Synthesis of ferrite grade $\gamma$-$\text{Fe}_2\text{O}_3$

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Abstract. Iron(II) carboxylate–hydrazinates: Ferrous fumarato–hydrazinate (FFH), FeC$_4$H$_4$O$_4$2N$_2$H$_4$; ferrous succinato–hydrazinate (FSH), FeC$_4$H$_6$O$_4$2N$_2$H$_4$; ferrous maleato–hydrazinate (FEM), FeC$_4$H$_6$O$_4$2N$_2$H$_4$; ferrous malato–hydrazinate (FMH), FeC$_4$H$_6$O$_4$1.5N$_2$H$_4$.H$_2$O; and ferrous tartrato–hydrazinate (FTH), FeC$_4$H$_8$O$_6$.N$_2$.H$_2$.O are being synthesized for the first time. These decompose (autocatalytically) in an ordinary atmosphere to mainly $\gamma$-$\text{Fe}_2\text{O}_3$, while the unhydrazinated iron(II) carboxylates in air yield $\alpha$-$\text{Fe}_2\text{O}_3$, but the controlled atmosphere of moisture requires for the oxalates to stabilize the metastable $\gamma$-$\text{Fe}_2\text{O}_3$. The hydrazine released during heating reacts with atmospheric oxygen liberating enormous energy,

$$N_2H_4 + O_2 \rightarrow N_2 + H_2O; \Delta H_2O = -621 \text{ kJ/mol},$$

which enables to oxidatively decompose the dehydrazinated complex to $\gamma$-$\text{Fe}_2\text{O}_3$. The reaction products $N_2 + H_2O$ provide the necessary atmosphere of moisture needed for the stabilization of the metastable oxide.

The synthesis, characterization and thermal decomposition (DTA/TG) of the iron(II) carboxylato–hydrazinates are discussed to explain the suitability of $\gamma$-$\text{Fe}_2\text{O}_3$ in the ferrite synthesis.

Keywords. Carboxylate; hydrazine; metastable oxide; ferrite.

1. Introduction

Technologically important ferrites of general formula, MFe$_2$O$_4$ (M = divalent metal) are generally synthesized by a solid state reaction between $\text{Fe}_2O_3$ and MO. The solid state reactions are normally sluggish in nature, and hence, in ceramic technique granulations are done to get reactive fine particles of the starting materials, compacted and then heat treated to very high temperatures, >1000°C. Many a times the repeated grinding and heat treatments are given to achieve a single phase ferrite of desired composition. Reactivity of sluggish solid state reactions are enhanced by choosing defective starting materials by intentionally adding foreign impurities called as doping. Structural compatibility also plays an important role. In ferrites synthesis the iron oxide in hexagonal corundum structure form, $\alpha$-$\text{Fe}_2\text{O}_3$, is made to react with the cubic divalent metal oxides, MO, to get cubic spinel, MFe$_2$O$_4$. Here, at high temperatures the $\alpha$-$\text{Fe}_2O_3$ transforms into cubic spinel magnetite, Fe$_3$O$_4$, which then reacts easily with the cubic MO resulting into cubic spinel. However, it has been observed (Huhn 1987; Tuat et al 1992; Shrotri et al 1992) that the iron oxide in cubic spinel form, $\gamma$-$\text{Fe}_2\text{O}_3$, as a starting material in ferrites synthesis enhances the solid state reaction and a better quality material could be obtained. The cubic spinel, $\gamma$-$\text{Fe}_2\text{O}_3$, is a defective oxide with vacancy ordered structure of unit cell structure, (Fe$^{3+}$)$_8$ [Fe$^{3+}$]$^{16/3}$ [Fe$^{3+}$]$^{4/3}$[Fe$^{3+}$]$^{8/3}$]O$_{32}$, where ( ), [ ] and $\square$ represent tetrahedral, octahedral and vacant sites, respectively. This defective cubic oxide reacts easily with the cubic MO giving cubic spinel easily. And, such enhanced reactivity of $\gamma$-$\text{Fe}_2\text{O}_3$ in ferrite, MgFe$_2$O$_4$ synthesis has been realized by us (Verenkar 1997; Sawant 1998; Rane et al 1999) that confirms the fact that cubic defective iron oxide, $\gamma$-$\text{Fe}_2\text{O}_3$, is a better starting material in ferrites manufacture. This is also in conformity with certain solid state reactions which are favoured if they are carried out at the phase transformation temperature of one of the reactants (Hedvaal effect); formation of CoAl$_2$O$_4$ is easier at the $\gamma \rightarrow \alpha$ transformation of Al$_2$O$_3$. Thus, the enhanced reactivity of cubic $\gamma$-$\text{Fe}_2\text{O}_3$ is the combined effect of its structural compatibility, defective structure and its transformation to $\alpha$-$\text{Fe}_2\text{O}_3$ during the heat treatment with cubic MO. In the synthesis of LiMn ferrite it was observed (Sano and Tamaura 1999) that $\gamma$-$\text{Fe}_2\text{O}_3$ is more stable than even other cubic spinel oxide, magnetite, Fe$_3$O$_4$, (Fe$^{3+}$)$_8$[Fe$^{3+}$]$^{6}$[Fe$^{3+}$]$^{6}$]O$_{32}$, may be because it is not defective.

