CHAPTER III

STUDY OF $\gamma$-Fe$_2$O$_3$

Part I

Studies on the synthesis, characterisation and decomposition of iron oxyhydroxides

Part II

Studies on the synthesis of $\gamma$-Fe$_2$O$_3$ from iron (II) carboxylato-hydrazinate
Gamma ferric oxide, $\gamma$-Fe$_2$O$_3$ (maghemite), a ferrimagnetic material, finds use as, a magnetic tape material in electronic industry, as well as, a catalyst in chemical industry. It is also reported to be used as a raw material in ferrite industry for the preparation of ferrites, in place of usual $\alpha$-Fe$_2$O$_3$ and found to increase the rate of spinelization. A systematic study of the synthesis of $\gamma$-Fe$_2$O$_3$ from precursor method can give additional information in optimising different properties of this industrially important material. So it was felt necessary to understand the formation of $\gamma$-Fe$_2$O$_3$ from the precursors.

As we are envisaging the utilisation of iron ore reject to synthesise active iron oxide useful in ferrites preparation, such information on the various
methods of preparation of $\gamma$-Fe$_2$O$_3$ may help us in adopting an easier method to prepare the oxide from chemically beneficiated iron ores (acid extracts).

3.1 Literature survey on $\gamma$-Fe$_2$O$_3$ preparation

A good recording material must possess a coercivity value in the range of 250 Oe to 1200 Oe to prevent accidental erasure but not so high that the magnetisation cannot be reversed. Particles having acicular shape with a length to width ratio of 3:1 to 10:1 and an average length of 0.6 $\mu$m act as a good recording material, since the shape anisotropy confers a coercivity of 250 - 400 Oe $\gamma$-Fe$_2$O$_3$ is the most commonly used magnetic recording material. The acicular shaped particles with a length to width ratio of approximately equal to 6:1, an average length of 0.6 $\mu$m, saturation magnetization of 71 to 75 emu/g and coercivity of about 250 - 300 Oe are generally used.

The particle size distribution and shape, thus, play an important role in such applications. The literature survey reveals that a lot of stress is being given on these, during the synthesis of $\gamma$-Fe$_2$O$_3$. In our present investigation, our main aim was to prepare active iron oxide (mainly $\gamma$-Fe$_2$O$_3$) to be used as a raw material in the synthesis of ferrite (MgFe$_2$O$_4$) and, hence, an elaborate study of synthesis of $\gamma$-Fe$_2$O$_3$ was carried out.

$\alpha$-FeOOH is commercially utilized in the synthesis of $\gamma$-Fe$_2$O$_3$, which is a multistage process (eqn.7). The $\alpha$-FeOOH is first dehydrated to $\alpha$-Fe$_2$O$_3$, then reduced to Fe$_3$O$_4$ and finally oxidised to $\gamma$-Fe$_2$O$_3$. Although this process is cumbersome, it is best suitable to obtain a needle shape $\gamma$-Fe$_2$O$_3$ from acicular $\alpha$-FeOOH.
This reduction oxidation method was first developed by Camras [311]. He further recommended another reduction of $\gamma$-Fe$_2$O$_3$ to Fe$_3$O$_4$ and reoxidation to $\gamma$-Fe$_2$O$_3$ to have improved magnetic properties. Dehydration and reduction at high temperature, however, may give a sintering effect.

Boronius et al [312] pointed out that the unwanted sintering of the particles that takes place during reduction and oxidation can be prevented by coating the particles of $\alpha$-FeOOH by inorganic chemicals like, sodium silicate. Woditsch et al [313] used silicon oil instead of sodium silicate and claimed higher coercivity due to this treatment.

The thermal transformation of goethite in alkali-halide disks has been widely investigated [314-317]. These works have shown that in diluted alkali iodide disks (0.1 - 0.5%), spinel structures such as maghemite or magnetite are obtained by adequate treatment. But, when the initial concentration of $\alpha$-FeOOH in the salt mixture is higher (~33%), the final products are protohematite and hematite.

Osmond [318] in 1951 studied the reduction - oxidation of $\alpha$-Fe$_2$O$_3$ to get $\gamma$-Fe$_2$O$_3$ . Thereafter, this method was used by other researchers [247,267,319-335] to prepare $\gamma$-Fe$_2$O$_3$.

The $\gamma$-Fe$_2$O$_3$ particles formed by reduction - oxidation of $\alpha$-Fe$_2$O$_3$ usually show some cation ordering. [266,326], while those prepared by the decomposition of $\gamma$-FeOOH have been reported to produce disordered structure [336-337].

The transformation of $\gamma$-FeOOH to $\gamma$-Fe$_2$O$_3$ has been studied by many workers [335-356]. Many investigators [337,339-340] reported that those $\gamma$-Fe$_2$O$_3$ which are prepared by low-temperature calcination of $\gamma$-FeOOH conserve the con-
figuration of cation atoms in the mother $\gamma$-FeOOH. This means that the dehydration reaction proceeds by shifting and re-stacking the structure already existing in the mother crystal.

The structure of oxides / oxyhydroxides of metals are built up of close-packed oxy / hydroxyl layers. When one form of oxide or oxyhydroxide transforms into another, the change may be effected simply by removing or adding close-packed oxy / hydroxyl layers from or to the original structures. Thus, one might expect to find an oriented relationship between the original and transformed products. Such a relationship which is not limited to any particular type of crystal, was observed by Galdsztanb [357-358] in the transformation of $\alpha$-FeOOH to $\alpha$-Fe$_2$O$_3$.

This sort of inter-relationship can be explained in terms of topotaxy, a term proposed by Gorter to denote the transformation from one crystalline phase to another, where there are definite oriented relationships between the axis of the original and transformed crystals.

