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Synthesis of sodium ferrite by precursor and combustion methods: A comparative study

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Abstract

Thermal decomposition of sodium ferricarboxylate precursors, $Na_3[Fe(L)_6].xH_2O$ (L = formate, acetate, propionate, butyrate) has been carried out in flowing air atmosphere from ambient temperature to 850 °C. Various physico-chemical techniques i.e. TG, DTG, DSC, XRD, IR, Mössbauer spectroscopy, etc. have been employed to characterize the intermediates and end products. After dehydration, the anhydrous complexes undergo decomposition to yield various intermediates i.e. sodium propionate/oxalate/carbonate and α-Fe_2O_3 in the temperature range 260–285 °C. A subsequent decomposition of sodium carbonate leads to the formation of sodium oxide in the successive stages. Finally, nanosized ferrites of the stoichiometry, $NaFeO_2$ have been obtained above 760 °C as a result of solid-state reaction between α-Fe_2O_3 and Na_2O. The same ferrite has also been prepared by the combustion method at comparatively lower temperature (400 °C) and in less time than that of precursor/conventional ceramic methods.

Keywords: A. Calcination; B. X-ray method; Mössbauer spectroscopy; D. Ferrites

1. Introduction

Mixed metallic oxides are designated as an important class of compounds and among them ferrites are most prominent by virtue of their high electrical resistivity, thermodynamic stability, electro-catalytic activity and resistance to corrosion. Ferrites are regarded as better magnetic materials than pure metals because of their high resistivity, lower cost, easier manufacture and superior magnetization properties. Alkali metal ferrites have attracted a considerable attention owing to their potential application in high capacity batteries, electrochromic displays, waste-water cleaning, low magnetization ferrofluids, intercalation electrodes in rechargeable batteries and as strong oxidizing agents [1–7]. The structural stability of ordered rocksalt structures with composition AMO_2 (A = alkali metal; M = transition metal) has also been investigated as a function of size and charge of the cations [8]. Metal ferricarboxylates have proven to be very suitable precursors for the synthesis of powdered ferrites (precursor method) due to their complexing ability, sensitivity towards oxidation state and ease of decomposition. On the other side, the combustion method involves the formation of stoichiometrically pure and single-phase nanoparticle ferrite from a highly exothermic redox chemical reaction [9,10]. Another reason for undertaking such investigation is to synthesize ferrite powders at lower temperature and shorter time than usually observed in conventional ceramic method. The ceramic method, which is the most common technique for bulk preparation of ferrites, involves high temperature sintering of reactant oxides coupled with frequent milling. Since high sintering temperature results in particle coarsening and aggregation, nanoparticle ferrites cannot be obtained by this method [11,12].

2. Experimental procedure

Sodium ferricarboxylate precursors, $Na_3[Fe(L)_6].xH_2O$ (L = formate, acetate, propionate, butyrate), were prepared by mixing stoichiometric quantities of aqueous solutions of ferric nitrate, respective sodium carboxylate and respective carboxylic acid. The reaction mixture was stirred vigorously and then concentrated on water bath until a brown colored product formed. The product was filtered, washed with cold

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water, dried and stored in vacuum desiccator. The identity of the complexes (precursors) was established by chemical analysis. The percentage of iron was determined spectrophotometrically using 1,10-phenanthroline [13]. Sodium content in each precursor was determined flame photometrically.

For the preparation of ferrites by combustion method, the stoichiometric quantities of aqueous solutions of $NaNO_3$, $Fe(NO_3)_3.9H_2O$ and oxalyl dihydrazide ($C_2H_6N_4O_2$) were mixed in a pyrex dish and the reaction mixture was combusted in a muffle furnace maintained at 400 °C. The entire combustion process was over in 30 min to yield the ferrite by the redox reaction:

$$\begin{aligned} &NaNO_3(aq) + Fe(NO_3)_3(aq) + 2C_2H_6N_4O_2(aq) \\ &\quad \rightarrow NaFeO_2 + 4CO_2(g) + 6N_2(g) + 6H_2O(g) \end{aligned}$$

The experimental details for recording IR, XRD, TG-DTG-DSC and SEM are reported elsewhere [14]. The Mössbauer studies were performed at Technical University of Braunschewig, Braunschewig (Germany) using a conventional transmission spectrometer in a constant acceleration mode. A $^{57}Co/Rh$ γ-ray source was used. The velocity scale was calibrated relative to ^{57}Fe in Rh. For the identification of intermediates and products, the precursors were also calcined isothermally in nickel crucibles. The variation in temperature was kept within ±5 °C during isothermal calcinations.