Considering the importance of $\gamma$-$\text{Fe}_2\text{O}_3$ in the synthesis of ferrites, we (Rane et al 1981; Moye et al 1993; Verenkar 1997; Sawant 1998) have been investigating an easier method of preparation of this oxide from various precursors such as iron(II) oxalate, formate, iron hydroxides and iron oxyhydroxides and their hydrazinates. Especially the iron(II) carboxylate, ferrous oxalate dihydrate, FeC$_2$O$_4$.2H$_2$O, is a widely studied precursor in the synthe-
sis of Fe$_2$O$_3$. In air the ferrous oxalate decomposes to α-
Fe$_2$O$_3$, while in a controlled atmosphere of a known partial
pressure of moisture the decomposed product is mainly γ-Fe$_2$O$_3$. However, the ferrous oxalate on hydra-
zination yields complexes of known composition such as
FeC$_2$O$_4$·2NH$_4$, FeC$_2$O$_4$·2H$_2$O and these decompose
catalytically at an ordinary temperature and pressure
into mainly γ-Fe$_2$O$_3$. This easy formation of the γ-Fe$_2$O$_3$
has also been observed (Sawant 1998) in iron(II) formates.

Hydrazine method has opened up a new area of coordi-
nation chemistry involving metals ranging from transition,
lanthanides to actinides (Athavale and Padmanabh Iyer
1967; Ferrari et al 1966; Braibanti et al 1968; Sharov
1977; Sharov et al 1977; Ravindranathan and Patil 1987;
Kikkawa et al 1995; Goto et al 1996; Patil et al 1997;
Yasodhai and Govindarajan 1999). The thermal products
of hydrazinated complexes produce high reactivity metal/
mixed metal oxides due to explosive decomposition.

The metal carboxylates are in general pyrophoric in
nature and the decomposition at low temperatures in-
volves the release of enormous amount of volatile gas products
leading them to very fine oxide products of high surface
area. The hydrazination of the oxalates further makes
them to explosively decompose giving still finer oxide
products. Since we observed the easy formation of γ-
Fe$_2$O$_3$ from the hydrazinated iron(II) oxalate as compared to
the rigorous temperature and atmosphere control need
for the formation of the oxide from the unhydrazinated
carboxylate, we have been studying hydrazine method to
prepare the oxide from other iron(II) carboxylates: ferrous
fumarate, ferrous succinate, ferrous maleonate, ferrous
tartrate, ferrous maleate and ferrous malate.

The ferrous-fumarate, -succinate, -malonate and tartrate
are found to decompose to mainly α-Fe$_2$O$_3$ in air (Ven-
kataranam et al 1987, 1989; Rahman et al 1988; Venkata-
raman and Mukhedkar 1990; Nikumbh et al 1993) and
like ferrous oxalate (Rane et al 1981) they too decompose
to γ-Fe$_2$O$_3$ in a controlled atmosphere of moisture. We
present here preparation and decomposition of hydrazine
complexes of these and two other (ferrous malate and maleate complexes), prepared for the first time.

2. Preparation and characterization

2.1 Preparation: Solution and equilibration method

A requisite quantity of sodium salts of fumaric, succinic,
maleic and malic acid was added to a known amount of
hydrazine hydrate (95–99%) in an inert atmosphere of
nitrogen and stirred well for 2–3 h and then a freshly pre-
pared ferrous chloride was run down till the precipitation
was complete. The contents were further stirred for
another 60 min in the N$_2$ atmosphere. The precipitate
was then filtered, washed with alcohol and then dried. Malonic
acid was used in the preparation instead of its sodium salt.