The transformation of $\gamma$-FeOOH $\rightarrow$ $\gamma$-Fe$_2$O$_3$ $\rightarrow$ $\alpha$-Fe$_2$O$_3$ was studied by Bernal et al [337] using single crystals of $\gamma$-FeOOH. The (100) of $\gamma$-FeOOH is parallel to one of the cubic axes (001) of $\gamma$-Fe$_2$O$_3$. The mechanism of the transformation of $\gamma$-FeOOH to $\gamma$-Fe$_2$O$_3$ involves the removal of half of the hydroxyl group together with the hydrogen in the adjoining hydroxyl sheet, water molecules. There is also a shift of an half oxygen ion in the (100) direction. The resulting strain due to the shift explains the disorder in the $\gamma$-Fe$_2$O$_3$ crystal. The transformation of $\gamma$-Fe$_2$O$_3$ to $\alpha$-Fe$_2$O$_3$ does not involve any loss or gain of material but only a
restacking of close-packed oxygen atoms (cubic to hexagonal) on the (111) faces of \( \gamma-\text{Fe}_2\text{O}_3 \).

Although a simple elimination of water on dehydration of \( \gamma-\text{FeOOH} \) topotactically transforms it easily into \( \gamma-\text{Fe}_2\text{O}_3 \), commercially \( \gamma-\text{Fe}_2\text{O}_3 \) is prepared from \( \alpha-\text{FOOH} \) by reduction - oxidation method (eqn 7). This is mainly because \( \gamma-\text{Fe}_2\text{O}_3 \) synthesized from \( \gamma-\text{FeOOH} \) shows lower saturation magnetization values than that obtained from controlled oxidation of \( \text{Fe}_3\text{O}_4 \). A plausible reason given for such superior properties for the \( \gamma-\text{Fe}_2\text{O}_3 \), obtained from \( \text{Fe}_3\text{O}_4 \) oxidation, is based on the consideration of easy diffusion of \( \text{Fe}^{3+} \) ion through the spinel framework that already present in \( \text{Fe}_3\text{O}_4 \) to give a well ordered vacancies, on the so called 'Lithium sites' (Actually \( \text{Fe}_{64}\text{O}_{96}, \{\text{Fe}_{24}^{\text{Tetrahedral}}[\text{Fe}_{36}^{\text{Octahedral}} (\text{Fe}_{4}^{\text{Li-sites}} \Box \_8^{\text{Li-sites}})\text{O}_{96}]\} \) of \( \gamma-\text{Fe}_2\text{O}_3 \) [342, 352].

On the other hand, defect spinel \( \gamma-\text{Fe}_2\text{O}_3 \), of framework of \( [\text{FeO}_6] \) octahedra with edge and corner sharing that formed from the corrugated layers of \( [\text{FeO}_6] \) octahedra of \( \gamma-\text{FeOOH} \), has no sufficient time and occasion for \( \text{Fe}^{3+} \) ions to diffuse through the developing framework of \( \gamma-\text{Fe}_2\text{O}_3 \), to occupy the lithium sites for giving well ordered \( \gamma-\text{Fe}_2\text{O}_3 \).

The thermal decomposition of \( \gamma-\text{FeOOH} \) yields \( \gamma-\text{Fe}_2\text{O}_3 \). Alternative procedures of dehydrating \( \gamma-\text{FeOOH} \) have been described, which include intercalation reactions [341] and mechanochemical processes. With regards to the mechanochemical dehydration, it is well known that dry grinding of lepidocrocite \( \gamma-\text{FeOOH} \), leads to \( \alpha-\text{Fe}_2\text{O}_3 \) [359-361]. Such behaviour is also found in other phases of iron oxyhydroxide such as, goethite, \( \alpha-\text{FeOOH}, [362] \) or akaganeite,\( \beta-\text{FeOOH}, [363] \).
But the mechanochemical treatment of $\gamma$-FeOOH in wet medium [343,364-365] was shown to yield $\gamma$-Fe$_2$O$_3$.

It has been suggested [365] that in dry milling water released, due to the dehydration, reaches to such a high partial pressure of water vapour in the grinding vessel which is sufficient to accelerate the transformation of the formed $\gamma$-Fe$_2$O$_3$ into $\alpha$-Fe$_2$O$_3$. On the other hand, in wet grinding the non-aqueous medium helps in optimizing the water vapour partial pressure over the dehydrating particles of $\gamma$-FeOOH. This partial pressure is adequate in stabilizing the $\gamma$-Fe$_2$O$_3$.

Effect of the partial pressure of water vapour on the thermal decomposition of $\gamma$-FeOOH has been studied [350] and established that an increase in water vapour accelerates the transformation of $\gamma$-Fe$_2$O$_3$ to $\alpha$-Fe$_2$O$_3$. The explanation given for this is that, the particles of the $\gamma$-Fe$_2$O$_3$ that formed in fine size get coalesced with the increasing partial pressure of water vapour, thereby, increasing the particle size. The larger particles influence the phase transformation.

A mild transformation of $\gamma$-FeOOH to $\gamma$-Fe$_2$O$_3$ is also achieved using organic reagents [341]. When $\gamma$-FeOOH is treated with organic bases (pyridine, n-hexylamine) at temperature of 120 - 140$^\circ$C, it is quantitatively converted into the topotactically related $\gamma$-Fe$_2$O$_3$. Here, the first step is an intercalation of the organic base in the host lattice of $\gamma$-FeOOH. The second and relatively faster step is a sequential elimination of water from the interlayer where the base plays the role of a catalyst.

