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PREPARATION, THERMAL, XRD, CHEMICAL AND FTIR SPECTRAL ANALYSIS OF $NiMn_2O_4$ NANOPARTICLES AND RESPECTIVE PRECURSOR

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Metal carboxylato-hydrazinates are very good precursors for the synthesis of metal as well as mixed metal oxides as these decompose to nanosized oxides with high surface area most of the times at comparatively lower temperatures. In the present study one such novel precursor nickel manganese fumarato-hydrazinate ($NiMn_2(C_4H_2O_4)_3 \cdot 6N_2H_4$) has been prepared and characterized by XRD, FTIR and chemical analysis. The thermal decomposition of the precursor has also been studied by isothermal, differential thermal and thermogravimetric analysis. The precursor shows two-step dehydrazination followed by decarboxylation to form $NiMn_2O_4$. The infrared spectra show N–N stretching frequency at 965 cm^{-1}, which confirm the bidentate bridging hydrazine. XRD confirms the formation of single phase $NiMn_2O_4$.

Keywords: *chemical, FTIR spectral analysis, metal carboxylato-hydrazinates,* $NiMn_2O_4$*, thermal, XRD*

Introduction

The chemistry of hydrazine is interesting not only because it has a potent N–N bond, two free electron pairs and four substitutable hydrogen atoms but also because it forms various complexes with transition metals. Thermal reactivity of metal hydrazine complexes is of a great interest since the stability of complexes changes dramatically, depending upon the anions as well as the cation [1]. Secondly, hydrazine being a fuel not only supports combustion but also lowers the decomposition temperature of the metal complexes [2–4]. These complexes are important as precursors to obtain simple as well as mixed ultrafine metal oxides, which can have interesting electrical, magnetic and catalytic properties. Nanomaterials have attracted increasing interest of researchers all over the world. Therefore, many authors have synthesized and characterized various nanomaterials [5–21]. We are reporting here the preparation and characterization of nickel manganese fumarato-hydrazinate and its thermal decomposition to $NiMn_2O_4$ nanoparticles.

Experimental

Preparation of nickel manganese fumarato-hydrazinate

The method of preparation of nickel manganese fumarato-hydrazinate is similar to the one described elsewhere [22]. A requisite quantity of sodium fumarate in aqueous medium was stirred with hydrazine hydrate, $N_2H_4 \cdot H_2O$ (99–100%) in an inert atmosphere for 2 h. To this solution, a solution containing nickel and manganese chloride in stoichiometric amount was added dropwise with constant stirring in an inert atmosphere. The precipitate thus obtained was then filtered, washed with ethanol, dried with diethyl ether and stored in a vacuum desiccator.

Methods

Hydrazine content of the complex was analyzed titration using KIO_3 as titrant [23]. The percentage of nickel and manganese was estimated by the standard methods given in the Vogel's textbook [23]. The elemental analysis of the precursor as well as $NiMn_2O_4$ nanoparticles was also carried out using atomic absorption spectrophotometer (model AAS 201 Chemito Instrument).

Infrared analysis of the complex and its thermal products ($NiMn_2O_4$ nanoparticles) was done on Shimadzu FTIR, model 8101 A.

Simultaneous differential thermal analysis (DTA) and thermogravimetric (TG) analysis of the complex was done on PL-STA 1500 Analyzer (Rheometric Scientific, UK), from RT to 900°C in air. The heating rate was maintained at 10°C min^{-1}.

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Table 1 Chemical and thermal analysis of nickel manganese fumarato-hydrazinate

Precursor	Nickel/%		Manganese/%		Hydrazine/%		Total mass loss/%		TG mass loss-DTA peaks		
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Temp. range/°C	Mass loss/%	Exo/endo peaks/°C
Nickel manganese fumarato-hydrazinate $NiMn_2(C_4H_2O_4)_3 \cdot 6N_2H_4$									rT–250	22.2	246.5 (exo)
									250–288	4.55	exo hump
									288–344	35.75	310.7 (exo)
	8.33	8.35	15.08	15.63	27.0	27.32	66.8	66.89	344–900	2.0	321.3 (exo)

The isothermal and the total mass loss studies of the complex were carried out at various predetermined temperatures. The isothermal products were also chemically analysed for the hydrazine content and characterized by infrared spectral analysis.

Autocatalytic decomposition of the complex

The dried complex was spread on a Petri dish and a burning splinter was brought near to it, when small portion of it caught fire. A red glow that formed immediately spread on the entire bulk completing the total decomposition of the complex in an ordinary atmosphere.

X-ray diffraction (XRD) pattern of the autocatalytically decomposed end product of the complex ($NiMn_2O_4$ nanoparticles) as well as the sintered $NiMn_2O_4$ nanoparticles at 900°C was obtained using Scintage X-ray powder diffractometer using CuK_α radiations and Ni filter. The observed d values were compared with the JCPDS file for $NiMn_2O_4$ to identify the phases [24].

