Note

Physico-chemical studies on the thermal analysis of some sodium ferricarboxylates

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Abstract

The thermal decompositions of sodium ferricarboxylates containing uni-, bi- and tridentate ligands, namely formate, oxalate and citrate, were studied up to 1073 K in static air atmosphere employing Mössbauer and infrared spectroscopic techniques, and nonisothermal methods (TG, DTA, DTG). Except for the citrate complex, the thermolysis proceeds without the formation of any iron(II) intermediate. The particle size of the α-Fe_2O_3 formed during the decomposition increases with increasing decomposition temperature. Finally, a solid state reaction between α-Fe_2O_3 and sodium carbonate/oxide occurs leading to the formation of fine particles of α-$NaFeO_2$.

Keywords: Coupled technique; Decomposition; DTA; DTG; Ferrite; IRS; Ligand; Mössbauer; Sodium ferricarboxylate; TG

1. Introduction

Because of their sensitivity towards oxidation state and complexing ability, iron carboxylates are used extensively as inorganic precursors for the preparation of ferrites. Ferrites have wide application in radio, television, microwave and satellite communications, bubble devices, audio-video and digital recording, and as perma-

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nent magnets [1]. It would, therefore, be advantageous to obtain ferrites under convenient conditions, rather than via the conventional ceramic method which involves milling the compound, and thus introducing lattice defects and strains into the ferrites obtained. The preparation of ferrites by thermolysis of iron carboxylate precursors prepared by a liquid-mix technique (the method adopted by us) does not involve any milling, and the ferrites are formed at much lower temperatures.

2. Experimental

The method of preparation and characterization of sodium hexa(formato)ferrate(III) pentahydrate, sodium tris(oxalato)ferrate(III) tetrahydrate and sodium bis(citrato)ferrate(III) pentahydrate have been reported elsewhere [2–4]. These precursors were calcined up to 1073 K in static air atmosphere for 3–4 h. The experimental details of the Mössbauer, infrared and thermal analyses have been reported elsewhere [5]. All Mössbauer spectra were recorded at 298 ± 2 K and were fitted to Lorentzian line shapes.

3. Results and discussion

The Mössbauer parameters of all the complexes are listed in Table 1.

3.1. Sodium hexa(formato)ferrate(III) pentahydrate, $Na_3[Fe(HCOO)_6] \cdot 5H_2O$

The Mössbauer spectrum of this complex at 298 K (room temperature) shows a doublet (Fig. 1, curve a) with isomer shift δ and quadrupole splitting ΔE_Q values of

Table 1
Mössbauer data of products from thermolysis of sodium ferricarboxylates

Parameter	298 K (room temp.)	473 K	573 K	773 K	973 K
$Na_3[Fe(HCOO)_6] \cdot 5H_2O$					
δ (mm s^{-1}) [a]	0.44	0.40	0.40	0.40	0.32
ΔE_Q (mm s^{-1}) [b]	0.62	–	–	–	0.64
HI [c]	–	476	486	490	–
$Na_3[Fe(C_2O_4)_3] \cdot 4H_2O$					
δ	0.15	0.21	0.31	0.34	0.36
ΔE_Q	–	–	0.60	0.20	0.67
HI	–	–	–	480	–
$Na_3[Fe(C_6H_5O_7)_2] \cdot 5H_2O$					
δ	0.47	1.15	0.31	0.35	0.37
ΔE_Q	0.65	2.59	–	–	0.52
HI	–	–	469	480	–