Slightly impure samples of $\gamma$-FeOOH that contain a small (5%) amount of $\alpha$-FeOOH are transformed quantitatively into $\alpha$-Fe$_2$O$_3$ under the above conditions.
but, pure $\alpha$-FeOOH is unaffected. The fact that $\alpha$-FeOOH is unaffected by pyridine or n-hexylamine under these conditions shows that this base assisted transformation is strongly structure dependent. It is observed [343] that the mechano-chemically prepared maghemite increases in its thermal stability due to the higher crystallinity of ground micro crystals, as revealed by the values of crystallite size and micro strains. It is also known that maghemite stores significant amounts of energy when submitted to dry milling [366-368] and, that, this fact causes alterations in its thermal behaviour, related with heat released processes and changes in the temperature of the thermally promoted phase transition of maghemite $\rightarrow$ hematite.

Magnetic and electric fields are also tried to assist dehydration and dehydroxylation of inorganic hydroxy compounds [369]. Clarke and Hall [335] have studied the preparation and interconversion of iron (III) oxide, hydroxides and oxyhydroxides and their characterization, by X-ray diffraction and small angle neutron scattering (SANS). Thus, the studies on the decomposition of iron oxyhydroxides seems to be quite thoroughly investigated.

A reverse transformation of thermodynamically more stable $\alpha$-Fe$_2$O$_3$ state to metastable $\gamma$-Fe$_2$O$_3$ state by grinding process is also reported [370]. Matsumoto et al [371] synthesized $\gamma$-Fe$_2$O$_3$ from amorphous Fe(OH)$_3$. Dovey et al [372] used iron oxalate and formate to prepare maghemite. First these precursors were decomposed in a mixture of steam, nitrogen and carbon dioxide to obtain Fe$_3$O$_4$ which was then dampened and heated in an oven between 100-200°C to convert it to $\gamma$-Fe$_2$O$_3$. Van Oosterhout et al. [235] were able to prepare $\gamma$-Fe$_2$O$_3$ by decom-
posing ferrous oxalate dihydrate in an atmosphere of steam and nitrogen, followed by oxidation in a mixture of air and water. Anantharaman et al [57] too prepared γ-Fe₂O₃ from ferrous oxalate dihydrate. They first decomposed the precursor in moist nitrogen at 562 °C to yield Fe₃O₄ which was then oxidised by dry air to acicular γ-Fe₂O₃ at 302 °C. The resulting γ-Fe₂O₃ had saturation magnetization ~70 emu/g, coercive force ~300 °C and squareness ratio ~0.6-0.65.

According to Venkatesh Rao et al [270], the ferrous oxalate dihydrate containing traces of moisture decomposes in air under the ambient of its own gaseous products at ~300 °C to γ-Fe₂O₃. However, the decomposition is highly exothermic, so that, the local oxidative heating leads to unavoidable contamination with α-Fe₂O₃. The final product had a saturation magnetization of 70emu/g, coercive force ~250 °C and ratio of remanence to saturation ~0.6. Tsyrnorechki et al [373-374] prepared γ-Fe₂O₃ by heating FeC₂O₄.2H₂O at 350 °C for 24 h in an atmosphere containing 4 to 5% oxygen.

Rane et al [264] too prepared γ-Fe₂O₃ from ferrous oxalate dihydrate by adopting a procedure almost similar to the procedures mentioned above. The decomposition was done in a controlled atmosphere of water vapours with nitrogen as a carrier gas and air for oxidation. They found that water helps in supressing the release of lattice water which later forms oxygen and hydrogen. The hydrogen enters the lattice to form γ-Fe₂O₃ having hydrogen ion H⁺ in the octahedral vacancies.

According to Aharoni et al [257], γ-Fe₂O₃ consists of solid solution of (Fe³⁺)₈ [Fe³⁺₁/₃, Fe²⁺₂/₃]O₂ and (Fe³⁺) [H⁺₄, Fe²⁺₁₂]O₃. They showed that
when $\gamma$-Fe$_2$O$_3$ was heated, hydrogen was evolved, in amounts of about 70% of that required to give the formula Fe$_8$[H$_4$Fe$_{12}$]O$_{32}$. Nikumbh, Rane and Mukhedkar [280] in their studies of direct current electrical conductivity of $\gamma$-Fe$_2$O$_3$ observed a kink in log $\sigma$ versus 1/T around 177°C, indicating the removal of hydrogen from the octahedral site.

A simple single step hydrazine method of preparation of $\gamma$-Fe$_2$O$_3$ has been studied by many researchers. Moye Rane and Kamat Dalal [278] autocatalytically decomposed ferrous oxalato-hydrazinates, FeC$_2$O$_4$.N$_2$H$_4$ and FeC$_2$O$_4$.2N$_2$H$_4$, prepared both by solution and equilibration method, to synthesize $\gamma$-Fe$_2$O$_3$. Patil et al [375-376] prepared magnetic ferric oxide by thermally decomposing iron hydrazino carboxylate hydrazinate [Fe(N$_2$H$_3$COO)$_2$(N$_2$H$_4$)$_2$], as well as, hydrazinium iron hydrazino carboxylate [N$_2$H$_5$Fe(N$_2$H$_3$COO)$_3$.H$_2$O]. These complexes exhibit autocatalytic decomposition, once ignited.

According to Patil et al [377-378], the decomposition / combustion of FeC$_2$O$_4$(N$_2$H$_4$)$_2$ in air at ~200°C yields a mixture of $\gamma$- and $\alpha$-Fe$_2$O$_3$, while Fe(N$_2$H$_3$COO)$_2$(N$_2$H$_4$)$_2$ gives exclusively $\gamma$-Fe$_2$O$_3$. The crystallite sizes of $\gamma$-Fe$_2$O$_3$ were in the range of 170-250 Å and the surface area was 40 m$^2$/g. Temperature profile measurement of FeC$_2$O$_4$(N$_2$H$_4$)$_2$ [379] showed that the maximum temperature attained during the combustion is 600°C, although ignition occurs at ~200°C. On the other hand, in the case of Fe(N$_2$H$_3$COO)$_2$(N$_2$H$_4$)$_2$, the combustion releases heat amounting to the temperature ~425°C. This difference in the exothermicity of the combustion of FeC$_2$O$_4$ (N$_2$H$_4$)$_2$ and Fe(N$_2$H$_3$COO)$_2$ (N$_2$H$_4$)$_2$ is probably re-
sponsible for the formation of a mixture of $\gamma$- and $\alpha$-Fe$_2$O$_3$ in the former and, ex-
clusively $\gamma$-Fe$_2$O$_3$ in the latter.

