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Low temperature cobaltite formation using mixed metal oxalate hydrazinate precursor

K. C. PATIL, D. GAJAPATHY, V. R. PAI VERNEKER
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Oxide spinels such as ferrites, cobaltites and chromites are of importance because of their use as catalysts and oxide electrode materials [1]. The commonest method for the preparation of these spinels consists of preparing an intimate physical mixture of the appropriate individual oxides or carbonates and heating this mixture to a temperature sufficiently high to cause the reaction of one oxide with the other and the formation of a new phase. In this process of prolonged high temperature calcination the surface area of the specimens is considerably reduced and consequently it becomes impossible to use them as catalysts. Of the various methods used to synthesize these oxide spinels the precursor technique is more advantageous because the precursors achieve excellent stoichiometry, low trace impurity content and homogeneity approaching the maximum theoretically possible. The principle advantage of the precursor method is that the two methods are mixed on an atomic scale so that greater reactivity and more homogeneous products result than by heating a mixture of ball milled oxides. Many precursors such as pyridinates [2] and ammoniates [3] have been reported. Though stoichiometric oxides are obtained by this method the temperatures of decomposition are as high as 1000° C. Recently we have reported [4] the synthesis of spinel ferrites using mixed metal oxalate hydrazinate precursors at temperatures as low as 120 to 200° C. It was thought appropriate to attempt the synthesis of other oxide materials such as cobaltites by extending this method.

Precursors of the formula $MgCo_2(C_2O_4)(N_2H_4)_5$ and $NiCo_2(C_2O_4)_3(N_2H_4)_6$ were prepared by either of the following methods.

(i) Electrolytic grade magnesium/nickel and cobalt powders in the stoichiometric ratio (1:2) were dissolved in a solution of ammonium oxalate (6 parts) in hydrazine hydrate. It takes a few hours for the metal powders to completely go into solution

$$Mg + 2Co + 3(NH_4)_2C_2O_4 \cdot H_2O +$$
$$5N_2H_4H_2O \rightarrow MgCo_2(C_2O_4)_3(N_2H_4)_3(N_2H_4)_5 +$$
$$6NH_3 + 8H_2O + 3H_2$$

$$Ni + 2Co + 3(NH_4)_2C_2O_4 \cdot H_2O +$$
$$6N_2H_4 \cdot H_2O \rightarrow NiCo_2(C_2O_4)_3(N_2H_4)_6 +$$
$$6NH_3 + 9H_2O + 3H_2$$

(ii) Electrolytic grade cobalt powder (0.08 mol) was dissolved in a solution of magnesium/nickel acetate (0.04 mol) in 400 ml of 1:1 acetic acid. When the metal powder had completely dissolved a solution of oxalic acid (0.124 mol) was added to precipitate the corresponding double oxalate hydrates. Such a procedure for the preparation of double oxalate hydrates has been reported in the literature [5]. These double oxalate hydrates were converted into the corresponding hydrazinates by treating them with hydrazine hydrate.

Both the methods yield the hydrazinates with the same composition.

The results of the chemical analysis of the precursors [$MgCo_2(C_2O_4)_3(N_2H_4)_5$: % Mg–4.05 (4.30), % Co–20.62 (20.82), % $C_2O_4^{2-}$–47.72 (46.61), % N_2H_4–28.18 (28.26); $NiCo_2(C_2O_4)_3(N_2H_4)_6$: % Ni–9.62 (9.28), % Co–18.90 (18.63), % $C_2O_4^{2-}$–42.67 (41.74), % N_2H_4–31.12 (30.35); theoretical values are given in the brackets] are in very good agreement with the assigned composition.

Infrared spectra of the samples were recorded as nujol mulls on a Perkin Elmer PE 599 spectrophotometer. The spectra (Table I) confirm the presence of coordinated oxalate and hydrazine. The spectra have characteristic absorptions of bidentate oxalate [6] at 1650, 1320, 1300 and

TABLE I Infrared spectra data of $MCo_2(C_2O_4)_3(N_2H_4)_x$ (M = Mg, Ni)

$MgCo_2(C_2O_4)_3(N_2H_4)_5$	$NiCo_2(C_2O_4)_3(N_2H_4)_6$	Assignment
3320	3320	NH stretching
3150	3250	
	3160	
1650	1640	OCO asym. stretching
1320	1345	OCO sym. stretching
1300		
1205	1205	NH_2 twisting
1120	1190	
	1120	
960	970	N–N stretching
830	820	OCO bending
780	785	
650	660	NH_2 rocking
560	545	M–O stretching
500	500	OCO bending + CCO bending
365	350	M–N stretching

780 cm^{-1} and bidentate bridging hydrazine [7] at 3320, 3150, 1205, 1120 and 960 cm^{-1}.

Differential thermal analysis (DTA) experiments were done using an instrument described elsewhere [8] fitted with an omniscribe strip chart recorder. DTA shows that both $MgCo_2(C_2O_4)_3(N_2H_4)_5$ and $NiCo_2(C_2O_4)_3(N_2H_4)_6$ decompose exothermically; the peak temperatures being 272 and 223° C, respectively. Thermogravimetric (TG) data confirm that in both the cases the decomposition is single step. Observed weight losses in TG are in agreement for the formation of $MgCo_2O_4$ (% weight loss observed was 62, the required being 63.7) and $NiCo_2O_4$ (% weight loss observed was 63, the required being 61.9) from these precursors. Thermogravimetric analysis was carried out on a stanton Redcraft TG 750 thermobalance. Platinum cups were used for both DTA and TG experiments and the experiments were done in air.

Formation of cobaltites as the final products of decomposition was confirmed by X-ray diffraction pattern. The powder diffraction patterns of both residues are characteristic of cobaltite spinels with $a = 0.811$ and 0.813 nm which conforms to the literature value [9] for $MgCo_2O_4$ and $NiCo_2O_4$, respectively. The X-ray diffraction patterns were recorded on a Philips PW 1050/70 diffractometer using Co$K\alpha$ radiation.

Formation of cobaltites were also confirmed by infrared data. Infrared spectra show absorptions due to metal oxygen stretching from tetrahedral and octahedral sites at 650 cm^{-1} and 550 cm^{-1}, respectively, in analogy with data on ferrites [10] and other spinel oxides [11].

When the precursors were ignited in air they decomposed autocatalytically to yield the cobaltites. Once ignited the combustion was self sustained. Similar phenomenon has been observed [12] in the case of simple transition metal oxalate hydrazinates. The autocatalytic behaviour and the low temperature decomposition are due to the exothermic decomposition of oxalate and hydrazine in air; hydrazine being a fuel sustains combustion.

The same procedure of synthesis using hydrazinates could be used to synthesize other oxide materials which find applications as semiconductors, catalysts, electric and magnetic devices etc.

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