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Combustion Synthesis and Properties of Fine Particle Spinel Manganites

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Fine particle spinel manganites have been prepared by thermal decomposition of the precursors $N_2H_5M_{1/3}Mn_{2/3}(N_2H_3COO)_3 \cdot H_2O$ (M = Co and Ni) and $M_{1/3}Mn_{2/3}(N_2H_3COO)_2 \cdot 2H_2O$ (M = Mg and Zn), as well as by the combustion of redox mixtures containing M(II) nitrate (M = Mg, Co, Ni, Cu, and Zn), Mn(II) nitrate, and maleic hydrazide (MH) in the required molar ratio. Both the precursor and redox mixtures undergo self-propagating, gas-producing, exothermic reactions once ignited at 250–375°C to yield corresponding manganites in less than 5 min. Formation of single phase products was confirmed by X-ray powder diffraction patterns. The manganites are of submicrometer size and have surface area in the range 20–76 m^2/g. © 1993 Academic Press, Inc.

1. Introduction

Spinel manganite oxide materials are technologically important due to their electrical, magnetic, and catalytic properties (*1*). It has been found that copper–manganese oxides are powerful oxidation catalysts in the combustion of organic compounds (*2*). Transport properties (*3–6*), Seebeck coefficients (*3–6*), low temperature magnetization (*3, 7*), magnetic susceptibility (*5*), and neutron diffraction spectra (*8*) of spinel manganites have been reported. The inverse spinel, $NiMn_2O_4$, is a mixed-valent oxide. Its electrical properties together with those of its range of solid solutions ($Ni_xMn_{3-x}O_4$, $0.57 \leq x \leq 1$) are important in the commercial manufacture of negative temperature coefficient (NTC) thermistors (*9*). Chemical synthesis (*10*) of mixed metal oxides at relatively low temperatures has attracted considerable attention in recent years. Low-temperature preparations yield materials with small particle size and high surface area. They also allow stabilization of phases having cations in higher valence states and/or with metastable structures.

The conventional ceramic route (*11*) to the preparation of these spinel mixed metal oxides involves high temperature firing of the component oxides or carbonates with frequent regrindings. The wet chemical methods (*12*) also require high reaction temperatures. Earlier, we reported the metal hydrazine carboxylate precursor method for the preparation of ferrites (*13, 14*) and cobaltites (*15*). We now extend this method to the preparation of spinel manganites. Fine particle manganites have also been prepared by the novel combustion process developed in our laboratory for the preparation of α-alumina (*16*), aluminates (*17*), ferrites (*18*), high T_c cuprates (*19, 20*), and dielectric oxide materials (*21*).

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TABLE I

CHEMICAL ANALYSIS DATA OF $M_{1/3}Mn_{2/3}(N_2H_3COO)_2 \cdot 2H_2O$ (M = Mg AND Zn) AND $N_2H_5M_{1/3}Mn_{2/3}(N_2H_3COO)_3 \cdot H_2O$ (M = Co AND Ni)

	%M		%Mn		%Hydrazine	
M	Obsvd	Theor	Obsvd	Theor	Obsvd	Theor
Mg	3.56	3.51	15.80	15.56	27.81	27.78
Zn	8.89	8.91	14.93	14.98	26.31	26.22
Co	5.87	5.90	10.93	11.01	38.55	38.55
Ni	5.85	5.88	10.95	10.90	38.54	38.56

2.1. Experimental

(a) Preparation of Manganites by the Precursor Method

The ligand $N_2H_3COO^-$ was prepared by the reaction of ammonium carbonate with hydrazine hydrate or by saturating $N_2H_4 \cdot H_2O$ with CO_2(g) as reported earlier (*22*).

An aqueous solution containing metal(II) sulfate (M = Co, Ni, Mg, and Zn) and manganese(II) sulphate in the molar ratio (1 : 2) was treated with the ligand $N_2H_5COON_2H_3$ until the precipitate just dissolved. When this clear solution was kept exposed to air, crystals separated out in a couple of weeks. The crystals were washed with alcohol and dried over P_2O_5 in a vacuum dessicator. The chemical composition of the precursors was fixed as $N_2H_5M_{1/3}Mn_{2/3}(N_2H_3COO)_3 \cdot H_2O$ (M = Co and Ni) and $M_{1/3}Mn_{2/3}(N_2H_3COO)_2 \cdot 2H_2O$ (M = Mg and Zn) by chemical analysis, IR, and TG-DTA (Tables I and II). On being heated at 250°C the precursors undergo self-sustained decomposition and yield foamy, voluminous single-phase spinel manganites.