Patil [185] reported the preparation of $\gamma$-Fe$_2$O$_3$ by the combustion of redox
compound $[\text{N}_2\text{H}_5\text{Fe(N}_2\text{H}_3\text{C}_0\text{O})_3\cdot\text{H}_2\text{O}]$ and redox mixtures such as Fe(NO$_3$)$_3$ and
C$_3$H$_8$N$_4$O$_2$ (malonic dihydrazide, MDH). He compared the properties of $\gamma$-Fe$_2$O$_3$
prepared by both combustion processes and found that, the surface area of the ox-
ide powder prepared by the combustion of redox compound is higher than that ob-
tained by the combustion of redox mixture. This is because redox compounds un-
dergo flameless (smouldering) combustion, whereas redox mixtures burn with a
flame.

A mixture of $\alpha$- and $\gamma$-Fe$_2$O$_3$ (mainly) was obtained by autocombustion of
iron sulphite hydrazine hydrate [380].

Excepting iron, the hydrazine complexes of the other metals, such as, man-
ganese, nickel, cobalt, zinc, have also been studied by many reseachers. The differ-
ent metal hydrazine complexes are metal acetate hydrazinate[381], metal formate
hydrazinate [382-383], metal propionate hydrazinate [384], bis hydrazine metal
maleates and fumarates [385] and bis hydrazine metal malonates and succinates
[386]. Recently, the preparation, characteristics and thermal analysis of iron ace-
tate hydrazinate have been reported [387].

Some reseachers [371,388] used hydrothermal processes for the preparation
of $\gamma$-Fe$_2$O$_3$. Many have used spray pyrolysis / roasting for the preparation of
$\gamma$-Fe$_2$O$_3$ [247,333,389-391]. Spherical $\gamma$-Fe$_2$O$_3$ particles of nanometer size can be
directly obtained by spray pyrolysis of iron salt solution [391]. These particles have
different states of aggregation, depending on the precursor salt used and were found to be superparamagnetic. The iron salt solutions used, by Morales et al [333] for the preparation of $\gamma$-Fe$_2$O$_3$ by spray pyrolysis, were iron (III) nitrate which gave compact spherical aggregates of small crystallites ($\sim$6nm), and iron (II) ammonium citrate which gave hollow spheres of crystallites size $\sim$ 4nm.

Cabanas [392] reported the synthesis of spherical gamma iron-oxide particles by an aerosol technique.

A composite of polyaniline (PANI) containing iron oxides [393] with nanometer size was synthesized by a chemical method. Kroll et al [394] have reported in-situ preparation of nano crystalline gamma Fe$_2$O$_3$ in iron (II) cross-linked alginate gels. A microemulsion-mediated chemical reaction [395] was used to synthesize acicular particles of gamma Fe$_2$O$_3$, with an equivalent spherical diameter (ESD) of 7-8 nm. It was observed that each microemulsion droplet gives birth to a single particle of $\gamma$-Fe$_2$O$_3$. Thus, it may be possible to control size and shape of $\gamma$-Fe$_2$O$_3$.

Many researchers [396-397] have studied the direct preparation of high coercivity $\gamma$-Fe$_2$O$_3$ thin films for magnetic recording, by chemical vapour pyrolysis technique. Deng et al [398] prepared $\gamma$-Fe$_2$O$_3$ by a low temperature flux method. Abe et al [399] prepared nanoparticles of Fe$_2$O$_3$ through encapsulation into the pores of MCM-41(molecular sieve). The bandgap of the resulting Fe$_2$O$_3$ particles is widened from 2.1 to 4.1 eV, owing to the quantum size effect. Nanoparticles of $\gamma$-Fe$_2$O$_3$ were prepared in silica matrix by sol-gel process [400]. Da Costa et al
prepared $\gamma$-Fe$_2$O$_3$ by heating the product of a sol-gel reaction between iron (III) nitrate and ethylene glycol.

Ziolo et al [402] have reported the matrix-mediated synthesis of nanocrystalline $\gamma$-Fe$_2$O$_3$. A new magnetic material, with appreciable optical transmission in the visible region at room temperature, has been isolated as a $\gamma$-Fe$_2$O$_3$/Polymer nanocomposite.

Batis - Landoulsi and Vergnon [403] prepared $\gamma$-Fe$_2$O$_3$ from vapours of ferric chloride by reaction in an oxygen-hydrogen flame ($2727^\circ$C).

This chapter is divided into two parts: part I and part II. In part I of this chapter we are presenting our results of the studies on the synthesis, characterization and decomposition of iron oxyhydroxides: $\gamma$-FeOOH, $\alpha$-FeOOH amorphous FeOOH and their hydrazinated complexes. The raw material (iron salts) used for the preparation of iron oxyhydroxide is obtained by chemical beneficiation of iron ore rejects. Part II deals with the study of the synthesis and characterization of novel iron (II) carboxylates: ferrous fumarato - hydrazinate, ferrous succinato - hydrazinate, ferrous malonato - hydrazinate, ferrous tartrato - hydrazinate, ferrous maleato - hydrazinate and ferrous malato - hydrazinate and their thermal decomposition.
Studies on the synthesis, characterisation and decomposition of iron oxyhydroxides
3.2 Experimental: Preparation characterisation and thermal decomposition

3.2.1 Chemical beneficiation of iron ore reject.

a) Direct precipitation of iron(III)hydroxides

In our present study we have chemically beneficia ted an iron ore reject dump sample of Goan origin containing, 35.5 % Fe, 3.30 % Al₂O₃, 40.28 % SiO₂
and, traces of oxides of manganese, calcium and magnesium. The moisture percentage in it was 9.86.

