-x}O_4$ (M = copper, magnesium, nickel, zinc) by thermal decomposition of M(II)–Co(II) hydroxide nitrate mixed crystals [7–10] have shown that: (1) precursors with an M/Co atomic ratio ranging from 0 to 0.5 decompose to the corresponding oxide spinels; (2) the thermal decomposition of the mixed crystals is accompanied by the partial oxidation of Co(II) to Co(III) and the formation of intermediate M(II)–CO(II)–Co(III) oxide hydroxide nitrates which have preserved the initial layered-type structure of the precursor; (3) there are definite orientation relationships between the crystallographic directions of the precursors and their oxide products [10, 11]; (4) the spinel lattice of the products is formed under conditions allowing no long-range diffusion cationic transport.

It is evident that the relatively low decomposition temperature of the precursors and their specific heterodesmic (layered) structure which facilitates collective shear and collapse transformation, are factors favouring the diffusionless topotactic formation of the spinel lattice. In the case of the above mechanism, the cationic distribution in the product should be biographically associated with that of the precursor. This assumption is supported by the results of some earlier investigations which show that: (1) the statistical distribution of both kinds of metal ions in the precursor is preserved in the spinel product [12]; and (2) the cationic deficiency of the oxide product is determined by the structural similarity between the spinel and the precursor [13].

The above results have another important meaning: the cationic distribution of the M(II)–Co oxide spinels can be controlled to a certain extent using precursors with preset lattice site occupancies of the cations. Mixed crystals of the structural type of the layered zinc hydroxide nitrate dihydrate, $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, are of particular interest. The cationic sublattice of this salt consists of octa- and tetrahedrally coordinated Zn^{2+} ions in a ratio of 3/2 [14]. It is assumed that the structure of cobalt hydroxide nitrate, $Co_7(OH)_{12}(NO_3)_2$, is topologically similar to that of the above mentioned zinc salt [15]. These solids, when put in contact with aqueous solution containing other divalent metal ions, easily exchange the weakly bonded tetrahedrally coordinated divalent cations [16] which offers another possibility for the preparation of precursors representing ordered substitutional solid solutions.

The present paper contains results from studies on the preparation of Zn(II)–Co(II) hydroxide nitrates and hydroxides with different cationic distribution and on the oxide products of their thermal decomposition.

2. Experimental techniques

2.1. Sample preparation

To elucidate the effect of the precursor on the inversion degree of the product spinel phase, three kinds of samples were synthesized.

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Sample I. A 0.5 M NaOH solution and a 0.11 M $Zn(NO_3)_2$ solution (100 ml each) were added simultaneously with stirring to a boiling $Co(NO_3)_2$ solution (14 ml). The precipitation of the M^{2+} ions was incomplete: $OH^-/M^{2+} = 1.3$. This allowed the experiment to be performed in air without oxidation of the Co^{2+} ions to Co^{3+} [17]. The conditions were chosen according to our previous investigations [8, 18] with a view to obtaining single-phase mixed hydroxide nitrate crystals.

Sample II. 100 ml nitrate solution containing Zn^{2+} and Co^{2+} ions (1.2×10^{-2} and 2.4×10^{-2} g atoms, respectively) was added with continuous stirring at 60° C to 120 ml 0.5 M NaOH solution. The suspension obtained was aged for 4 h. To prevent oxidation of Co(II), an inert (helium) atmosphere was used.

Sample III. Double-layered cobalt hydroxide nitrate, $Co_7(OH)_{12}(NO_3)_2$, was synthesized by precipitation. For that purpose a 0.5 m NaOH solution (100 ml) was added to the 0.75 M $Co(NO_3)_2$ solution (50 ml) containing $NaNO_3$ ($1\,g\,mol\,l^{-1}$). The suspension volume was maintained constant during the precipitation and the water losses due to evaporation were compensated by a suitable rate of addition of the NaOH solution. A 3 M solution of $Zn(NO_3)_2$ was added to the suspension obtained. The mixture was heated in a sealed glass ampoule for 48 h at 120° C with continuous shaking.

The precursor precipitates were filtered, washed with water and ethanol, then dried at 60° C.