3. Results and discussion

3.1. Precursor method

IR spectrum of sodium hexa(formato)ferrate (III) precursor shows a broad band centered at about 3280 cm^{-1} due to ν(O–H) of lattice water and a small but distinct shoulder at 2910 cm^{-1} due to ν(C–H) of the formate group. Intense bands in the ranges 1630–1655 and 1380–1410 cm^{-1} are attributed to ν_{asy}(C=O) and ν_{sym}(C=O) of the coordinated formate groups [15], respectively. A small but distinct band at 580 cm^{-1} due to ν(Fe–O) suggests the presence of Fe–O (carboxylate) bonding [16]. The other precursors display almost similar IR spectra.

Mössbauer spectra of the precursors exhibit a doublet (Fig. 1) with isomer shift (δ) and quadrupole splitting (Δ) values in the ranges 0.29–0.34 and 0.60–0.80 mm s^{-1}, respectively. These values correspond to ferric ions in octahedral coordination [17]. The coordination number of six for iron is satisfied by six formate ligands which bind to iron through oxygen atoms of the carboxylate groups. The outer cation (Na^+) and water molecules seem to be responsible for linking together the complex ion, $[Fe(L)_6]^{3-}$. The fits of the spectra of these precursors result in a relatively narrow Lorentzian line half-width ($\Gamma \sim 0.13$ mm s^{-1}) indicating that these precursors are in paramagnetic state. The decomposition behaviour of each precursor complex is discussed separately:

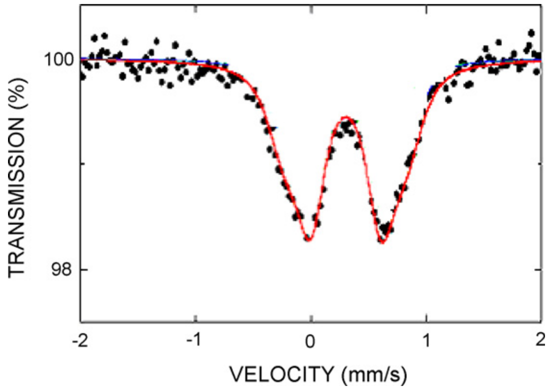

Fig. 1. Mössbauer spectrum of sodium ferriformate dihydrate.

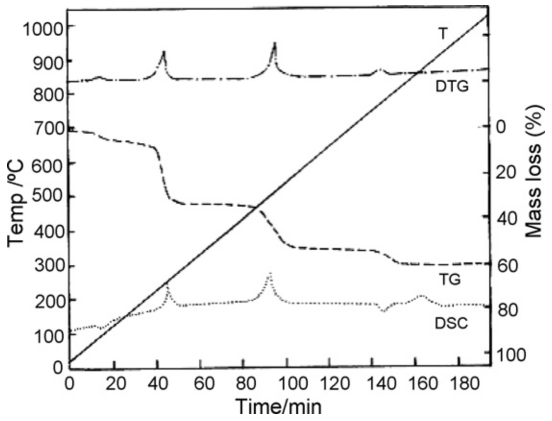

Fig. 2. Simultaneous TG–DTG–DSC curves of sodium ferriformate dihydrate.

3.1.1. Sodium hexa(formato)ferrate(III)dihydrate, $Na_3[Fe(HCOO)_6].2H_2O$

Fig. 2 shows the simultaneous TG–DTG–DSC curves of sodium hexa(formato)ferrate(III) dihydrate in flowing air atmosphere at a heating rate of 5 °C min^{-1}. The complex undergoes dehydration till weight loss of 8% is reached at 150 °C (calc. loss = 8.3%). The corresponding DSC (endotherm) and DTG peaks lie at 90 and 95 °C, respectively. After remaining stable up to 215 °C, the anhydrous complex undergoes oxidative decomposition to yield Fe_2O_3 and sodium oxalate until weight loss of 34.6% is reached at 280 °C (calc. loss = 34.8%). Corresponding to this step, DSC shows an exotherm at 250 °C accompanied by an enthalpy change (ΔH) of −82.75 kJ mol^{-1}. DTG also shows a respective distinct signal at 252 °C. The conversion of formate into oxalate during thermolysis has been reported in literature [18]. These intermediates remain stable up to 500 °C as indicated by the presence of an arrest in TG. The presence of Fe_2O_3 has been confirmed by the Mössbauer spectrum of the residue from precursor calcined at 500 °C for 30 min. It displayed a symmetrical sextet due to magnetic hyperfine interactions (Fig. 3) with parameters (Table 1) in close agreement to those reported for α-Fe_2O_3 of bulk size [19]. As heating continues, sodium oxalate gets decomposed into sodium carbonate as confirmed by weight loss of 53% at 580 °C (calc. loss = 53.3%). Corresponding to this step, there exists a DTG peak at 520 °C that is exo in DSC. At higher temperature, sodium carbonate decomposes into sodium oxide with the evolution of CO_2 as indicated by weight loss of 60% at 800 °C.