The sample was first crushed and brought to a size of -100 mesh. Each time 20g of this sample was taken in a conical flask and dissolved by adding 50 % HCl solution. First, 50 ml of 50 % HCl solution and 2-3 drops of Conc. HNO₃ was added to 20g of the sample and the mixture was boiled on a sand bath. Then, again 5ml of the HCl solution was added to the mixture and continued boiling. This was repeated till all the particles of the iron oxide are dissolved and only white coloured SiO₂ is seen at the bottom of the flask. This SiO₂ is then removed by filtration.

The filtrate which is called as acid extract contains chlorides of Fe, Al and trace elements. To this filtrate 20 % NaOH was added, drop by drop, with constant stirring. Iron (III) ions only start precipitating in the acidic pH as Iron (III) hydroxides. Since the solubility product (Kₐ) of Fe(OH)₃ is less than that of Al(OH)₃ and hydroxides of other trace elements [404], the Fe(OH)₃ can be selectively precipitated out. The precipitated iron hydroxide was filtered and washed with hot, water repeatedly till it is free from alkali and chloride ions.

b) Synthesis of ferric nitrate and ferrous chloride from iron ore rejects

The iron hydroxide obtained from iron ore (section 3.2.1.a) was then converted into ferric nitrate and ferrous chloride.

Ferric nitrate: The iron hydroxide was first neutralised by adding nitric acid solution and then concentrated on the water bath. The ferric nitrate slowly crystallises,
as the solution cools to room temperature. These crystals were then removed and washed with alcohol, dried and stored in the desiccator.

Ferrous chloride: The iron hydroxide was converted to ferric chloride by adding hydrochloric acid solution. This solution was then reduced to ferrous state by adding pure iron metal powder and requisite quantity of conc. HCl and then boiling the mixture in an atmosphere of CO₂. These salts were then used in the synthesis of iron oxyhydroxides.

3.2.2 Synthesis of Iron oxyhydroxides from ferric nitrate and ferrous chloride prepared from ferric hydroxide of iron ore

Iron oxyhydroxides: γ-FeOOH, α-FeOOH and amorphous FeOOH are synthesised, as follows, by using ferric nitrate and ferrous chloride, prepared from ferric hydroxide of iron ore, as in section 3.2.1.b.

a) Synthesis of γ-FeOOH

γ-FeOOH was prepared as per the method of Fricke and Zerrweck [405]. A solution of freshly prepared ferrous chloride (0.15 M, 750ml) was added to the aqueous solution of (CH₃)₆ N₄ (42 g in 150ml), drop by drop. A blue green precipitate of Fe(OH)₂ is formed. To this then an aqueous NaNO₂ solution (10.5g in 150ml) was added slowly with stirring and the mixture was heated to about 60°C and allowed to stand 3 hours. The reddish orange precipitate formed was filtered and washed with warm water till free of chloride ions and dried.
b) Synthesis of α-FeOOH

α-FeOOH was synthesized following the method described by the Fricke and Ackermann [406]. A cold solution of 81g of ferric nitrate in 200ml of water was slowly poured with vigorous stirring into an ammonia solution. The hydroxide precipitated was washed repeatedly by decantation. The slurry was then stirred with sufficient concentrated KOH to give a mixture 2N approximately and allowed to stand for 3-4 h. Finally, steam was bubbled through the solution for 2 h. The precipitate was then washed with calculated amount of NH₄Cl which removed the excess KOH. The precipitate was filtered, washed with water and dried.

c) Synthesis of amorphous FeOOH

The method similar to Kung et al [407] is used here. 20.2g ferric nitrate in 500 ml of water was added to 0.1 M NH₃ solution. The pH of the solution was maintained at 10.5 by adding conc. NH₃ to obtain the precipitate which was then filtered and washed untill the filtrate showed the pH of distilled water. The precipitate was dried in over at 60 °C.

3.2.3. Hydrazination of ferric hydroxide and iron oxyhydroxides

a) Equilibration method.

A requisite amount of the iron oxyhydroxide was taken in a petridish and kept in a desiccator containing hydrazine hydrate (99 - 100 %) for few days.

A specially designed reactor, however, enabled us to monitor the hydrazine uptake by titrimetric method using KIO₃ as titrant.
The set up for the hydrazine equilibration consists of a round bottom flask with two necks of standard joints. A separating funnel with a side arm is fitted to one of the necks of the round bottom flask.

A dry iron oxyhydroxide sample was placed in the separating funnel using glass wool as a plug. Through the second neck of the round bottom flask dry nitrogen was bubbled (10 bubbles/min.) into the hydrazine hydrate (99-100%), placed in the flask. Separating funnel was closed with stopper and the arm provided to it was used to flush out the nitrogen gas carrying unreacted hydrazine hydrate vapours by passing through an acidified water. When the hydrazine uptake of the sample reaches its saturation point (that is, just before sample turns black) the separating funnel was closed at the bottom. Then a known amount of conc. HCl was run down into it. The separating funnel was removed from the round bottom flask and the whole solution of the hydrazinated sample was run down in a reagent bottle and titration was carried out using KIO₃ and CCl₄ [299].

3.2.4 Characterization.

a) Chemical analysis.

i) Metal estimation

The estimation of iron content of iron oxyhydroxides and hydrazinated iron oxyhydroxides was carried out by standard potassium dichromate method [299].
ii) **Hydrazine estimation**

The hydrazine content was estimated titrimetrically using KI\(_3\) as titrant [299].