Results and discussion

Chemical formula determination of nickel manganese fumarato-hydrazinate

The infrared spectra of the complex (Fig. 1) show three bands in the region 3190–3348 cm^{-1} due to the N–H stretching frequencies. The N–N stretching frequency at 965 cm^{-1} confirms the bidentate bridging hydrazine molecules [25]. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1590 and 1370 cm^{-1}, respectively with the $\Delta\nu(\nu_{asy}-\nu_{sy})$ separation of 220 cm^{-1}, indicating the monodentate linkage of both carboxylate groups in the dianion. This IR data thus suggest that the nickel manganese fumarato-hydrazinate complex is formed.

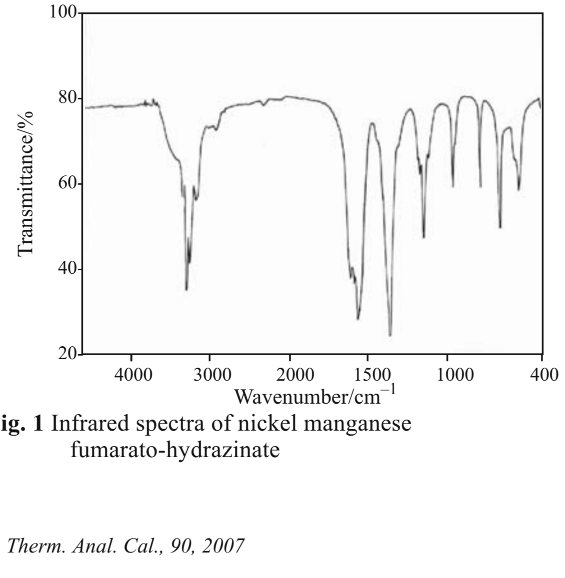

Fig. 1 Infrared spectra of nickel manganese fumarato-hydrazinate

A chemical formula, $NiMn_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ is determined for nickel manganese fumarato-hydrazinate based on the percentage of hydrazine (27.00), nickel (8.33) and manganese (15.08) which match closely with the calculated value of 27.32, 8.35 and 15.63% for hydrazine, nickel and manganese, respectively (Table 1). Similarly, the observed mass loss of 66.80% in total mass loss studies (~800°C) and 66.03% in isothermal mass loss studies (at 400°C) matches well with the calculated value 66.89%, based on the above formula.

Thermal analysis of the precursor and phase identification of the $NiMn_2O_4$ nanoparticles

Nickel manganese fumarato-hydrazinate decomposes in air thermally and autocatalytically to $NiMn_2O_4$. The ‘d’ values calculated from the X-ray diffraction pattern of the autocatalytically decomposed end product of the complex as well as the sintered $NiMn_2O_4$ nanoparticles at 900°C match well with the reported values [24].

TG-DTA, isothermal mass loss and hydrazine analysis

The TG-DTA curves of $NiMn_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ is shown in Fig. 2. The TG curve, from room temperature (RT) to 900°C shows four mass loss regions with two major ones [Table 1]. The mass losses of 22.2 and 4.55%, from rT to 250°C and from 250 to 288°C were due to the loss of five and one N_2H_4 molecules, respectively. DTA curve shows a sharp exothermic peak with a peak temperature at 246.5°C followed by an exothermic hump, was due to dehydrazination. The major mass loss of 35.75% on TG curve from 288 to 344°C is attributed to the decarboxylation of dehydrazinated fumarate precursor. DTA curve shows two exothermic peaks in this region with the peak temperature of 310.7 and 321.3°C due to the two-step oxidative decarboxylation. A marginal mass loss of 2% was observed from 344 to 900°C on TG curve due to the oxidation of unburned carbon. Isothermal mass loss studies carried out from rT to

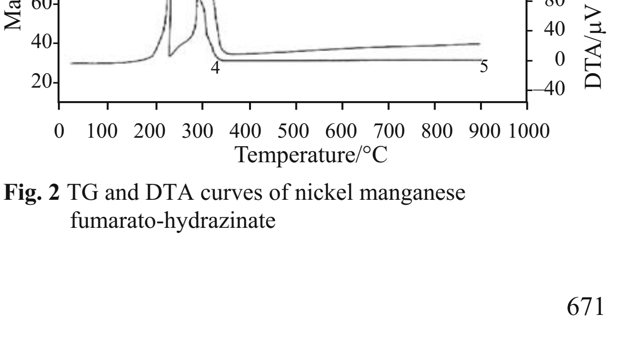

Fig. 2 TG and DTA curves of nickel manganese fumarato-hydrazinate

400°C with a temperature interval of 25°C show total dehydrazination around 150°C and mass loss of 66.03% at 400°C. It has been reported that the hydrazinated precursors releases hydrazine molecule in presence of air and between 150 to 300°C, which reacts explosively with atmospheric oxygen liberating enormous energy [22] sufficient to oxidatively decompose the dehydrazinated complex to its metal oxide. The single phase $NiMn_2O_4$ nanoparticles formation in the present study soon after the thermal decomposition has been confirmed by XRD.