(b) Preparation of Manganites by the Combustion Method

The stoichiometric composition of metal nitrate (oxidizer) and maleic hydrazide, $C_4H_4N_2O_2$ (fuel), was calculated using the total oxidizing and reducing valencies of the components which serve as the numerical coefficients for the stoichiometric balance so that the equivalence ratio, Φ_e, is unity and the heat evolved is maximum (*23*). Accordingly, the molar ratio of divalent metal nitrate to maleic hydrazide becomes 1 : 0.625.

In a typical experiment, $Mn(NO_3)_2 \cdot 4H_2O$ (8.5234 g) and $Ni(NO_3)_2 \cdot 6H_2O$ (4.9374 g) were taken in a Pyrex dish and dissolved in

TABLE II

THERMOANALYTICAL AND IR DATA OF THE PRECURSORS

Precursor	DTA peak temp (°C)	% Weight loss		Product	IR (cm^{-1})
		Obsvd	Reqd		
$Mg_{1/3}Mn_{2/3}(hc)_2 \cdot 2H_2O$	225 (exo)	71.00	71.37	$MgMn_2O_4$	990
$Zn_{1/3}Mn_{2/3}(hc)_2 \cdot 2H_2O$	240 (exo)	67.50	67.37	$ZnMn_2O_4$	990
$N_2H_5Co_{1/3}Mn_{2/3}(hc)_3 \cdot H_2O$	205(exo)	78.50	78.65	$CoMn_2O_4$	965,990
$N_2H_5Ni_{1/3}Mn_{2/3}(hc)_3 \cdot H_2O$	210(exo)	77.00	76.67	$NiMn_2O_4$	965,990

Note. hc = N_2H_3COO.

minimum amount of water to which $C_4H_4N_2O_2$ (MH) (4.0747 g) was added and the dish containing the solution was introduced into a muffle furnace (l = 28 cm, b = 17 cm, h = 9 cm) maintained at 375 ± 10°C. The mixture boiled, frothed, and ignited to yield voluminous and foamy $NiMn_2O_4$ that occupied the entire volume of the container in less than 5 min. The formation of single-phase $NiMn_2O_4$ was confirmed by powder X-ray diffraction.

2.2. Physical Methods

The X-ray powder diffraction patterns were recorded using a Philips Model PW 1050/70 X-ray diffractometer using Cu$K\alpha$ radiation with Ni filter. Simultaneous TG-DTA experiments were carried out using an ULVAC Sinku-Riko TA-1500 instrument. The IR spectra of the precursors were recorded as a Nujol mull using a Perkin–Elmer 781 spectrophotometer. Particle size measurements were carried out using a Micron Photo Sizer Model SKC-2000 employing sedimentation and light scattering principles. The BET surface areas of the oxides were measured by nitrogen adsorption employing a Micromeritics Accusorb 2100E instrument. The powder densities were determined using a pycnometer employing xylene as the medium.

3.1. Results and Discussion

The results of chemical analysis (Table I) of the precursors show that they are solid solutions of the corresponding metal hydrazine carboxylates. It is known (*22*) that Mn^{2+} and Mg^{2+} react with $N_2H_5COON_2H_3$ to yield $M(N_2H_3COO)_2 \cdot XH_2O$ and with Co^{2+}, Ni^{2+}, and Zn^{2+} to give $N_2H_5M(N_2H_3COO)_3 \cdot XH_2O$. It is natural that solid solutions of $Mn(N_2H_3COO)_2 \cdot XH_2O$ with Mg^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} should form an $M_{1/3}Mn_{2/3}(N_2H_3COO)_2 \cdot XH_2O$-type precursor. However, only Mg^{2+} and Zn^{2+} gave such precursors, while Co^{2+} and Ni^{2+} formed $N_2H_5M(N_2H_3COO)_3 \cdot H_2O$-type complexes. This is confirmed by the IR and TG-DTA data (Table II). Infrared spectra of the precursors show characteristic absorptions of ν_{N-N} of N_2H_3 at 990 cm^{-1} in all the compounds (*22*). Only cobalt and nickel precursors show an absorption at 965 cm^{-1} characteristic of the ν_{N-N} of ionic $N_2H_5^+$ (*13*, *15*) in addition to the absorption at 990 cm^{-1} of N_2H_3. The TG-DTA (Fig. 1) curves of the precursors show single-step decomposition. The exothermic peak (200–240°C) was attributed to the oxidation of $N_2H_3COO^-$ by atmospheric oxygen. The TG weight loss observed (Table II) is in good agreement with the formation of MMn_2O_4 (spinel manganites) from the decomposition of the precursors.