As the hydrazine equilibrated iron oxyhydroxides on exposure to air decompose spontaneously to oxides, the estimation of hydrazine uptake was difficult to monitor. Hence, a specially designed reactor, however, enabled us to follow up the hydrazine uptake titrimetrically.

**b) Infrared analysis**

Infrared spectra of the oxyhydroxides and their thermal products were obtained on Shimadzu FTIR instrument, model 8101.

c) **Density measurements.**

Pycnometric density of the oxyhydroxides and their thermal products was measured at room temperature using CCl\(_4\) the reference liquid.

d) **X-ray diffraction analysis**

X-ray diffraction patterns of the decomposed products of iron oxyhydroxides were obtained by using Philips X-ray diffractometer model PW 1710 with Cu K\(\alpha\) radiations and Nickel as a filter, as well as, by using Rigaku D Max II X-ray diffractometer with Cu and Fe targets. The inter planar spacings, \(d_{hlk}\), values were compared with JCPDS files for metallic Fe [408] and the iron oxides such as \(\alpha\)-Fe\(_2\)O\(_3\) [409], \(\alpha\)-Fe\(_2\)O\(_3\) [410-411], Fe\(_3\)O\(_4\) [412] and FeO [413].
e) Magnetic characterization

The saturation magnetization values of the thermal products of iron oxyhydroxides and autocatalytically decomposed hydrazinated oxyhydroxides were measured, using an alternating current hysteresis loop tracer described. The saturation magnetization values, $\sigma_s$, in emu/g were calculated using Ni as a standard.

f) Mössbauer Spectroscopy

The thermal products of amorphous FeOOH are studied by Mössbauer spectroscopy. The Mössbauer spectra were taken at -183 and 27°C using a constant acceleration spectrometer and a $^{57}$Co/Rh source. The isomer shifts are quoted with reference to $\alpha$-Fe.

3.2.5 Thermal analysis and decomposition

a) Thermogravimetric (TG) analysis and Isothermal weight loss studies

TG analysis of iron oxyhydroxides was done on Rigaku TAS 1000 instrument in $N_2$ atmosphere. Isothermal mass loss studies were carried out on the complexes at different predetermined temperature, in an oven by using platinum crucible.

b) Thermal decomposition in different atmosphere

The thermal decomposition of the iron oxyhydroxides was carried out in different atmospheres like, Air, dry $N_2$, $N_2/H_2O/Air$, dry$N_2/Methanol$, dry $N_2$/Isopropyl alcohol and dry $N_2$/cyclohexane at 300°C.
The assembly used for this purpose (Fig. 3.1) comprises of a hollow cylindrical glass tube of 5cm diameter with one end tapering into a small tube which is the inlet for the carrier gas, while the other end is fixed with a cork having an outlet for the carrier gas. Inside this glass tube another hollow glass tube is inserted, having diameter of 4cms and wound with a metallic wire. The one end of this wire is removed out through the cork which can be used to rotate the wound glass tube through 360°, for the uniform heating of the sample which is kept inside it. This assembly is inserted into a temperature controlled tubular furnace built in our laboratory. The assembly is kept in such a way that the sample to be decomposed lies exactly in the heating zone of the furnace. The heating rate of 5°/min. was maintained.

The carrier gas N₂ is first purified, by passing through the traps of conc. H₂SO₄, pyrogallol and calcium chloride, to make it dry and free of oxygen. For maintaining the required partial pressure of vapours of methanol (MeOH), isopropyl alcohol (IPA) cyclohexane etc, a dry N₂ was bubbled through these liquids, contained in a flask kept on a heating mantle at the desired temperature. The carrier gas with the partial pressure of these vapours was made to pass through a preheater which, in turn is connected to the tapering end of the hollow cylindrical tube containing another tube with the sample. A pulse of air was also made to enter the reaction zone whenever required.
FIG. 3.1 Assembly for controlled atmospheric decomposition
i. Air decomposition

The iron oxyhydroxides: $\gamma$-FeOOH, $\alpha$-FeOOH and amorphous FeOOH were decomposed in a tubular furnace at 300° C, in an ordinary atmosphere.

ii. $N_2$ atmosphere

The sample tube was inserted in the tubular furnace. The inlet was connected to the $N_2$ gas cylinder via the purification train. The decomposition was carried out at 300° C. The sample tube was rotated during decomposition, intermittently.

iii. $N_2 + H_2O + Air$ atmosphere

The iron oxyhydroxide sample was taken in the sample tube and inserted in the furnace. $N_2$ as a carrier gas was bubbled in the hot water (kept at 60° C), at the rate of 15-20 bubbles/min. The water vapours with carrier gas was passed in the sample tube via preheater and the temperature of the furnace was raised at a rate of 5° C/min. till it reaches 270° C. At this stage, air is passed instead of $N_2$, till the temperature reaches to 300° C. The sample was rotated after every 5 minutes during decomposition. After the completion of the decomposition, the sample tube was cooled to room temperature, by passing only $N_2$ gas.

iv. Dry $N_2 + MeOH$ atmosphere

After placing the iron oxyhydroxide sample in the tubular furnace, the inlet of the sample tube was connected to the flask containing a pure and warm methyl alcohol (MeOH). Dry $N_2$ gas was bubbled at the rate of 15 -20 bubbles / min.
MeOH solution. The MeOH vapours were carried through a preheater to the sample tube along with N₂ gas. The temperature of the furnace was increased to 300°C. The sample tube was rotated frequently during heating. The sample tube was cooled to room temperature in the N₂ atmosphere.

v. Dry N₂ + IPA atmosphere.