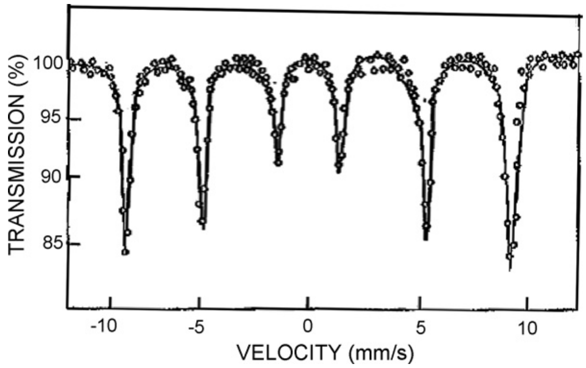

Fig. 3. Mössbauer spectrum of the precursor calcined at 500 °C for 30 min.

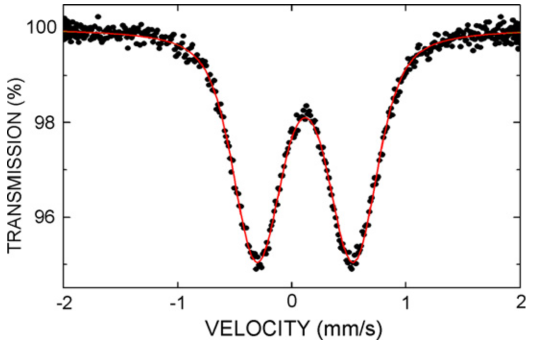

Fig. 4. Mössbauer spectrum of the final thermolysis product of sodium ferriformate dihydrate.

DSC shows an endotherm at 780 °C, characteristic of the evolution of CO_2. Finally, sodium oxide and α-Fe_2O_3 undergo solid-state reaction above 800 °C to yield sodium ferrite, α-$NaFeO_2$ as reflected by an exotherm above 800 °C in DSC. To get pure ferrite, $NaFeO_2$, the unreacted Na_2O was removed from the final thermolysis residue by its repeated washings with water [20]. XRD powder pattern of the final residue shows the existence of α-$NaFeO_2$ [21]. The identity of the ferrite as α-$NaFeO_2$ has also been confirmed by Mössbauer spectrum (Fig. 4) of the final residue that shows a doublet with hyperfine parameters ($\delta = 0.12$ mm s^{-1}, $\Delta = 0.85$ mm s^{-1}) corresponding to ferric (Fe^{3+}) ions in tetrahedral co-ordination [17,22]. The relatively narrow Lorentzian line half-width ($\Gamma = 0.13$ mm s^{-1}) indicates that the ferrite is in paramagnetic state. SEM micrograph reveals that the average particle size of α-$NaFeO_2$ obtained is 45 nm.

3.1.2. Sodium hexa(acetato)ferrate(III)decahydrate, $Na_3[Fe(CH_3COO)_6].10H_2O$

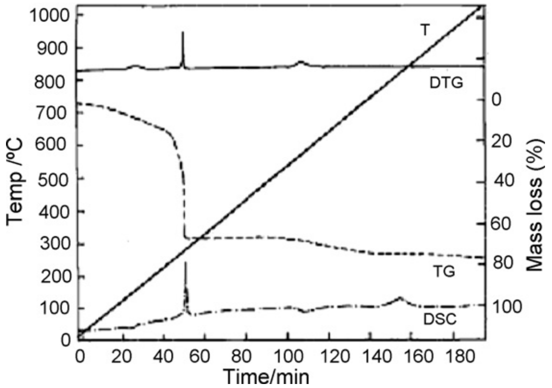

Fig. 5. Simultaneous TG–DTG–DSC curves of sodium ferriacetate decahydrate.