[a] With respect to natural iron. [b] Uncertainty in δ and ΔE_Q is ±0.04 mm s^{-1}. [c] Internal magnetic field with uncertainty of ±5 kOe.
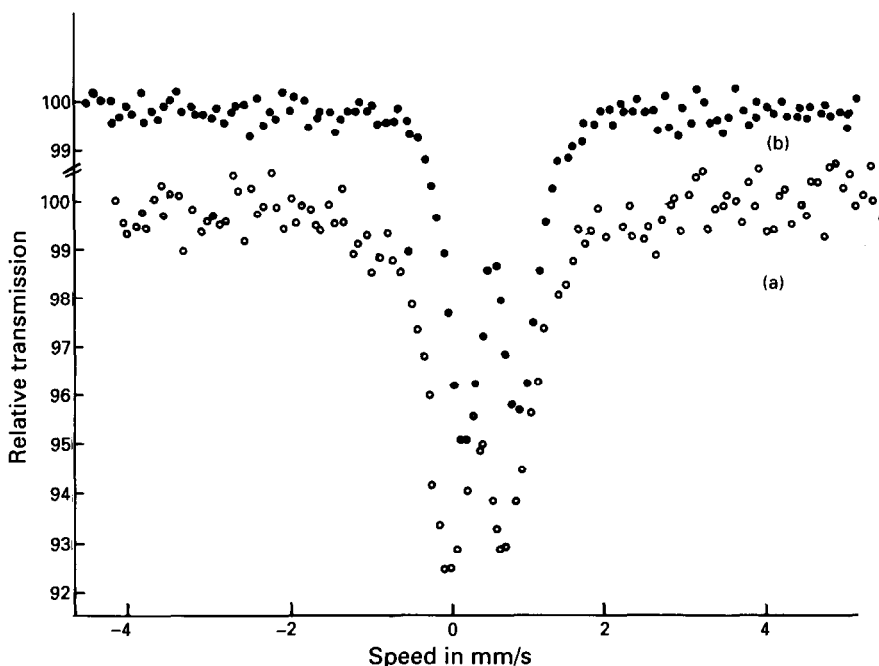
Fig. 1. Room-temperature Mössbauer spectra of sodium hexa(formato)ferrate(III) pentahydrate: (a) uncalcined; (b) calcined at 973 K.

0.44 and 0.62 mm s^{-1} respectively. These values are in agreement with those reported for high-spin iron(III) octahedral complexes [6].

