Application of Mössbauer spectroscopy in thermal decomposition studies of some metal ferricarboxylates

B S Randhawa* & K Gandotra

Department of Chemistry, Guru Nanak Dev University, Amritsar143 005

Received 15 February 2007; revised 27 July 2007; accepted 10 August 2007

The thermal decomposition of magnesium and calcium hexa(formato)ferrates(III), $M_3[Fe(HCOO)_6]_2\times H_2O$, has been carried out in flowing air atmosphere from ambient temperature to 700°C. Various physico-chemical techniques i.e. TG, DTG, DSC, XRD, IR, Mössbauer spectroscopy etc. have been employed to characterize the intermediates/end products. After dehydration, the anhydrous complexes undergo decomposition to yield an iron(II) oxalate intermediate in the temperature range 100-130°C. A subsequent oxidative decomposition of iron(II) species leads to the formation of $\alpha$-Fe$_2$O$_3$ and respective alkaline earth metal carbonate/oxide in successive stages. Finally, nanosized ferrites of the stoichiometry, MgFe$_2$O$_4$ and Ca$_2$Fe$_2$O$_5$ have been obtained as a result of solid-state reaction between $\alpha$-Fe$_2$O$_3$ and a fraction of MO. The obtention of ferrites at a temperature much lower than possible in conventional ceramic method, is a special feature of the method used.

Keywords: Mössbauer spectroscopy, X-ray diffraction, Ferrites, Metal ferricarboxylates

IPC Code: G01J3/28

1 Introduction

The study of mode of thermal decomposition of metal ferricarboxylates, is of technical importance as their end products i.e., ferrites find an extensive application in radio, television, microwave and satellite communication, bubble devices, audio-video and digital recording as permanent magnets. Magnesium ferrite is especially used in transformer cores and magnetic recording devices. The ceramic method 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/aggregation and milling imparts defects/strains in the product (ferrite), the obtention of nanosized ferrites is not possible by this technique. The precursor technique, involves thermolysis of metal ferricarboxylate precursors and provides a better route to prepare nanoferrites at lower temperature in shorter time. This novel technique has successfully been employed for the production of alkaline earth metal ferrites from the thermolysis of their respective ferrioxalate/malonate/maleate/citrate precursors. The preparation of magnesium and calcium ferrites from their formate precursors has been undertaken.

2 Experimental Details

Alkaline earth metal hexa(formato)ferrates(III), $M_3[Fe(HCOO)_6]_2\times H_2O$ [M=Mg,Ca] were prepared by mixing stoichiometric quantities of aqueous solutions of ferric chloride, respective alkaline earth metal formate and formic acid. The reaction mixture was stirred vigorously and then concentrated on water bath until a brown coloured product formed. The product was filtered, washed with cold water, dried and stored in vacuum desiccator. The identity of the complexes (precursors) was established by elemental/chemical analysis. The percentage of iron was determined spectrophotometrically using 1,10-phenanthroline. Magnesium and calcium contents were determined by atomic absorption spectroscopy.

The experimental details for recording IR, simultaneous TG-DTG-DSC, SEM and XRD powder data are reported elsewhere. The Mössbauer studies were performed at Laboratorie de Physique, University du Maine, France, using conventional transmission spectrometer with constant acceleration drive and isomer shift values are reported with respect to pure iron absorber. For the identification of intermediates and products, the complexes were also calcined isothermally in nickel crucibles. The variation in temperature was kept ±5°C during isothermal calcination.

3 Results and Discussion

IR spectrum of magnesium hexa(formato)ferrate(III)-dodecahydrate shows a broad band centered at about 3310 cm$^{-1}$ due to $\nu$(O-H) of lattice water and a small
but distinct shoulder at 2900 cm$^{-1}$ due to $\nu$(C-H) of the formate group. A broad band centered around 1630 cm$^{-1}$ and a strong band at 1380 cm$^{-1}$ are attributed to $\nu_{as}(C=O)$ and $\nu_{sym}(C=O)$ of the coordinated carboxylate groups$^{14}$, respectively. A small but distinct band at 580 cm$^{-1}$ due to $\nu$(Fe-O) suggests the presence of Fe-O(carboxylate) bonding$^{15}$. Calcium hexa(formato)ferrate(III)sesquihydrate shows almost a similar IR spectrum.

Mössbauer spectra of the precursors exhibit a doublet (Fig. 1) with isomer shift ($\delta$) and quadrupole splitting ($\Delta$) values of 0.36, 0.54 mms$^{-1}$, respectively for magnesium and 0.38, 0.63 mms$^{-1}$ for calcium ferriformates, respectively. These parameters are in close agreement to those reported for high spin Fe(III) complexes with octahedral geometry.$^{16}$ 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 (Mg$^{2+}$, Ca$^{2+}$) and water molecules seem to be responsible for linking together the complex ion,[Fe(HCOO)$_6$]$^{3-}$. The high spin nature of iron (III) in these complexes has also been confirmed by their magnetic susceptibility values of 5.77 and 5.82 $\mu_B$, respectively.