Ferrous tartrate was prepared from ferrous ammonium
sulphate and sodium tartrate and the dry ferrous tartrate
was then equilibrated over hydrazine atmosphere by stor-
ing in a petri dish in a desiccator containing hydrazine
hydrate. (Caution: hydrazine and hydrazine derivatives
were carcinogenic. They were handled carefully in a fume
cupboard.)

2.2 Characterization

Hydrazine content of all the complexes and the inter-
mediate thermal products was analyzed titrimetrically
using KIO$_4$. The percentage of iron, carbon and hydrogen
was estimated by standard analytical techniques. Infrared
band regions were detected using a FTIR spectrometer
(Shimadzu FTIR, model 8101A) of complexes and their
thermal intermediate products. Pyknometric density of the
complexes was also determined.

2.3 Thermal decomposition: isothermal, DTA/TG

Simultaneous differential thermal analysis (DTA) and
thermogravimetric (TG) analysis were done on STA 1500
instrument from room temperature (RT) to 700°C. Iso-
thermal weight loss studies were carried out at various
temperatures established based on DTA/TG traces. All
hydrazinate complexes decomposed autocatalytically when
the samples were spread in a petri dish and a burning
splinter brought near to it. Initially a glow was formed
which then spread throughout the bulk, thereby, comple-
ting the decomposition in an ordinary atmosphere. Weight
loss studies of these were also done.

2.4 Phase identification, microstructure (SEM) and
magnetic characteristics

X-ray powder diffraction (XRD) studies of all the thermal
products were carried out on Rigaku D MAX II diffracto-
meter using Cu and Fe targets. Phase identification was
done by comparing the observed d$_{ab}$ values with the
JCPDS file Nos 24–81 and 25–1402. Scanning electron
micrographs (SEM) of all the thermal products were taken
on Cambridge Stereoscan S 250 MK III. Saturation ma-
gnetization values, $J_S$, in emu/g of the thermal products
were measured on a high field hysteresis loop trace
described by Likhite et al (1965) and supplied by M/s
Arun Electronics, Mumbai.

3. Results and discussion

3.1 Chemical formula

Important infrared band positions, chemical contents of
hydrazine, iron, carbon, hydrogen and isothermal weight
losses of all the complexes are shown in table 1 and from these chemical formulas are fixed as
(i) ferrous fumarato–hydrazinate (FFH), FeC₆H₄O₂:2N₂H₄,
(ii) ferrous succinato–hydrazinate (FSH), FeC₆H₄O₂:2N₂H₄,
(iii) ferrous maleato–hydrazinate (FEH), FeC₆H₄O₂:2N₂H₄,
(iv) ferrous malato–hydrazinate (FMH), FeC₆H₄O₂:2N₂H₄,
(v) ferrous malonato–hydrazinate (FMM), FeC₆H₄O₂:1:5N₂H₂H₂O and (vi) ferrous tartrato–hydrazinate (FTH)
FeC₆H₄O₄:2N₂H₂H₂O.

There are distinctly two categories of complexes: FMH and FTH which have water of crystallization, while the others without any water of crystallization.

3.2 Thermal analysis

DTA/TG traces of all complexes are shown in figure 1. (FFH) FeC₆H₄O₂:2N₂H₄, (FSH) FeC₆H₄O₂:2N₂H₄, (FEH) FeC₆H₄O₂:2N₂H₄, (FLH) FeC₆H₄O₄:2N₂H₄ all with no water of crystallization show multistep exothermic peaks with corresponding weight loss steps. The samples with water of crystallization, (FMM) FeC₆H₄O₂:1:5N₂H₂H₂O and (FTH) FeC₆H₄O₄:2N₂H₂H₂O, however, indicate mainly one intense exothermic peak with corresponding weight loss.

The intermediate thermal products obtained at different fixed temperatures in the range RT–350°C were analyzed for the hydrazine contents in them (table 2). All dehydrazinate complexes indicated loss of hydrazine at ~ 150°C in steps, but then it was difficult to monitor such reactions, as the removal of the second hydrazine molecule immediately sets in an intense oxidative decomposition of the dehydrazinated complex. In fact, the exothermic reaction releases so much energy due to explosive oxidation of the liberated hydrazine, N₂H₄, with the atmospheric oxygen (Schmidt 1984),

\[ \text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}; \quad \Delta H = -621 \text{ kJ/mol}, \]

that the heat is sufficient to oxidatively decompose the dehydrazinated complex into metal oxide.

