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Low-Temperature Preparation of Fine-Particle Cobaltites

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A novel solid-solution precursor method for the preparation of fine-particle cobaltites at low temperatures has been described. The precursors, hydrazinium metal hydrazinecarboxylate hydrates, $N_2H_5M_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$, where M = Mg, Mn, Fe, Co, Ni, and Zn, decompose in air <250°C to yield corresponding metal cobaltites, MCo_2O_4. Formation of cobaltites has been confirmed by thermogravimetry (TG) weight loss, IR, and X-ray diffraction. Combustion of the precursor in air yields fine-particle cobaltites with surface areas in the range of 12–115 $m^2 g^{-1}$ and particle sizes of 1–40 μm. Low decomposition temperatures of the precursors accompanied by the evolution of large amounts of gases appear to control the particle size of the cobaltites. © 1987 Academic Press, Inc.

1. Introduction

Cobaltites are of importance because of their use as catalysts and oxide electrode materials (*1*). The conventional procedure for the preparation of spinel oxides is the ceramic method (*2, 3*) which cannot be employed for certain cobaltites, e.g., $NiCo_2O_4$ and $ZnCo_2O_4$, because of their instability at higher temperatures (>400°C) (*4*). Apart from the difficulty in the preparation, the surface area of the cobaltites prepared by the ceramic method is considerably low and, consequently, they are unsuitable as catalysts. A number of attempts have been made to bring down the cobaltite formation temperature by using either the "wet method" (*5, 6*), in which the metals are precipitated as hydroxides, which are then aged and calcined below 400°C, or the precursor method (*7, 8*), in which the metals are coprecipitated as oxalates and decomposed. Among all the methods, the precursor technique is advantageous, since it achieves excellent stoichiometry and low impurity content and provides a route to higher surface area complex oxides.

Hydrazinium metal hydrazinecarboxylate hydrates, $N_2H_5M(N_2H_3COO)_3 \cdot H_2O$ (M = Fe, Co, Ni, and Zn), are known (*9*) to yield corresponding metal oxides at low temperatures. The crystal structure of $N_2H_5Ni(N_2H_3COO)_3 \cdot H_2O$ is known (*10*) and is isomorphous with the corresponding Fe, Co, and Zn analogs (*11*). Since the ionic radii of Mg^{2+} and Mn^{2+} are comparable with Co^{2+}, they are expected to form solid-solution precursors having the composition $N_2H_5M_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$, where M = Mg, Mn, Fe, Ni, and Zn for the preparation of cobaltites at low temperatures. Here, we report the preparation of high-surface-area, fine-particle cobaltites by the thermal decomposition of these solid-solu-

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tion precursors. Fine-particle cobaltites have been characterized by X-ray powder diffraction (XRD), IR spectra, surface area, particle size, and electrical conductivity measurements.

2. Experimental

2.1 Synthesis and Chemical Analysis

The solid-solution hydrazine precursors $N_2H_5M_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$, where M = Mg, Mn, Fe, Ni, and Zn, were prepared by the reaction of an aqueous solution of M^{2+} and Co^{2+} ions in the mole ratio of 1 : 2 with $N_2H_3COON_2H_5$ or N_2H_3COOH in $N_2H_4 \cdot H_2O$ (*9*). The resulting solution was kept open to atmosphere. Crystalline solids separated from the solution in a couple of days. The crystals were washed with alcohol and ether and dried over P_2O_5 in a vacuum desiccator. The composition of the compounds was fixed by chemical analysis. The cobalt content in these precursors was determined by separating cobalt as the $Co(C_{10}H_6ONO)_3$ complex using α-nitroso β-naphthol (*12*). The filtrate during these separations containing the divalent metal ions (Mg, Mn, Ni, and Zn) was treated with chloroform to remove excess α-nitroso β-naphthol, and the metal ions were estimated by titration with standard EDTA solution. In the case of iron complex, iron was first separated using cupferron (*12*) and cobalt estimated by titration with EDTA. Hydrazine content in these precursors was estimated volumetrically by titration with 0.025 M potassium iodate solution under Andrew's condition (*13*).