Thermal decomposition of alkaline earth metal hexa(formato)ferrates(III), $M_3[Fe(HCOO)_6]_2\times H_2O$ [$M= M_g, C_a$], occurs in four major consecutive steps. The details of thermal analysis of these complexes have been presented in Table 1.

### 3.1 Magnesium hexa(formato)ferrate(III)dodecahydrate, $M_g[Fe(HCOO)_6]_2\times 12H_2O$

The presence of $Fe_2O_3$ formed during decomposition has been confirmed by recording Mössbauer spectrum of the residue obtained by calcining the parent complex at 250°C for 30 min (Fig. 2). The Mössbauer spectrum displayed a doublet with isomer shift ($\delta$) and quadrupole splitting ($\Delta$) values of 0.28 and 0.55 mms$^{-1}$, respectively (Table 2). These parameters agree with those reported$^{17}$ for $\alpha-Fe_2O_3$ with particle size $< 10$ nm. The identity of the end product i.e. magnesium ferrite has been confirmed by recording its Mössbauer spectrum and XRD powder pattern.$^{18}$ Mössbauer spectrum of the end product (Fig. 3) exhibits two overlapping sextets with internal magnetic field values of 441 and 413 kOe for octahedral and tetrahedral sites, respectively. A computer analysis of the spectrum shows that there

---

**Fig. 1 — Mössbauer spectrum of magnesium ferriformate dodecahydrate**

---

<table>
<thead>
<tr>
<th>Complex</th>
<th>Heating Temp. (°C)</th>
<th>Mass loss (%)</th>
<th>DSC peak type/Temp. (°C)</th>
<th>Thermal Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_g[Fe(HCOO)_6]_2\times H_2O$</td>
<td>130</td>
<td>34.00</td>
<td>endotherm (doublet), 90,120</td>
<td>Simultaneous dehydration and endo-decomposition of precursor to $Fe_2C_2O_4$ and $MgC_2O_4$</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>47.20</td>
<td>exotherm, 195</td>
<td>Exo-decomposition of $Fe_2C_2O_4$ to $Fe_2O_3$</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>70.00</td>
<td>exotherm, 310</td>
<td>Exo-decomposition of $MgC_2O_4$ to $MgO$</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>—</td>
<td>exotherm, 410</td>
<td>Solid-state reaction between MgO and $\alpha-Fe_2O_3$ yielding ferrite, $MgFe_2O_4$</td>
</tr>
<tr>
<td></td>
<td>&gt;100</td>
<td>15.60</td>
<td>Broad endotherm, 85</td>
<td>Simultaneous dehydration and endo-decomposition of precursor to $Fe_2C_2O_4$ and $CaC_2O_4$</td>
</tr>
<tr>
<td>$Ca_3[Fe(HCOO)_6]_2\times 1.5H_2O$</td>
<td>305</td>
<td>32.80</td>
<td>exotherm, 290</td>
<td>Exo-decomposition of $Fe_2C_2O_4$ to $\alpha-Fe_2O_3$</td>
</tr>
<tr>
<td></td>
<td>415</td>
<td>42.45</td>
<td>exotherm, 400</td>
<td>Exo-decomposition of $CaC_2O_4$ to $CaCO_3$</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>52.50</td>
<td>endotherms, 560, 615</td>
<td>Endo-decomposition of $CaCO_3$ to $CaO$</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>—</td>
<td>exotherm, 670</td>
<td>Solid-state reaction between $CaO$ and $\alpha-Fe_2O_3$ yielding ferrite, $Ca_3Fe_2O_5$</td>
</tr>
</tbody>
</table>
There are two cationic sites, i.e., octahedral and tetrahedral with cationic (Fe$^{3+}$) distribution of 51% and 49%, respectively. Mössbauer parameters presented in Table 2 are in agreement with those reported for MgFe$_2$O$_4$. SEM micrograph which reveals the formation of MgFe$_2$O$_4$ with an average particle size of 30 nm.