Conclusions

- Nickel manganese fumarato-hydrazinate can be synthesized easily from sodium fumarate, nickel chloride, manganese chloride and hydrazine hydrate in an inert atmosphere at room temperature.
- Chemical analysis, total mass loss and infrared spectral studies of the complex confirms the formation of the complex with formula $NiMn_2(C_4H_2O_4)_3 \cdot 6N_2H_4$.
- The precursor decomposes autocatalytically once ignited to form $NiMn_2O_4$ nanoparticles.
- TG-DTA studies of the complex show two-step dehydrazination followed by decarboxylation to form $NiMn_2O_4$ nanoparticles.
- XRD confirms the formation of the single phase $NiMn_2O_4$ nanoparticles.

References

1 K. C. Patil, Proc. Ind. Acad. Sci. (Chem. Sci.), 96 (1986) 459.
2 R. A. Porob, S. Z. Khan, S. C. Mojumdar and V. M. S. Verenkar, J. Therm. Anal. Cal., 86 (2006) 605.
3 A. More, V. M. S. Verenkar and S. C. Mojumdar, Nano Letters, to be submitted.
4 A. More, S. C. Mojumdar, S. Parab and V. M. S. Verenkar, Preparation, Purification and Characterization of Nanoparticle Ferrite From Novel Fumarato-Hydrazinate Precursor, 15th CTAS Annual Workshop and Exhibition, May 17–18, 2005, National Research Council Canada, Boucherville, Québec J4B 6Y4, Canada, p. 22.
5 H. Matsuyama and J. F. Young, J. Mater. Res., 14 (1999) 3379.
6 S. C. Mojumdar and L. Raki, J. Therm. Anal. Cal., 82 (2005) 89.
7 H. Matsuyama and J. F. Young, J. Mater. Res., 14 (1999) 16.
8 S. C. Mojumdar and L. Raki, J. Therm. Anal. Cal., 86 (2006) 651.
9 H. Matsuyama and J. F. Young, Chem. Mater., 11 (1999) 3389.
10 S. C. Mojumdar, L. Raki, N. Mathis, K. Schmidt and S. Lang, J. Therm. Anal. Cal., 86 (2006) 119.
11 M. Alexandre and P. Dubois, Mater. Sci. Eng., 28 (2000) 1.
12 S. C. Mojumdar, Res. J. Chem. Environ., 9 (2005) 23.
13 P. Cavert, Potential application of nanotubes, in: T. W. Ebbesen (Ed.), Carbon Nanotubes, CRC Press, Boca Raton, FL, 1997, pp. 277–292.
14 S. C. Mojumdar and L. Raki, J. Therm. Anal. Cal., 86 (2006) 99.
15 M. Drábik, L. Gáliková, K. G. Varshney and M. A. Quraishi, J. Therm. Anal. Cal., 76 (2004) 91.
16 G. K. D. Pushpalal, J. Mater. Sci., 35 (2000) 981.
17 S. C. Mojumdar, J. Therm. Anal. Cal., 64 (2001) 1133.
18 B. X. Li, W. Q. Liang, W. S. Zhang and Z. He, J. Chin. Cer. Soc., 28 (2000) 325.
19 S. C. Mojumdar, Thermophysics 2001, October 23-25, 2001, Račková Dolina, High Tatras, Slovakia, pp. 93–98.
20 K. Kendal, A. J. Howard and J. D. Birchal, Philos. Trans. R. Soc., A310 (1983) 139.
21 S. C. Mojumdar, B. Chowdhury, K. G. Varshney and K. Mazanec, J. Therm. Anal. Cal., 78 (2004) 135.
22 Satyavan Y. Sawant, K. R. Kannan and V. M. S. Verenkar, in Proc. 13th Nat. Symp. on Thermal Analysis, B.A.R.C., Mumbai, 2002 (Eds. C. G. S. Pillai, K. L. Ramakumar, P. V. Ravindran and V. Venugopal), Indian Thermal Analysis Society, Mumbai (2002) 154.
23 I. Vogel, ‘A Text Book of Quantitative Inorganic Analysis’, 4th Edition, Longman, UK (1985).
24 JCPDS, Powder diffraction file No. 1-1110.
25 A. Braibanti, F. Dallavalle, M. A. Pellinghelli and E. Leporati, Inorg. Chem., 7 (1968) 1430.

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