2.2 Instrumentation

Infrared spectra of the precursors were recorded using a Perkin–Elmer Model 781 instrument and those of the cobaltites by a Perkin–Elmer Model 580 instrument employing Nujol mulls and KBr pellets.

The mode of decomposition of the precursors was studied by simultaneous thermogravimetry (TG)–derivative thermogravimetry (DTG)–differential thermal analysis (DTA) employing an ULVAC Sinku–Riko TA 1500 instrument. All experiments were carried out in air. The heating rate employed was 10°C/min. Platinum cups were used as sample and reference holders. Alumina was the reference material used. Samples of 3-5 mg were used for each run.

The XRD patterns of the precursors and cobaltites were recorded using a Philips diffractometer (PW 1050/70) employing Co$K\alpha$ and Fe$K\alpha$ radiation.

The BET surface area of the cobaltites was measured by nitrogen adsorption employing a Micromeritics Accusorb 2100 E instrument.

Particle size distribution of the cobaltites was found using Micron Photosizer SKC 2000, based on light scattering principle by sedimentation method.

For the purpose of obtaining electrical conductivity measurements, sintering of the cobaltites was done after pressing them into pellets with 1% polyvinyl alcohol (binder). A uniaxial pressure of 6 ton/cm^2 was applied for pelletizing. To remove the binder, the pellets were heated at 300°C for 6 h. With the exception of $NiCo_2O_4$ and $ZnCo_2O_4$ all other pellets were further sintered in air at 800°C for 12 hr. The densities of the cobaltite powders and sintered pellets were evaluated using a pycnometer. The sintered pellets achieved nearly 95% of theoretical density. Order of magnitude estimates of room temperature resistivities were made by two probe measurements. Measurements were done on a General Radio 1608 A impedance bridge. Colloidal silver paint was used as electrode material.

3. Results and Discussion

The preparation, crystal structure (*10*), and infrared spectra (*9*) of hydrazinium

TABLE I

UNIT CELL DIMENSIONS FOR THE MONOCLINIC HYDRAZINIUM METAL HYDRAZINECARBOXYLATE HYDRATES AND THEIR SOLID SOLUTIONS

Complex	a (Å)	b (Å)	c (Å)	$\beta°$	V (Å^3)
$N_2H_5Ni(N_2H_3COO)_3 \cdot H_2O$[a]	12.129	10.858	10.255	121.1	1156
$N_2H_5Co(N_2H_3COO)_3 \cdot H_2O$	12.106	10.873	10.252	121.10(0)	1155
$N_2H_5Mg_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$	12.133	10.892	10.229	121.09(9)	1157
$N_2H_5Mn_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$	12.147	10.941	10.245	121.09(9)	1166
$N_2H_5Fe_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$	12.193	10.980	10.299	121.09(9)	1180
$N_2H_5Ni_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$	12.138	10.979	10.283	121.08(7)	1173
$N_2H_5Zn_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$	12.128	10.916	10.276	121.09(9)	1165

[a] Ref. (*10*).

nickel hydrazinecarboxylate hydrate, $N_2H_5Ni(N_2H_3COO)_3 \cdot H_2O$, have been studied. The X-ray powder diffraction patterns of the solid solution precursors, $N_2H_5M_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$ (M = Mg, Mn, Fe, Ni, and Zn), are identical to that of $N_2H_5Ni(N_2H_3COO)_3 \cdot H_2O$, indicating the formation of solid solutions; typical XRD patterns of $N_2H_5Zn(N_2H_3COO)_3 \cdot H_2O$, $N_2H_5Co(N_2H_3COO)_3 \cdot H_2O$, and $N_2H_5Zn_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$ are shown in Fig. 1. The cell parameters and unit cell volumes of the precursors calculated from XRD data are given in Table I. The chemical analysis (Table II) of the precursors conform to the desired composition $N_2H_5M_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$ (M = Mg, Mn, Fe, Ni, and Zn), showing that the atomic ratio of M/Co is 1 : 2 within experimental error.