The IPA vapours formed by bubbling the dry N₂ gas through warm isopropyl alcohol (A.R.Grade) at the rate of 15 bubbles/min were carried by N₂ gas through the preheater into the glass tube containing sample, kept in a tubular furnace. The sample was heated slowly in this atmosphere upto 300°C and then cooled by passing N₂ gas. During heating, the sample tube was rotated after every 4-5 minutes, for the uniform heating of the sample.

vi. Dry N₂ + Cyclohexane atmosphere

The iron oxyhydroxide is placed in the sample tube which was then inserted into the tubular furnace. The dry N₂ gas was bubbled into the warm and pure cyclohexane. The cyclohexane fumes formed along with the N₂ gas were made to enter into the preheater which is connected to the sample tube. The furnace containing sample tube was heated at a rate of 5°C/min. till the temperature reaches to 300°C. The sample was rotated through 360°C during decomposition, after every 5 minutes. While cooling the decomposed sample, only N₂ gas was passed through it till the room temperature is attained.
c) **Autocatalytic decomposition of hydrazinated iron hydroxides and iron oxyhydroxides.**

Iron hydroxides and iron oxyhydroxides on equilibrating in hydrazine hydrate atmosphere, in a desiccator, change their colour indicating the hydrazine uptake by them. A reddish orange $\gamma$-FeOOH and reddish brown amorphous FeOOH turned black after seven days of the equilibration, while the yellow $\alpha$-FeOOH shows no change in colour. On exposure to air the hydrazinated $\gamma$-FeOOH and amorphous FeOOH decomposed autocatalytically, while $\alpha$-FeOOH only fumed.

3.2.6 Hydrazine equilibration studies of iron oxyhydroxides by electrical conductivity measurements

a) **Variation of electrical conductivity on hydrazination as a function of time**

Although the specially built reactor enabled us the estimation of the hydrazine uptake by iron oxyhydroxides titrimetrically, the colour change observed in the hydrazine equilibration of these and chemical analysis indicated that the products consists of oxides of Fe$^{2+}$ and Fe$^{3+}$. Hence, along with the hydrazine content estimation, it was decided to measure electrical characteristic of these iron oxyhydroxides during the hydrazine uptake, as there occurs reduction of Fe$^{3+}$ ions to Fe$^{2+}$ on hydrazination and these ferric and ferrous ions may contribute to the enhanced electrical conductivity in the products that formed.

A specially built set up was used for the measurement of direct current electrical conductivity during the hydrazination of the iron oxyhydroxides. The iron oxyhydroxides in the pellet form were pressed between platinum electrodes in
a conductivity cell designed for such work. The conductivity cell was placed in the reactor containing hydrazine hydrate atmosphere and the leads were connected to a multimeter and the resistance measurements were done as a function of time. From the dimensions of the pellet, the resistance values were converted into resistivity and conductivity.

3.3 Results and Discussion

A chemical formulas for iron oxyhydroxides and hydrazinated iron oxyhydroxides were fixed based on chemical analysis, ir and thermal analysis. Decomposition of these precursors was carried out and the thermal products were X-ray characterized to establish the phase formation. The thermal products were then systematically studied to understand their magnetic characteristics. A plausible mechanism for the formation of the iron oxides was proposed.

3.3.1 Fixation of chemical formulas

a) Chemical formulas of iron oxyhydroxides.

i Chemical analysis

The iron contents of 59.0 % for $\gamma$-FeOOH, 60.0 % for $\alpha$-FeOOH and 54.0 % for amorphous FeOOH are observed. The calculated percentage of Fe for all these iron oxyhydroxides, considering formula FeOOH is 62.86. The iron contents of all these iron oxyhydroxides are, thus, found to be lower than the calculated ones.
ii. Infra red analysis

Infra red band positions of O-H stretching, O-H bending and Fe-O stretching are given in Table 3.1 for these iron oxyhydroxides. The O-H stretching, O-H bending and Fe-O stretching are respectively found at 2890, 1020 and 747 cm\(^{-1}\) for \(\gamma\)-FeOOH and at 3100, 904 and 774 cm\(^{-1}\) for \(\alpha\)-FeOOH. Amorphous FeOOH, however, shows two absorption peaks O-H stretching, 3100 cm\(^{-1}\); Fe-O stretching, 775 cm\(^{-1}\). These band positions are agreeing well with the reported band positions for \(\gamma\)-FeOOH and \(\alpha\)-FeOOH [356, 414].

iii Pycnometric density

The densities of \(\gamma\)-FeOOH, amorphous FeOOH and \(\alpha\)-FeOOH are 1.54, 1.73 and 2.66 respectively (Table 3.1).

iv TG and total mass loss

Iron oxyhydroxides decompose in air \(\sim 300^\circ\)C giving iron oxide, Fe\(_2\)O\(_3\). The total mass loss observed \(\sim 300^\circ\)C in air [Table 3.1] is 15.62 % for \(\gamma\)-FeOOH; 13.76 % for \(\alpha\)-FeOOH and 22.9 % for amorphous FeOOH. Total mass loss observed on TG in nitrogen is, for \(\gamma\)-FeOOH -15 %; for \(\alpha\)-FeOOH -15 % and amorphous FeOOH -23 %. Considering formula FeOOH for all these oxyhydroxides, the calculated weight loss for Fe\(_2\)O\(_3\) formation is 10.13 %. Thus, an increased weight loss is observed for all these iron oxyhydroxides. These observations indicate that these iron oxyhydroxides consist of an additional water which may be present as water of hydration.
Based on these observations in TG and total mass loss studies, the chemical formula for these iron oxyhydroxide are fixed as, \( \gamma\text{-FeOOH \cdot 0.3H}_2\text{O} \), \( \alpha\text{-FeOOH \cdot 0.2H}_2\text{O} \) and amorphous \( \text{FeOOH \cdot 0.8H}_2\text{O} \). These formulas now agree well with the iron contents calculated with the observed values by chemical analysis (Table 3.1). The iron contents, thus, observed and calculated (in bracket) show closeness in the values, confirming the formulas fixed as given above.