2.2. Sample characterization

The M(II) in the samples were determined complexometrically as a sum of Zn(II) and Co(II) by back titration with a $ZnSO_4$ solution. The content of Co(II) was determined by oxidation to Co(III) with hydrogen peroxide in a neutral medium [19]; Co(III) was established iodometrically; and NO_3^-, by the method of Devarda.

The X-ray diffraction (XRD) analyses of the precursors and their products were performed with a powder diffractometer using Co*Kα* radiation and scintillation registration.

Transmission electron microscope (TEM) observations and selected-area electron diffraction (SAED) studies on the decomposition of the precursors under electron irradiation *in situ* were carried out on samples deposited on a carbon substrate. Another technique was used to investigate the thermal decomposition in air: precursor samples were deposited on a clean mica surface and treated thermally at 350° C for 1 h. The decomposition products were carefully covered with a carbon film. The film, along with the particles fixed on it, was separated from the substrate and transferred to the microscope chamber.

The paramagnetic susceptibility of the spinel products obtained by thermal decomposition of the samples in air at 250° C for 2 h was measured using a Faraday-type magnetic balance in the temperature range 20 to 250° C. Published data [20, 21] on the magnetic moments of different cations (Table I) were used in the calculation of the effective magnetic moments, μ_{eff}, of spinels with different cationic distributions.

TABLE I Magnetic moments, μ_{eff}, of cobalt ions with different valences and coordination (BM)

Ion	Co_o^{2+}	Co_t^{2+}	LS Co_o^{3+}	LS Co_t^{3+}	HS Co_t^{3+}
μ_{eff}	5.1	4.88	0.0	3.6	5.1

o, t = octa- and tetrahedral coordination, respectively.
LS, HS = low and high spin states, respectively.

The diffuse reflectance spectra (DRS) were recorded in the range 250 to 2500 nm with a "Beckman UV" spectrophotometer, using $BaSO_4$ as a standard.

3. Results and discussions

3.1. Sample I

Sample I consists of single-phase mixed crystals formed as a result of a partial isodimorphous replacement of Co^{2+} ions in the double-layered cobalt hydroxide nitrate by Zn^{2+} ions [8]. The mixed crystals have the composition $Zn_{1.66}Co_{3.34}(OH)_{8.82}(NO_3)_{1.28}(H_2O)_{2.23}$ and the lattice type of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$. In accordance with our previous study [8] the thermal decomposition of the mixed crystals proceeded in three stages. During the first stage the salt transformed into its anhydrous form, the interlayer distance, d_{200}, decreasing from 0.974 to 0.926 nm. During the second stage, the interlayer distance smoothly decreased down to 0.76 nm, a value which is characteristic of an intermediate oxide hydroxide nitrate phase with the composition $Zn_{1.66}Co_{3.44}O_{2.78}(OH)_{4.55}(NO_3)_{1.28}$. The first and second stages are associated with dehydration processes alone. The M/NO_3 ratio does not change, but some of the Co^{2+} ions are oxidized to Co^{3+}. The intermediate oxide hydroxide nitrate which has an XRD pattern similar to that of the layered double hydroxide $Co_3Zn_2(OH)_{10} \cdot 2H_2O$ reported by Günter and Oswald [22], transforms during the third stage to a zinc–cobalt spinel, evolving H_2O and nitrogen oxides.

The DRS of the sample (Fig. 1a) contain bands at 588, 658 and 1540 nm characteristic of Co^{2+} in tetrahedral coordination and a band at 1235 nm which corresponds to octahedrally coordinated Co^{2+} ions [23]. The relative intensity of the bands does not change during the first (Fig. 1b) or second (Fig. 1c) stages of thermal decomposition. Comparison between the intensity distribution in the DRS of the coprecipitated sample I (Fig. 1a), the nonsubstituted double-layered cobalt hydroxide nitrate (Fig. 1e) and the ion-exchanged sample III (Fig. 1f) shows that Co^{2+} ions are distributed over both tetrahedral and octahedral lattice sites. The absence of superstructure lines in the XRD spectra indicates that the substitution is not ordered. It should be noted that a similar type of cation distribution in coprecipitated hydroxy salts was observed earlier [16].

The TEM photographs and the SAED patterns of the precursor and the product of its decomposition are shown in Figs 2 and 3, respectively.

The sample I crystallites are plate-like and exhibit well-developed (1 0 0) faces. The SAED pattern contains reflections from the [1 0 0] zone (the [0 0 1] zone of the pseudohexagonal lattice). In the microscope chamber the sample decomposes to two oxide phases.