Fig. 5 shows the simultaneous TG–DTG–DSC thermograms of sodium ferriacetate decahydrate at a heating rate of 5 °C min^{-1}. The precursor undergoes a partial dehydration yielding sodium ferriacetate pentahydrate at weight loss of 14% at 235 °C (calc. loss = 13.7%). The corresponding DTG peak lies at 140 °C that is endotherm in DSC. Sodium ferriacetate pentahydrate then undergoes an exothermic decomposition to sodium carbonate and Fe_2O_3 till weight loss 64% is reached at 285 °C (calc. loss = 63.7%). Corresponding to this step, DSC shows a sharp exotherm at 280 °C with $\Delta H = -328$ kJ mol^{-1}. The respective DTG peak also lies at 280 °C. The formation of Fe_2O_3 has been confirmed by recording Mössbauer spectrum of the residue obtained by isothermal firing of the precursor at 300 °C for 30 min. Mössbauer parameters of the residue were similar to those reported [19] for α-Fe_2O_3 of bulk size. As heating continues, sodium carbonate undergoes a gradual decomposition into sodium oxide along with the evolution of CO_2 until weight loss of 73.5% is reached at 760 °C (calc. loss = 73.7%). The evolution of CO_2 is supported by a characteristic endotherm at 590 °C in DSC. DTG also shows a corresponding small signal. Finally, a solid-state reaction occurs between α-Fe_2O_3 and Na_2O above 760 °C yielding

Table 1
Room temperature Mössbauer parameters for the thermolysis products from precursor and combustion methods

Precursor method L	Temperature of calcination(°C)	δ (mm s^{-1})[a]	Δ (mm s^{-1})	Γ (mm s^{-1})	B (kOe)	Assignment
HCOO	500	0.45	–	–	514	α-Fe_2O_3
	>800	0.12	0.85	0.13	–	α-$NaFeO_2$
CH_3COO	300	0.42	–	–	510	α-Fe_2O_3
	>800	0.13	0.86	0.14	–	α-$NaFeO_2$
C_2H_5COO	300	0.44	–	–	512	α-Fe_2O_3
	>800	0.12	0.86	0.13	–	α-$NaFeO_2$
C_3H_7COO	300	0.42	–	–	511	α-Fe_2O_3
	>800	0.12	0.87	0.12	–	α-$NaFeO_2$
Combustion method	400	0.22	0.60	0.23	–	α-$NaFeO_2$

[a] w.r.t. pure iron absorber, Γ: Lorentzian line half-width, B: internal magnetic field.

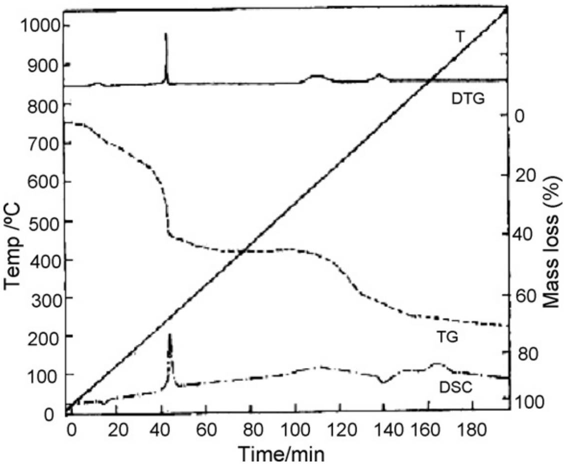

Fig. 6. Simultaneous TG–DTG–DSC curves of sodium ferripropionate dihydrate.

sodium ferrite, $NaFeO_2$ at weight loss of 74.5% (calc. loss = 74.8%). The identity of the ferrite as α-$NaFeO_2$ has been confirmed by recording XRD and Mössbauer data of the end product after removing the unreacted Na_2O. SEM micrograph shows the average particle size of α-$NaFeO_2$ obtained to be 42 nm.