The hydrazinate complexes with water of crystallization, however, showed one step reaction with intense exothermic peak. Majority contents of hydrazine and water were lost (table 2) below 100°C and then there occurred further decomposition due to dehydrazinated complex. A total decomposition occurred at 180–200°C in (FMM) FeC₆H₄O₂:1:5N₂H₂H₂O. The FMM has 20.43(%) N₂H₄ which on heating to 50°C lost 7.85% weight and at 70° the loss was 9.5%, but the hydrazine content in these two temperatures remained, respectively, at 16-42 and 16-18%. Our calculation indicates that at ~ 70°C the complex releases one molecule of H₂O and half a molecule of N₂H₄ and the product at this stage must have 16-85(%) N₂H₄ which is close to the observed value of 16-18%. Then the complete removal of the remaining N₂H₄ takes place at ~ 170°C and a major weight loss occurs at ~ 180°C. These results indicate that the decomposition of FMM has a sequence: dehydrazination → dehydration → dehydrazination followed by oxidative decomposition.

### Table 1. Chemical analysis, density, IR, and total weight loss of iron(II) carboxylato–hydrazinates.

<table>
<thead>
<tr>
<th>Hydrazinates</th>
<th>Chemical analysis (%)</th>
<th>Density (g cm⁻³)</th>
<th>Infrared data (cm⁻¹)</th>
<th>Total weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeC₆H₄O₄</td>
<td>N₂H₄</td>
<td>27.16</td>
<td>27.35</td>
<td>1.38</td>
</tr>
<tr>
<td>2N₂H₄</td>
<td>Fe</td>
<td>24.00</td>
<td>25.88</td>
<td>19.30</td>
</tr>
<tr>
<td>1:5N₂H₂H₂O</td>
<td>C</td>
<td>3.96</td>
<td>4.27</td>
<td></td>
</tr>
<tr>
<td>FeC₆H₄O₄</td>
<td>N₂H₄</td>
<td>27.25</td>
<td>27.11</td>
<td>1.18</td>
</tr>
<tr>
<td>2N₂H₄</td>
<td>Fe</td>
<td>23.87</td>
<td>23.68</td>
<td>20.30</td>
</tr>
<tr>
<td>1:5N₂H₂H₂O</td>
<td>C</td>
<td>17.90</td>
<td>16.08</td>
<td>17.22</td>
</tr>
<tr>
<td>FeC₆H₄O₄</td>
<td>N₂H₄</td>
<td>20.43</td>
<td>21.46</td>
<td>1.51</td>
</tr>
<tr>
<td>1:5N₂H₂H₂O</td>
<td>Fe</td>
<td>24.25</td>
<td>24.95</td>
<td>17.90</td>
</tr>
<tr>
<td>N₂H₄H₂O</td>
<td>C</td>
<td>3.73</td>
<td>4.46</td>
<td></td>
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<tr>
<td>FeC₆H₄O₄</td>
<td>N₂H₄</td>
<td>25.50</td>
<td>25.17</td>
<td>1.22</td>
</tr>
<tr>
<td>2N₂H₄</td>
<td>Fe</td>
<td>25.50</td>
<td>25.17</td>
<td>17.22</td>
</tr>
<tr>
<td>FeC₆H₄O₄</td>
<td>N₂H₄</td>
<td>26.74</td>
<td>27.37</td>
<td>1.9</td>
</tr>
<tr>
<td>2N₂H₄</td>
<td>Fe</td>
<td>25.12</td>
<td>25.43</td>
<td>26.74</td>
</tr>
<tr>
<td>FeC₆H₄O₄</td>
<td>N₂H₄</td>
<td>22.80</td>
<td>22.16</td>
<td>1.86</td>
</tr>
</tbody>
</table>
The ferrous tartrato-hydrazinate (FTH) FeC₄H₂O₆·N₂H₄·H₂O, on the other hand, shows (table 2) water loss at ~ 60°C as the RT hydrazine content of 12-41% of the complex remains same at this temperature. Further heating leads to the removal of hydrazine. The sequence of reaction here is dehydration → dehydrazination followed immediately by oxidative decomposition. Thus, these two complexes with water of crystallization decompose exothermally in one step, while the complexes with no crystallization of water show multistep decompositions. Hence, the dehydrazination and dehydration together make the total decomposition process reactive as revealed by the single step exothermic reaction. The bis-hydrazine maleate and bis-hydrazine fumarate complexes of Co, Ni and Zn were also found (Govindrajan et al. 1995) to show single and multistep decompositions and they have suggested reactive and less reactive reactions in these systems yielding metal oxide products.