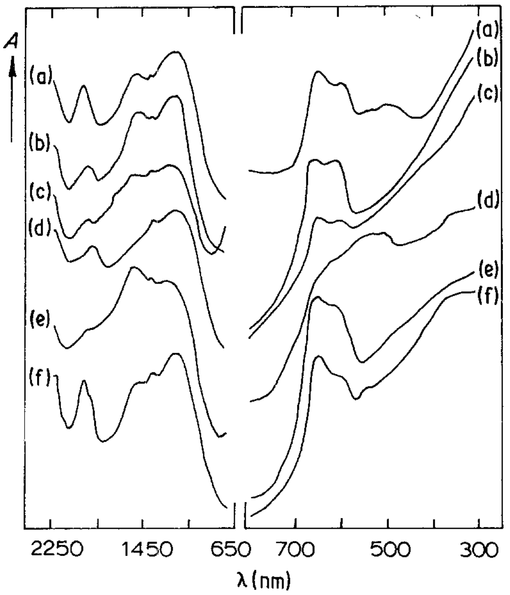

Figure 1 Diffuse reflectance spectra of (a) sample I; (b), (c) sample I at first and second stages of thermal decomposition, respectively, (d) sample II; (e) double-layered Co(II) hydroxide nitrate; (f) sample III.

Obviously, the high vacuum and the relatively low content of the NO_3^- ions which act as an oxidizing agent do not allow formation of Co^{3+} ions in quantities necessary for the spinel stoichiometry.

The product which is obtained by decomposition of the precursor in air is a polycrystalline pseudomorph (Fig. 3). Its SAED pattern can be indexed on the basis of a cubic spinel lattice whose three-fold axis is almost parallel to the (1 0 0) direction of the precursor. The spinel crystallites are misoriented in a degree allowing the appearance of diffraction spots belonging to the [1 1 1] and [1 1 2] zones. A similar phenomenon which is usually observed in the decomposition of a number of hydroxides and hydroxy salts is probably due to stresses arising from differences in the specific volumes of the precursor and the product (see, for instance, [24]).

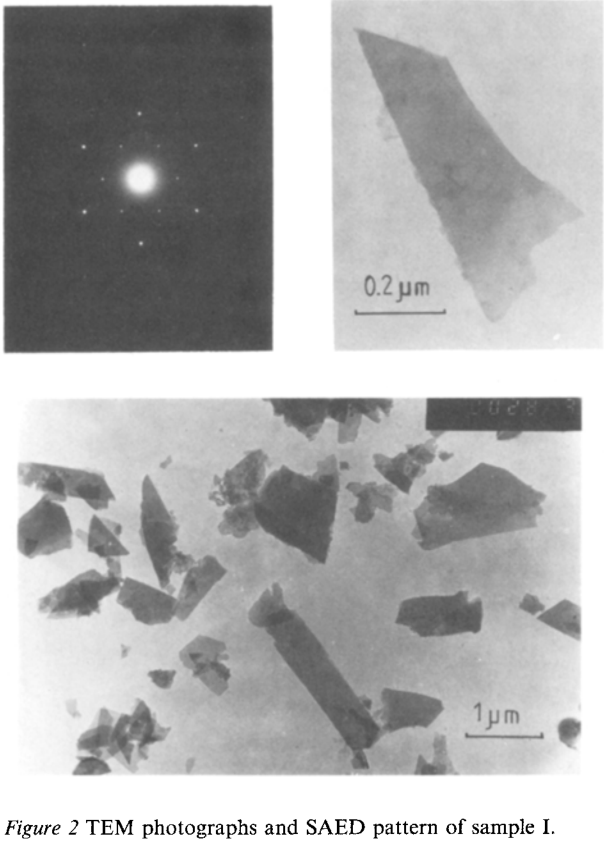

Figure 2 TEM photographs and SAED pattern of sample I.