Figure 2 shows the simultaneous DTG, DTA and TG curves recorded at a heating rate of 10 K min^{-1}. The DTG curve shows peaks at 333, 493, 542 and 918 K. There are corresponding peaks in the DTA curve indicating that the thermal effects are accompanied by weight loss. DTA shows an endothermic peak at 359 K, followed by an exothermal region from 400 to 945 K. Then there is another broad exothermal peak at about 973 K. TG shows a weight loss of 18.5% at 380 K, indicating the removal of five water molecules (calculated loss, 18.5%). A weight loss of 45.5% at 528 K in the TG curve suggests the formation of Fe_2O_3, along with sodium formate (calculated loss, 44.7%). The presence of sodium formate was confirmed from the infrared spectrum which shows distinct bands at 2900 cm^{-1} due to v(C–H), at 1610 cm^{-1} due to v_{asym}(C=O), and at 1400 and 1310 cm^{-1} due to v_{sym}(C=O) of the carboxylate [7]. A further weight loss of 52% at 593 K indicates the presence of Fe_2O_3 and sodium carbonate (calculated loss, 54.0%). The presence of Fe_2O_3 was confirmed by recording the Mössbauer spectrum of the complex calcined isothermally at 573 K which exhibits a six-line pattern (Fig. 3) due to magnetic hyperfine interaction, with isomer shift and internal magnetic field values of 0.40 mm s^{-1} and 486 kOe, respectively [8,9]. The infrared spectrum of the sample
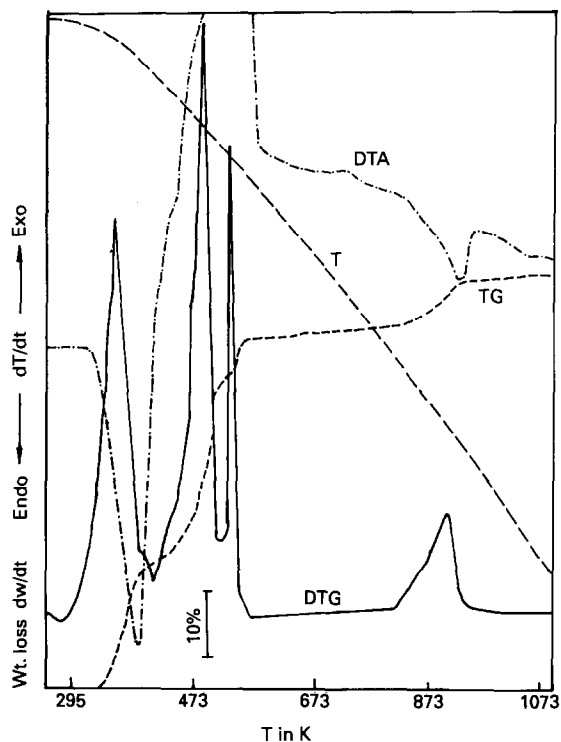
Fig. 2. Simultaneous DTG, DTA and TG curves for sodium hexa(formato)ferrate(III) pentahydrate at a heating rate of 10 K min^{-1}.
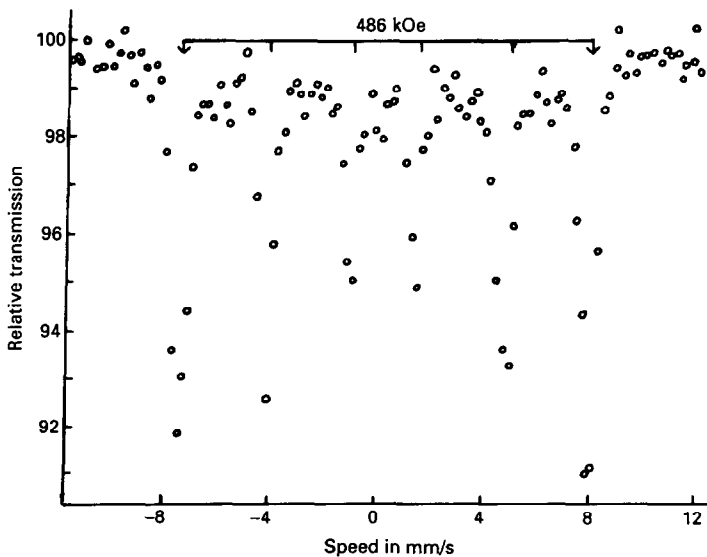

Fig. 3. Room-temperature Mössbauer spectrum of sodium hexa(formato)ferrate(III) pentahydrate calcined at 573 K.

shows an intense band at 1430 cm^{-1} due to sodium carbonate [10]. A final weight loss of 60% at 945 K suggests the formation of sodium ferrite, NaFeO$_2$ (calculated loss, 64.3%). The difference between the observed and calculated weight losses may be due to the presence of residual free unoxidised carbon along with the ferrite [11]. The formation of sodium ferrite was supported by the Mössbauer spectrum of the sample calcined isothermally at 973 K which displays a doublet (Fig. 1, curve b) with isomer shift and quadrupole values of 0.32 and 0.64 mm s^{-1}, respectively [12]. No change in Mössbauer parameters was observed on further heating up to 1073 K.