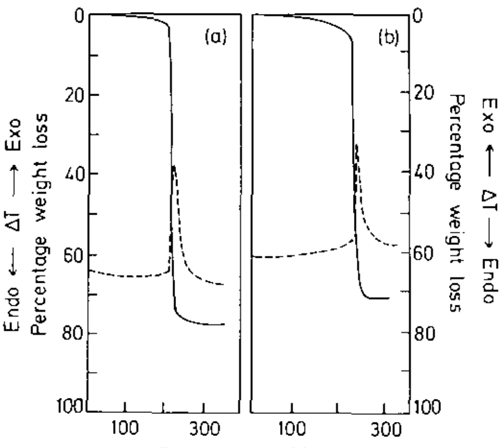

FIG. 1. Simultaneous TG-DTA of (a) $N_2H_5Ni_{1/3}Mn_{2/3}(N_2H_3COO)_3 \cdot H_2O$ and (b) $Mg_{1/3}Mn_{2/3}(N_2H_3COO)_2 \cdot 2H_2O$.

The formation of the manganites MMn_2O_4, where M = Mg, Co, Ni, Cu, and Zn, was confirmed by their characteristic powder X-ray diffraction patterns. The XRD patterns of $NiMn_2O_4$ prepared both by the thermal decomposition of the precursor and by combustion of redox mixture are

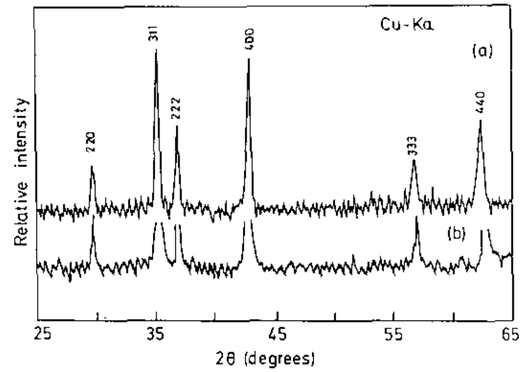

FIG. 2. X-ray powder diffraction patterns of $NiMn_2O_4$: (a) precursor method and (b) combustion method.

shown in Fig. 2. The XRD patterns show considerable line broadening, indicating the fine particle nature of the manganites. The lattice constant (a = 8.4191 Å) is in good agreement with the literature (a = 8.4190 Å) (*24*). The XRD patterns and the lattice constants of all the other manganites (Table III) are also in agreement with the literature (*24*). It is interesting to note that Mg, Co, and Zn manganites have tetragonal structures and nickel and copper manganites form cubic spinels. This observation is as expected (*25*).

The particulate properties of manganites, like density, surface area, and average agglomerate particle size have been summarized in Table III. The particle size distribution of $CoMn_2O_4$ prepared by both precursor and combustion methods are shown in Fig. 3. The average agglomerate size of $CoMn_2O_4$ calculated from the particle size distribution curve is 0.69 μm (Fig. 3a) and 0.70 μm (Fig. 3b); i.e., 50% of the particles have a mean diameter of 0.69 and 0.70 μm. The powder densities are in the range of 65–72% theoretical density. The surface area values of MMn_2O_4 prepared by metal hydrazine carboxylate precursor and combustion methods are comparable in the cases of $MgMn_2O_4$ (30 m^2/g) and $ZnMn_2O_4$ (60 m^2/g). However, there is no trend in the surface areas of the transition metal manganites although combustion derived manganites have surface areas in the range 30–56 m^2/g. Surprisingly $CoMn_2O_4$ prepared by the precursor method has the highest surface area (76 m^2/g) and $NiMn_2O_4$ the lowest (20 m^2/g). This may be due to the marked differ-