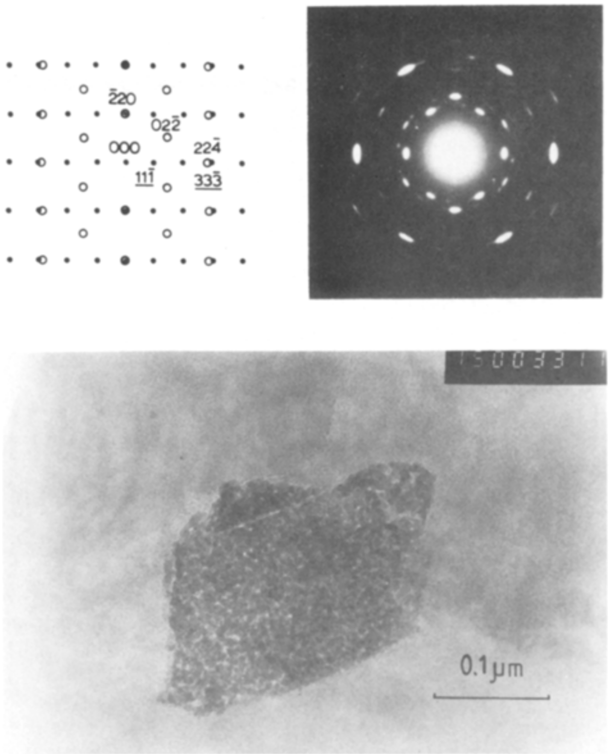

Figure 3 TEM photograph and SAED pattern of sample I decomposed thermally in air to a spinel pseudomorph; bottom right, indexed SAED pattern: $\overset{hkl}{\circ}$, spots from the [1 1 1] zone; $\underset{hkl}{\bullet}$, spots from the [1 1 2] zone.

The TEM and SAED studies definitely show that the formation of the spinel phase during the decomposition of the precursor in air is a topotactic process.

The effective magnetic moment per formula unit, μ_{eff}, of the final product is 2.6 BM. This value corresponds to a partially inverse spinel, $(Zn_{0.74}Co_{0.26})[Zn_{0.26}Co_{1.74}]O_4$, with Co^{3+} ions in the typical high-spin state.

3.2. Sample II

Sample II is a pink precipitate with the composition $Zn_{0.33}Co_{0.67}(OH)_2$. Its XRD pattern has three diffuse peaks corresponding to the (1 0 0), (1 1 0) and (2 0 0) reflections of a hydroxide phase with a brucite-like structure. The DRS (Fig. 1d) show bands characteristic of octahedrally coordinated Co^{2+} ions only. Hence, the structure of this hydroxide sample is of a simple single-layered type.

The thermal decomposition of sample II proceeds in one endothermic stage and leads to the formation of $ZnCo_2O_4$ spinel. The effective magnetic moment of the product is $\mu_{eff} = 3.4$ BM, which again corresponds to a partially inverse spinel with a cationic distribution $(Zn_{0.56}Co_{0.44})[Zn_{0.44}Co_{1.56}]O_4$.

3.3. Sample III

As already mentioned, the synthesis of sample III is preceded by the precipitation of double-layered hexagonal (a_0 = 0.313 and c_0 = 0.918 nm) cobalt hydroxide nitrate. Its DRS (Fig. 1e) show bands characteristic of tetra- and octahedrally coordinated Co^{2+} ions.

The replacement of Co^{2+} by Zn^{2+} ions causes an increase of the interlayer distance from 0.918 to 0.978 nm and transformation of the initial lattice to the $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ lattice type. The DRS of the Zn^{2+} substituted samples show a substantial decrease in intensity of the bands of tetrahedrally coordinated Co^{2+} ions in the parent lattice.

The product of decomposition of sample III is a single-phase spinel. Its paramagnetic susceptibility is very weak and allows no reliable calculation of the effective magnetic moment. In fact, the product has the cationic distribution of almost normal $Zn[Co_2]O_4$ spinel.

4. Conclusions

The formation of the zinc–cobalt oxide spinels from the corresponding hydroxide nitrate percursors with a double-layered lattice type occurs by the same diffusionless topotactic mechanism observed with the single-layered hydroxide nitrates. This conclusion is supported not only by the traditionally used XRD, TEM and SAED methods but also by the cationic distribution-sensitive DRS and magnetic measurements data.

Because with this specific mechanism of oxide-phase formation the cationic distribution of the precursor controls the cationic distribution of the product, it offers new possibilities for the preparation of complex inorganic oxide materials.

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Received 13 February
and accepted 29 April 1987