3.2. Sodium tris(oxalato)ferrate(III) tetrahydrate, Na$_3$[Fe(C$_2$O$_4$)$_3$] · 4H$_2$O

The room temperature Mössbauer spectrum of sodium tris(oxalato)ferrate(III) tetrahydrate shows a single broad absorption band (Fig. 4, curve a) due to the spin lattice relaxation effect. The isomer shift value of 0.15 mm s^{-1} is in agreement with the reported value for high-spin octahedral complexes [6]. TG shows that decomposition starts at 533 K. The Mössbauer spectrum of the complex heated isothermally at 573 K exhibits a doublet with isomer shift and quadrupole splitting values of 0.31 and 0.60 mm s^{-1}, respectively (Table 1), indicating the formation of α-Fe$_2$O$_3$ with particle sizes of less than 10 nm [8]. The infrared spectrum shows intense bands at 1640 and 1380 cm^{-1} due to sodium oxalate [7]. On further heating, the particle size of α-Fe$_2$O$_3$ increased and the sodium oxalate decomposed to sodium carbonate. Finally, at 973 K α-NaFeO$_2$ was formed (Fig. 4, curve b) due to the solid state reaction between α-Fe$_2$O$_3$ and sodium carbonate. The Mössbauer parameters remained unchanged up to 1073 K.
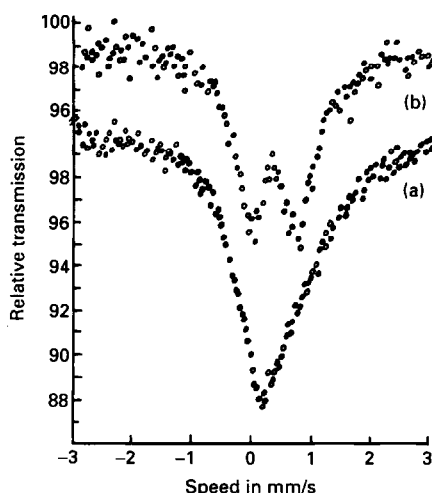

Fig. 4. Room-temperature Mössbauer spectra of sodium tris(oxalato)ferrate(III) tetrahydrate: (a) uncalcined; (b) calcined at 1073 K.
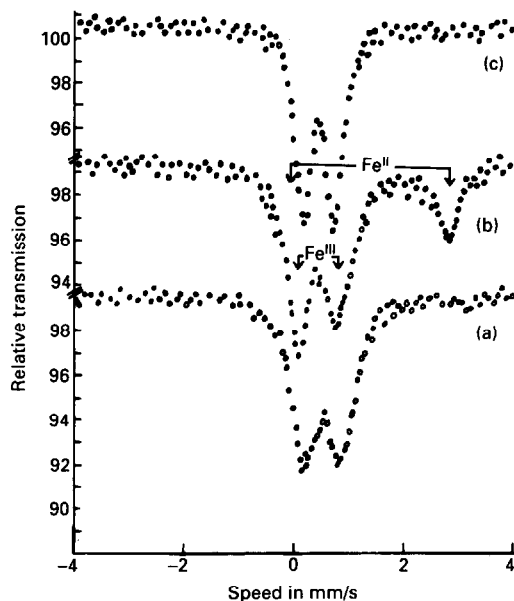
Fig. 5. Room-temperature Mössbauer spectra of sodium bis(citrato)ferrate(III) penthahydrate: (a) uncalcined; (b) calcined at 473 K; (c) calcined at 973 K.
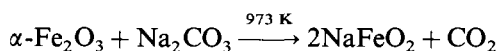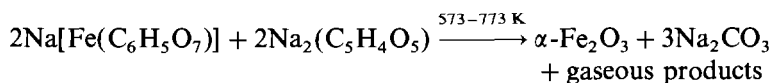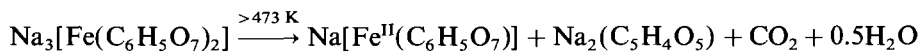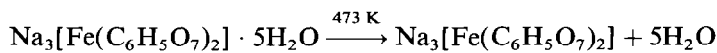
3.3. Sodium bis(citrato)ferrate(III) pentahydrate, $Na_3[Fe(C_6H_5O_7)_2] \cdot 5H_2O$