TABLE III

PARTICULATE PROPERTIES OF SPINEL MANGANITES DERIVED FROM PRECURSOR (A) AND COMBUSTION (B) METHODS

Material	Lattice const from XRD (A°)	Density[a] (g/cm^3)		Surface area (m^2/g)		Particle size (μm)	
		A	B	A	B	A	B
$MgMn_2O_4$ (tet.)	$a = b$ = 5.7588 c = 9.4044	2.90 (67.5)	2.95 (68.7)	27.88	30.08	4.85	0.71
$CoMn_2O_4$ (tet.)	$a = b$ = 5.7210 c = 9.2664	3.65 (71.5)	3.68 (72.1)	76.08	38.62	0.69	0.70
$NiMn_2O_4$ (cubic)	$a = b = c$ = 8.4191	3.40 (65.4)	3.62 (69.7)	20.00	42.80	5.32	0.86
$CuMn_2O_4$ (cubic)	$a = b = c$ = 8.3323	—	3.73 (69.3)	—	56.54	—	0.69
$ZnMn_2O_4$ (tet.)	$a = b$ = 5.6621 c = 9.3446	3.55 (67.5)	3.58 (68)	60.70	60.54	1.90	0.78

[a] Values in the parentheses are percentages of theoretical density.

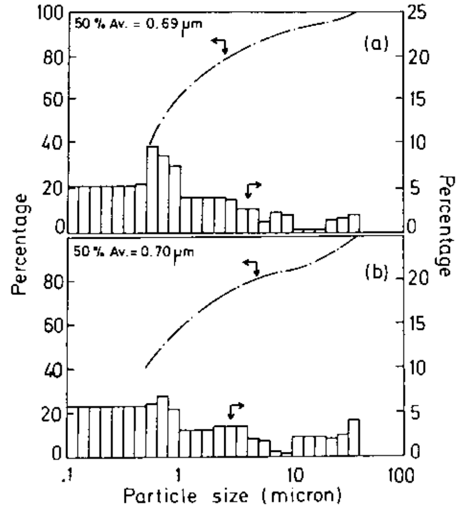

FIG. 3. Particle size distribution of $CoMn_2O_4$: (a) precursor method and (b) combustion method.

ence in the decomposition/combustion behavior of the precursors; i.e., the cobalt compound burns without flame (smoldering) whereas the nickel compound ignites (pyrophoric) and the product ($NiMn_2O_4$) appears to have sintered.

3.2. Mechanism

Formation of fine particle spinel manganites by the precursor method can be attributed to their low ignition temperatures and their liberation of a large amount of gases. The thermolysis reaction can be written as follows:

$$3(N_2H_5M_{1/3}Mn_{2/3}(N_2H_3COO)_3 \cdot H_2O) \quad (M = \text{Co and Ni}) \xrightarrow[250^\circ C]{\text{atmospheric } O_2} MMn_2O_4(s) + 9CO_2(g) + 12\,N_2(g) + 24H_2O(g)$$

$$3(M_{1/3}Mn_{2/3}(N_2H_3COO)_2 \cdot 2H_2O) \quad (M = \text{Mg and Zn}) \xrightarrow[250^\circ C]{\text{atmospheric } O_2} MMn_2O_4(s) + 6CO_2(g) + 6\,N_2(g) + 15H_2O(g).$$

Thus, the precursor method (solid state decomposition) can be considered as a combustion process which uses atmospheric oxygen for the combustion of the precursor which is fuel-rich. The decomposition is self-sustained, once initiated, and is accompanied by the liberation of gases like N_2, H_2O, and CO_2. This facilitates the formation of fine particle spinel manganites by dissipating the heat and inhibiting the sintering of the product. On the other hand, the combustion method involves solution pyrolysis which carries its own oxygen from metal nitrates. The exothermicity of the redox reaction provides the energy required to form the manganites. The reaction, being highly exothermic, is autocatalytic once initiated.

4. Conclusions

Thermal decomposition/combustion of the redox compounds $N_2H_5M_{1/3}Mn_{2/3}(N_2H_3COO)_3 \cdot H_2O$ (M = Co and Ni) and $M_{1/3}Mn_{2/3}(N_2H_3COO)_2 \cdot 2H_2O$ (M = Mg and Zn), and of mixtures of $M(NO_3)_2$ (M = Mg, Co, Ni, Cu, and Zn), $Mn(NO_3)_2 \cdot 4H_2O$, and MH (1 : 1 : 1.875 molar ratio) yield fine particle, single phase manganites. The particulate properties of manganites derived from both the methods are comparable.

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