3.3 Phase identification, microstructure (SEM) and magnetic characterization

The X-ray analysis of the thermal and autocatalytic decomposition products of all the complexes were found to be γ-Fe₂O₃. The d values observed and the reported ones of the γ-Fe₂O₃ are shown in table 3. Saturation magnetization values, Jₛ, in the range 18–43 emu/g are observed (Verenkar 1997) for all these oxide samples. The values found in the present investigation are low, however, Jₛ in the range 50–74 emu/g are also observed in the literature (Khalafalla and Morrish 1972; Coey and Khalafalla 1972).

Figure 1. DTA/TG traces of iron(II) carboxylato-hydrazinates.
Synthesis of ferrite grade $\gamma$-Fe$_2$O$_3$

One explanation for such low values in our studies may be due to some admixture of $\alpha$-Fe$_2$O$_3$ as found in our XRD patterns. This is expected in our method of preparation where explosive decomposition of the hydrazinated complexes release so much heat which eventually convert few $\gamma$-Fe$_2$O$_3$ particles into $\alpha$-Fe$_2$O$_3$. However, under the controlled atmosphere of moisture the unhydrazinated complexes did yield pure $\gamma$-Fe$_2$O$_3$ with $J_S$ of 74 emu/g. Although the autocatalytically decomposed hydrazine complexes did not yield $\gamma$-Fe$_2$O$_3$ of better magnetic characteristics, they are good enough for the purpose of ferrite preparation as revealed by our studies on MgFe$_2$O$_4$ (Rane et al 1999) as compared to the ferrite prepared from commercial grade $\alpha$-Fe$_2$O$_3$. Iron oxides consisting of large

Table 2. Isothermal weight loss and hydrazine analysis of iron(II) caboxylato–hydrazinates.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Hydrazinates</th>
<th>Isothermal/chemical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temp.(°C) Wt. Loss (%) % N$_3$H$_4$</td>
</tr>
<tr>
<td>1.</td>
<td>Ferrous fumarato–hydrazinates</td>
<td>RT – 27.16</td>
</tr>
<tr>
<td></td>
<td>(FFH) FeC$_3$H$_2$O$_4$·2N$_3$H$_4$</td>
<td>70 3.20 22.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90 15.35 5.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>110 19.50 2.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200 37.65 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td>310 64.15 –</td>
</tr>
<tr>
<td>2.</td>
<td>Ferrous succinato–hydrazinate</td>
<td>RT – 27.52</td>
</tr>
<tr>
<td></td>
<td>(FSH) FeC$_3$H$_4$O$_5$·2N$_3$H$_4$</td>
<td>50 1.2 27.52</td>
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<td></td>
<td></td>
<td>90 21.02 3.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140 25.20 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td>176 29.50 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td>193 56.65 –</td>
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<td></td>
<td></td>
<td>248 66.25 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td>310 67.10 –</td>
</tr>
<tr>
<td>3.</td>
<td>Ferrous maleato–hydrazinate</td>
<td>RT – 26.74</td>
</tr>
<tr>
<td></td>
<td>(FEH) FeC$_3$H$_2$O$_4$·2N$_3$H$_4$</td>
<td>58 2.5 25.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96 12.05 17.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>156 30.05 3.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>172 34.00 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td>182 55.55 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td>225 64.40 –</td>
</tr>
<tr>
<td></td>
<td>(FLH) FeC$_3$H$_4$O$_5$·2N$_3$H$_4$</td>
<td>50 6.4 21.95</td>
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<td></td>
<td></td>
<td>100 17.05 10.17</td>
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<td></td>
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<td>150 30.45 2.40</td>
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<td>300 66.55 –</td>
</tr>
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<td>5.</td>
<td>Ferrous malonato–hydrazinate</td>
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</tr>
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<td>(FMH) FeC$_3$H$_2$O$_5$·1.5N$_3$H$_6$H$_2$O</td>
<td>50 7.85 16.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70 9.50 16.18</td>
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<td>95 12.25 17.38</td>
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<td>120 18.00 13.62</td>
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<td>140 21.40 9.77</td>
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<td></td>
<td></td>
<td>150 24.90 9.61</td>
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<td></td>
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<td>170 32.00 5.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>182 63.10 –</td>
</tr>
<tr>
<td>6.</td>
<td>Ferrous tartrato–hydrazinate</td>
<td>RT – 12.41</td>
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<tr>
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<td>(FTH) FeC$_3$H$_4$O$_6$·N$_3$H$_4$·H$_2$O</td>
<td>62 6.00 12.41</td>
</tr>
<tr>
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<td>80 12.35 10.73</td>
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<td>102 16.00 7.13</td>
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<td>140 19.85 4.85</td>
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<td>160 22.50 2.40</td>
</tr>
<tr>
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<td>225 68.20 –</td>
</tr>
</tbody>
</table>
percentage of $\gamma$-Fe$_2$O$_3$ enhanced reactivity (Huhn 1987) to produce ZnFe$_2$O$_4$. In fact, the SEM studies on these synthetic cubic spinel $\gamma$-Fe$_2$O$_3$ particles in nano-metre size of high surface (BET) area of 50–90 m$^2$g$^{-1}$ reacted easily with the cubic MgO resulting in well densified cubic MgFe$_2$O$_4$ ferrite of better quality.