3.1.3. Sodium hexa(propionato)ferrate(III) dihydrate, $Na_3[Fe(CH_3CH_2COO)_6].2H_2O$

Fig. 6 shows the simultaneous TG–DTG–DSC curves of sodium hexa(propionato) ferrate (III) dehydrate in flowing air atmosphere at a heating rate of 5 °C min^{-1}. The complex undergoes dehydration till weight loss of 6.5% is reached at 100 °C (calc. loss = 6.01%). The corresponding DTG peak lies at 90 °C, which is endo in DSC. The anhydrous precursor undergoes oxidative decomposition into sodium propionate and Fe_2O_3, accompanied by weight loss of 37% at 260 °C (calc. loss = 37.1%). Corresponding to this step, DTG shows a sharp peak at 250 °C and DSC shows a sharp distinct exotherm at 255 °C with $\Delta H = -345.6$ kJ mol^{-1}. The intermediates remain stable up to 510 °C. The existence of Fe_2O_3 as α-Fe_2O_3 has been confirmed by Mössbauer parameters (Table 1) of the residue obtained by calcining the precursor isothermally at 300 °C for 30 min. After remaining stable up to 510 °C, sodium propionate decomposes into sodium carbonate as indicated by weight loss of 59.5% at 680 °C (calc. loss = 60%). DSC shows a broad peak at 610 °C while DTG displays the corresponding signal at 605 °C. As heating continues, sodium carbonate gets decomposed into sodium oxide at weight loss of 69.3% at 795 °C (calc. loss = 69%). The evolution of CO_2 in this step is supported by an endotherm in DSC at 740 °C. This is followed by a solid-state reaction between Na_2O and α-Fe_2O_3 to yield sodium ferrite, $NaFeO_2$. The identity of the end product as α-$NaFeO_2$ has been confirmed by recording the Mössbauer spectrum and XRD powder pattern of the end product. SEM analysis indicates that the average particle size of the ferrite obtained is of the order of 40 nm.

3.1.4. Sodium hexa(butyrato)ferrate(III), $Na_3Fe(CH_3CH_2CH_2COO)_6$

The decomposition pattern of this complex is almost similar to that observed for its acetato counterpart (except for the dehydration step as the former is anhydrous).

The above discussion leads to the following major consecutive steps for the aerial thermal decomposition of various sodium ferricarboxylates:

(i) Dehydration of the precursor, (ii) exo-decomposition of the anhydrous complex to α-Fe_2O_3 and respective sodium carboxylate, (iii) exo-decomposition of respective sodium carboxylate into Na_2CO_3, (iv) endo-decomposition of Na_2CO_3 to Na_2O and (v) solid-state reaction between α-Fe_2O_3 and Na_2O to yield sodium ferrite, α-$NaFeO_2$.

3.2. Combustion (solution-phase) method

The ferrite, α-$NaFeO_2$ obtained from the combustion of redox mixture has been characterized by XRD powder data and Mössbauer spectrum of the ferrite also shows a symmetric doublet with an isomer shift value of about 0.22 mm s^{-1}. This value corresponds to ferric ions in octahedral coordination [17]. This is contrary to those isomer shift values of the ferrite, obtained by precursor method, corresponding to Fe^{3+} ions in tetrahedral coordination. The characteristic feature of the Mössbauer spectrum of the ferrite, α-$NaFeO_2$ obtained from combustion method is that it displays a broad doublet with Lorentzian line half-width value of 0.23 mm s^{-1}, about twice that of resulting from the fits of the Mössbauer spectra of the ferrites obtained by precursor method. SEM analysis reveals that the average particle size of the ferrite is 20 nm.

4. Conclusions

In the combustion method, there is direct mixing of the cations on atomic scale. Oxalyl dihydrazide ($C_2H_6N_4O_2$) used in this method acts as a fuel for the combustion synthesis of ferrites. An enormous amount of heat and gases (CO_2, N_2, H_2O vapor) liberated during the exothermic redox chemical reaction not only reduces the external temperature required for the preparation of ferrites but also dissipates the heat, thus inhibiting the sintering of fine ferrite particles.

Unlike the solid precursor thermolysis method for the preparation of ferrites, the solution-phase combustion method is rapid and undergoes a direct conversion from the molecular mixture of the precursor solution to the final oxide (ferrite) product, avoiding the formation of intermediate phases that require inter-diffusion for complete reaction. Ferrite obtained in combustion method has smaller particle size (20 nm) than that obtained by precursor method (40–75 nm). The smaller the particle size of a material, the better are its magnetic properties.

Both these methods have certain advantages over the conventional ceramic method, viz. (i) ferrites are formed at lower temperature and in shorter time, (ii) stoichiometrically pure ferrites are obtained, (iii) ferrite particles of small size and greater surface area are obtained and (iv) no milling of starting materials is required (necessary in ceramic method) that can introduce lattice defects in the ferrite obtained which, in turn, affect its permanent magnetic properties.

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