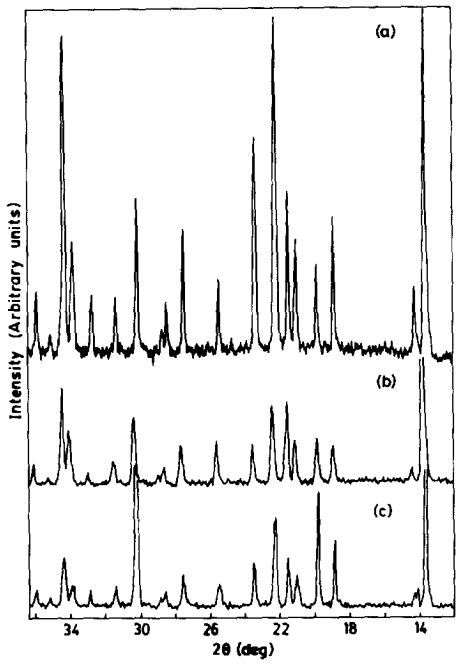

FIG. 1. X-ray powder diffraction patterns (Co$K\alpha$) for (a) $N_2H_5Zn(N_2H_3COO)_3 \cdot H_2O$, (b) $N_2H_5Co(N_2H_3COO)_3 \cdot H_2O$, and (c) $N_2H_5Zn_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$.

The infrared spectra of the precursors show the characteristic N–N stretching frequency of $N_2H_3COO^-$ in the region 900–1010 cm^{-1} and $N_2H_5^+$ ~965 cm^{-1} (*9*).

The TG–DTA data of the precursors are

TABLE II

CHEMICAL ANALYSIS DATA OF $N_2H_5M_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$ (M = Mg, Mn, Fe, Co, Ni, AND Zn)

	% Hydrazine		
M	Calcd	Obs	Mole ratio Co^{2+}/M^{2+}
Mg	39.58	39.39	2.03
Mn	38.36	39.02	2.02
Fe	38.33	39.01	1.98
Co	38.21	38.11	—
Ni	38.22	38.09	2.00
Zn	37.97	37.83	1.97

TABLE III

THERMAL DATA OF $N_2H_5M_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$ (M = Mg, Mn, Fe, Co, Ni, AND Zn)

	Thermogravimetry				
		% Final wt loss			
M	Temp. range (°C)	Obs	Calcd	DTA peak[a] temp. (°C)	Product
Mg	125–265	76	78.7	165, 215, 245	$MgCo_2O_4$
Mn	115–240	75.5	76.3	150, 230	$MnCo_2O_4$
Fe	120–235	77	76.26	125, 160, 205	$FeCo_2O_4$
Co	145–245	75.5	76.03	165, 190, 205, 240	Co_3O_4
Ni	140–245	77	76.05	160, 225	$NiCo_2O_4$
Zn	145–220	75	75.55	175, 205	$ZnCo_2O_4$

[a] All DTA peaks are exothermic.

summarized in Table III. A typical thermogram of $N_2H_5Mg_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$ is shown in Fig. 2. It can be seen that all the precursors decompose in more than one step to yield corresponding metal cobaltites, MCo_2O_4 being the final product. The observed weight loss in TG corresponds to the expected value. Whereas DTA of the precursors shows three distinct exotherms, the corresponding steps in TG are not well defined. The breaks in TG may correspond to $M_{1/3}Co_{2/3}(N_2H_3COO)_2(N_2H_4)_x$, where x = 1–2. Formation of such intermediates has been reported (*9, 14*) during the decomposition of $N_2H_5M(N_2H_3COO)_3 \cdot H_2O$, where M = Co and Zn. Isolation of these intermediates was not possible as the decomposition of the precursors, being autocatalytic, goes to completion.

Formation of cobaltites by the decomposition of the solid-solution precursors was confirmed by the IR spectra and XRD patterns of the residues. The fine-particle nature of the cobaltites was indicated by particle size analysis and surface area measurements. The results of IR spectra, XRD, surface area, and particle size analysis, as well as conductivity measurements of cobaltites, are summarized in Table IV. Infrared spectra of the cobaltites show absorption bands ~650 and ~550 cm^{-1} due to