The room-temperature Mössbauer spectrum of this complex shows a doublet (Fig. 5, curve a) with isomer shift and quadrupole splitting values of 0.47 and 0.65 mm s^{-1}, respectively. The values are close to those reported for high-spin iron(III) octahedral complexes [6]. TG shows that the decomposition begins above 473 K. The Mössbauer spectrum of the complex heated isothermally at 473 K displays two quadrupole doublets (Fig. 5, curve b), one for the parent complex and the other with isomer shift and quadrupole splitting values of 1.15 and 2.59 mm s^{-1}, due to the formation of iron(II) species [13]. At higher temperatures (573–773 K), α-Fe$_2$O$_3$ 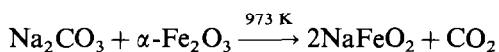of varying particle sizes is formed as shown by an increase in the magnetic field from 469 to 480 kOe (Table 1). At 973 K, a solid state reaction between α-Fe$_2$O$_3$ and sodium carbonate leads to the formation of fine particles of α-NaFeO$_2$ as supported by the Mössbauer spectrum (Fig. 5, curve c) with isomer shift and quadrupole splitting values of 0.37 and 0.52 mm s^{-1}, respectively, which remain stable up to 1073 K.

4. Conclusions

On the basis of various physico-chemical studies (Mössbauer, infrared, TG–DTA–DTG), the following mechanisms are proposed for the decomposition of

the complexes studied

$$Na_3[Fe(HCOO)_6] \cdot 5H_2O \xrightarrow{373\ K} Na_3[Fe(HCOO)_6] + 5H_2O$$

$$Na_3[Fe(HCOO)_6] \xrightarrow{400-528\ K} 0.5Fe_2O_3 + 3HCOONa + gaseous\ products$$

$$3HCOONa \xrightarrow{593\ K} 1.5Na_2CO_3 + gaseous\ products$$

$$Na_2CO_3 + \alpha\text{-}Fe_2O_3 \xrightarrow{973\ K} 2NaFeO_2 + CO_2$$

$$Na_3[Fe(C_2O_4)_3] \cdot 4H_2O \xrightarrow{473\ K} Na_3[Fe(C_2O_4)_3] + 4H_2O$$

$$2Na_3[Fe(C_2O_4)_3] \xrightarrow{573\ K} \alpha\text{-}Fe_2O_3 + 3Na_2(C_2O_4) + gaseous\ products$$

$$3Na_2(C_2O_4) \xrightarrow{773\ K} 3Na_2CO_3 + 3CO$$

$$Na_2CO_3 + \alpha\text{-}Fe_2O_3 \xrightarrow{973-1073\ K} 2NaFeO_2 + CO_2$$

$$Na_3[Fe(C_6H_5O_7)_2] \cdot 5H_2O \xrightarrow{473\ K} Na_3[Fe(C_6H_5O_7)_2] + 5H_2O$$

$$Na_3[Fe(C_6H_5O_7)_2] \xrightarrow{>473\ K} Na[Fe^{II}(C_6H_5O_7)] + Na_2(C_5H_4O_5) + CO_2 + 0.5H_2O$$

$$2Na[Fe(C_6H_5O_7)] + 2Na_2(C_5H_4O_5) \xrightarrow{573-773\ K} \alpha\text{-}Fe_2O_3 + 3Na_2CO_3 + gaseous\ products$$

$$\alpha\text{-}Fe_2O_3 + Na_2CO_3 \xrightarrow{973\ K} 2NaFeO_2 + CO_2$$

The decomposition of citrate into acetone dicarboxylate, i.e. $(C_5H_4O_5)^{2-}$, has been reported in the literature [14]. Sodium formate/oxalate/citrate, when present in the complex, decompose at lower temperatures than their respective pure salts due to (i) the catalytic action of the free $\alpha\text{-}Fe_2O_3$ present and (ii) the metastable structure of the formate/oxalate/citrate formed in the former case [15]. The ferrites were obtained by thermolysis of these precursors (prepared by the liquid-mix technique) at much lower temperatures than those of the ceramic method [11,16,17]. Another important feature of this method is that it does not involve the milling of the compound which is necessary in the ceramic method. The milling introduces lattice defects and strains in the ferrite obtained and thus affects its permanent magnetic properties [18].

Acknowledgement

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