### Table 2 — Mössbauer parameters for thermolysis products of Mg$_3$[Fe(HCOO)$_6$]$_2$.xH$_2$O at 300K

<table>
<thead>
<tr>
<th>M</th>
<th>Temperature of calcination, °C</th>
<th>δ* mms$^{-1}$</th>
<th>Δ mms$^{-1}$</th>
<th>B*, kOe</th>
<th>Internal magnetic field</th>
<th>Cationic (Fe$^{3+}$) distribution, %</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>250</td>
<td>0.28</td>
<td>0.55</td>
<td>—</td>
<td>51 (oct)</td>
<td>441</td>
<td>α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>0.38</td>
<td>0.01</td>
<td>441</td>
<td>51 (oct)</td>
<td>MgFe$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.22</td>
<td>0.05</td>
<td>413</td>
<td>49 (tet)</td>
<td>Fe$^{III}$C$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.26</td>
<td>0.60</td>
<td>—</td>
<td>—</td>
<td>Fe$^{III}$C$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>0.42</td>
<td>—</td>
<td>513</td>
<td>—</td>
<td>α-Fe$_3$O$_3$</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>700</td>
<td>0.35</td>
<td>0.50</td>
<td>508(S)</td>
<td>44.1 (oct)</td>
<td>Ca$_2$Fe$_2$O$_5$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.18</td>
<td>0.73</td>
<td>429(S)</td>
<td>48.5 (tet)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25</td>
<td>0.88</td>
<td>—</td>
<td>(CD)</td>
<td>7.4</td>
<td></td>
</tr>
</tbody>
</table>

# w.r.t pure iron absorber; * Internal magnetic field; S = sextet, CD = Central Doublet

3.2 Calcium hexa(formato)ferrate(III)sesquihydrate, Ca$_3$[Fe(HCOO)$_6$].1.5H$_2$O

The presence of iron(II) oxalate, formed from the simultaneous dehydration and decomposition of the precursor (Table 1), has been confirmed by recording the Mössbauer spectrum of the residue obtained by isothermal calcination of the parent complex at 200°C for 30 min. The Mössbauer spectrum (Fig. 4) consists of a quadrupole doublet having isomer shift and quadrupole splitting values of 1.22 and 1.71 mms$^{-1}$, respectively. The presence of Fe$_2$O$_3$ has also been confirmed by recording the Mössbauer spectrum of the residue obtained by firing the parent complex at 350°C for 30 min. The doublet displayed in the spectrum exhibited Mössbauer parameters (Table 2) almost similar to those observed for α-Fe$_2$O$_3$ (particle size < 10nm) formed during the thermolysis of magnesium complex. However, Mössbauer spectrum of the residue obtained by isothermal pyrolysis of the parent complex at 550°C for 30 min. displayed a symmetrical sextet due to magnetic hyperfine interactions (Fig. 5) with an isomer shift and internal magnetic field values of 0.42 mms$^{-1}$ and 513 kOe respectively. These parameters are in close agreement.
to those reported\textsuperscript{20} for $\alpha$-Fe$_2$O$_3$ of bulk size. An increase in particle size of $\alpha$-Fe$_2$O$_3$ (from <10nm to bulk size) with increasing temperature has been reported in literature\textsuperscript{21}. The identity of the calcium ferrite, Ca$_2$Fe$_2$O$_5$, has been confirmed by XRD powder pattern\textsuperscript{22} and Mössbauer spectrum (Fig. 6) of the final thermolysis residue. Mössbauer spectrum of the final residue exhibits a complex Zeeman pattern displaying two overlapping sextets along with a central doublet, the parameters for which suggest the formation of calcium ferrite, Ca$_2$Fe$_2$O$_5$ of mixed particle size\textsuperscript{23} (Table 2). The presence of a central doublet in addition to the sextets suggests the co-existence of ferrimagnetic and superparamagnetic phases of magnetic ferrite particles. A computer analysis shows that there are two cationic sites, i.e., octahedral and tetrahedral with cationic (Fe$^{3+}$) distribution of 44.1% and 48.5%, respectively, (Table 2). SEM micrograph reveals the formation of Ca$_2$Fe$_2$O$_5$ with an average grain size of 40 nm.

4 Conclusions
Because of their different electrostatic properties (polarizability, cationic size, etc.) magnesium and calcium ferriformates yield different products i.e., MgFe$_2$O$_4$ and Ca$_2$Fe$_2$O$_5$ during pyrolysis. Both precursors yield ferrites at lower temperature and in shorter time interval as compared to the conventional ceramic method\textsuperscript{24,25}. An advantage of the method used is that nanosized ferrites with an average particle size of 30-40 nm have been obtained. The room temperature saturation magnetization and Curie temperature values for ferromagnetic MgFe$_2$O$_4$ have been found to be 1655G and 675K, respectively. A comparatively lower magnitude of Curie temperature as compared to the reported\textsuperscript{1} value for bulk ferrite (710K) may be attributed to smaller particle size of the ferrite obtained. Ca$_2$Fe$_2$O$_5$ is reported to be antiferromagnetic\textsuperscript{23}.

Acknowledgement
The authors are thankful to Dr J M Greneche (Universite du Maine, Cedex, France) for Mössbauer recordings.

References
22 ASTM Card No.19-222