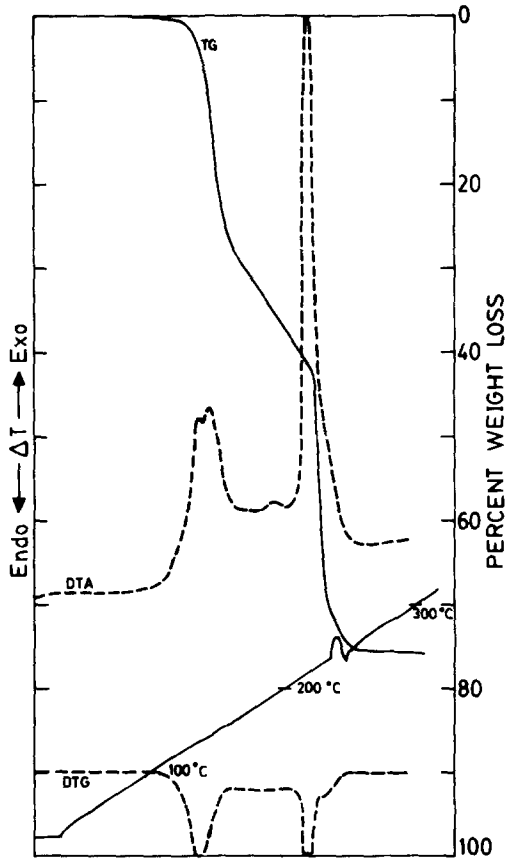

FIG. 2. Simultaneous TG–DTG–DTA of $N_2H_5Mg_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$.

the metal–oxygen stretching from tetrahedral and octahedral sites, respectively (*15*). X-ray powder diffraction patterns of the cobaltites correspond to those reported in the literature (*16*) with an "a" value ~8.1 Å. A typical XRD pattern of $MgCo_2O_4$ is shown in Fig. 3. The observed X-ray line

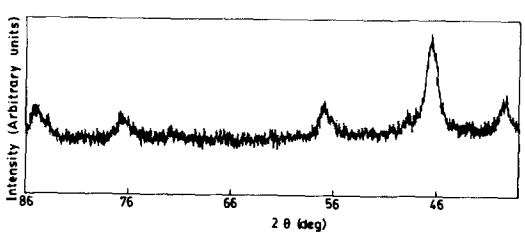

FIG. 3. X-ray powder diffraction pattern (Fe$K\alpha$) of $MgCo_2O_4$.

TABLE IV

SOME PROPERTIES OF COBALTITES (MCo_2O_4)

M	IR (cm^{-1}) ν_1	IR (cm^{-1}) ν_2	a (XRD) (Å)	Specific surface area ($m^2 g^{-1}$)	Average particle size (μm)	Crystallite size (XRD) (Å)	Conductivity $\Omega^{-1} cm^{-1}$
Mg	660	555	8.1303	47	2.20	101	10^{-4}
Mn	660	560	8.113	24	0.82	240	10^{-5}
Fe	650	555	8.222	116	4.35	65	10^{-3}
Co	670	570	8.108	18	1.52	275	10^{-5}
Ni	650	555	8.118	12.4	42	100	10^{-2}
Zn	650	560	8.172	65	4.56	138	10^{-6}

broadening is characteristic of the fine-particle nature of the cobaltites. The average crystallite sizes of the cobaltites calculated from the X-ray line broadening using the Debye–Scherrer formula are in the range of 65–250 Å (Table IV). The particle size analysis of cobaltites determined by the sedimentation technique showed that most of the particles are fine, with an average particle size ranging from 1 to 40 μm. The BET surface areas of the cobaltites vary from 12 to 115 $m^2 g^{-1}$, the low and high values corresponding to $NiCo_2O_4$ and $FeCo_2O_4$, respectively. It is rather surprising that there is a large variation in the surface area values of these cobaltites although they are all prepared from identical precursors. However, this fact was obvious from the combustion behavior of the precursors since magnesium, zinc, and iron precursors decomposed with swelling; although manganese, cobalt, and nickel precursors decomposed with swelling initially, the voluminous residues suddenly collapsed, indicating instantaneous sintering. The exact reason for the observed variation in the surface areas needs further investigation.

The conductivity values of the cobaltites are in the range of 10^{-2} to 10^{-6} Ω^{-1} cm^{-1}. The values for Co_3O_4 and $NiCo_2O_4$ are comparable with those reported in the literature (*1*).

Acknowledgments

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