4. Conclusions

(I) Iron(II) carboxylato–hydrazinates: ferrous fumarato–hydrazinate (FFH), FeC$_4$H$_6$O$_2$N$_2$H$_2$; ferrous succinato–hydrazinate (FSH), FeC$_4$H$_6$O$_2$N$_2$H$_2$; ferrous maleato–hydrazinate (FMH), FeC$_4$H$_6$O$_2$N$_2$H$_2$; ferrous malato–hydrazinate (FLH), FeC$_4$H$_6$O$_2$N$_2$H$_2$O; ferrous tartarato–hydrazinate (FTH), FeC$_4$H$_6$O$_2$N$_2$H$_2$O; are being easily synthesized.

(II) The iron(II) carboxylato–hydrazinates decompose (auto-catalytically) in an ordinary atmosphere mainly to $\gamma$-Fe$_2$O$_3$, while the unhydrazinated iron(II) carboxylates in air yield $\alpha$-Fe$_2$O$_3$, but the controlled atmosphere of moisture requires for the oxalates to stabilize the metastable $\gamma$-Fe$_2$O$_3$.

(III) Hydrazine method enables the synthesis of $\gamma$-Fe$_2$O$_3$ easily from the iron(II) carboxylates.

(IV) Uniform, nano-metre size, high surface area defect cubic spinel $\gamma$-Fe$_2$O$_3$ from iron(II) carboxylato–hydrazinates reacts easily with cubic MgO yielding high quality cubic spinel MgFe$_2$O$_4$, while with the commercial 0–2 μm size particles of $\alpha$-Fe$_2$O$_3$ one ends up with low performance ferrite due to the presence of unreacted $\alpha$-Fe$_2$O$_3$ as an admixture.

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| Table 3. X-ray data of iron oxides obtained by autocatalytic decomposition of iron(II) carboxylato–hydrazinate. |
|-------------------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| $\gamma$-Fe$_2$O$_3$ (reported) tetragonal      | d                 | 2.95              | 2.78              | 2.514             | 2.086             | 1.701             | 1.604             | 1.474             | 1.272             |
| $\gamma$-Fe$_2$O$_3$ (reported) cubic           | d                 | 2.95              | 2.78              | 2.52              | 2.08              | 1.70              | 1.61              | 1.48              | 1.27              |
| Fe$_2$O$_4$ (reported)                          | d                 | 2.967             | –                 | 2.532             | 2.099             | 1.715             | 1.616             | 1.485             | 1.281             |
| $\alpha$-Fe$_2$O$_3$ (reported) rhombohedral FFH| d                 | 3.66              | –                 | 2.69              | 2.51              | 2.20              | 1.838             | 1.69              | 1.452             |
| FSH (autocatalytic)                             | d                 | 2.97              | 2.777             | 2.70              | 2.519             | 2.08              | 1.84              | 1.69              | 1.603             |
| FMH (autocatalytic)                             | d                 | 2.97              | 2.78              | 2.70              | 2.524             | 2.09              | 1.84              | 1.69              | 1.607             |
| FTH (autocatalytic)                             | d                 | 2.95              | 2.771             | –                 | 2.53              | 2.09              | –                 | 1.718             | 1.61              |
| FEH (autocatalytic)                             | d                 | –                 | –                 | 2.70              | 2.526             | –                 | 1.84              | 1.697             | 1.604             | 1.484             |
| FLH (autocatalytic)                             | d (I/lo)          | 2.96              | 2.70              | 2.519             | –                 | 1.839             | 1.695             | 1.608             | 1.48              |
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