b) Hydrazine equilibration of iron oxyhydroxides

i. Equilibration in 80% and 99-100% hydrazine hydrate

Powdered as well as the compact (pellets used in the electrical conductivity measurements) samples of reddish orange \( \gamma\text{-FeOOH \cdot 0.3H}_2\text{O} \) and reddish brown amorphous \( \text{FeOOH \cdot 0.8H}_2\text{O} \) when placed in a desiccator containing 99-100% hydrazine hydrate turned black on the hydrazine equilibration. The yellow \( \alpha\text{-FeOOH \cdot 0.2H}_2\text{O} \), however, did not change its colour. On exposure to air these hydrazine equilibrated samples fumed with glow indicating intense decomposition taking place and the products obtained were now dull reddish brown in colour and magnetic in nature.

The equilibration when carried out in a desiccator containing 80% hydrazine hydrate also indicated the colour change, but they did not show spontaneous decomposition on exposure to air. The black products were magnetic in nature. The black coloured product of \( \gamma\text{-FeOOH} \) indicated 41.0% FeO content in it, while the product of amorphous FeOOH showed to consist of just 1.2% FeO (Table 3.2).
### TABLE 3.1 Chemical analysis, density, IR, total weight loss of iron-oxyhydroxides

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample</th>
<th>% Fe</th>
<th>Density</th>
<th>Infra Red Data, cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Total Weight Loss (%) in</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>g cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>Air (Isothermal)</td>
<td>N&lt;sub&gt;2&lt;/sub&gt; (TG)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Obs. (Calc.)</td>
<td>O-H stre.</td>
</tr>
<tr>
<td>1</td>
<td>γ-FeOOH·0.3 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>59.0</td>
<td>1.54</td>
<td>2890</td>
<td>1020</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(59.25)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Amorph. FeOOH·0.8 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>54.0</td>
<td>1.73</td>
<td>22.9</td>
<td>25.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(54.09)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>α-FeOOH·0.2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>60.0</td>
<td>2.66</td>
<td>3100</td>
<td>904</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(60.41)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3.2 Chemical analysis of iron oxyhydroxides on hydrazine equilibration in 80% N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample</th>
<th>% N&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</th>
<th>Colour Change after Equilibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>γ-FeOOH·0.3 H&lt;sub&gt;2&lt;/sub&gt;O (Reddish Orange)</td>
<td>10.4</td>
<td>Black (FeO 41%)</td>
</tr>
<tr>
<td>2</td>
<td>Amorph. FeOOH·0.8 H&lt;sub&gt;2&lt;/sub&gt;O (Reddish Brown)</td>
<td>10.8</td>
<td>Black (FeO 1.2%)</td>
</tr>
</tbody>
</table>
Yellow coloured $\alpha$-FeOOH did not show any change in colour on its exposure to hydrazine. On exposing to air hydrazinated $\alpha$-FeOOH fumed.

**ii. Hydrazine estimation**

The hydrazine equilibration studies carried out both in 99-100% and 80% hydrazine hydrate did not allow us to estimate the hydrazine uptake by these iron oxyhydroxides. Hence, a special set up described in section 3.2.3 that used for such hydrazine uptake study enabled us to analyse the hydrazine (Fig. 3.2) by titrimetric method. And, about 10.4% of hydrazine uptake was observed in $\gamma$-FeOOH $0.3\text{H}_2\text{O}$ (Table 3.2), while amorphous FeOOH$0.8\text{H}_2\text{O}$ showed 10.8% hydrazine in it. $\alpha$-FeOOH$0.2\text{H}_2\text{O}$, on the other hand, indicated just 1.5% hydrazine uptake. However, these results did not allow us to fix a chemical formula for these iron oxyhydroxide, as further studies like, ir, isothermal weight loss, DTA and TG analysis could not be carried out on these hydrazinated complexes due to their unstable nature.

As the black coloured product of hydrazine equilibrated $\gamma$-FeOOH is magnetic in nature and consist of 41% of FeO and the product of amorphous FeOOH is also magnetic in nature with 1.2% FeO (Table 3.2), it was felt that the electrical conductivity measurements on these iron oxyhydroxides during the hydrazine uptake may throw some light on the process of hydrazination. Also, as the black coloured products on exposure to air gave a dull brown product characterized as gamma ferric oxide, $\gamma$-Fe$_2$O$_3$, by xrd, the continuation of the electrical conductivity measurements on exposure to air should, therefore, indicate the phase transforma-
FIG. 3.2  Hydrazine estimation set up
tion of the black coloured magnetic product. Therefore, the electrical conductivity measurement were done on these iron oxyhydroxides during hydrazine equilibration.

iii. Variation of d.c. electrical conductivity during hydrazination as a function of time

The electrical conductivity of the iron oxyhydroxides in pellets form of 10 mm diameter and thickness of 2-3 mm were pressed between two circular platinum discs in a special conductivity cell built (section 3.2.6a) for such study. The whole assembly was then introduced in a desiccator containing hydrazine hydrate. The lead wires of the platinum electrodes were then connected to a multimeter. Resistance of the pellet was measured as a function of time. From the dimension of the pellet, the resistivity and then the conductivity values were plotted as log conductivity (σ) versus time in hours.

In Fig.3.3 the logσ vs. Time in hours plots of γ-FeOOH.0.3H₂O, amorphous FeOOH.0.8H₂O and α-FeOOH.0.2H₂O are shown. A room temperature conductivity value of 2.63 x 10⁻⁷ ohm⁻¹ cm⁻¹ of γ-FeOOH (curve A), on introducing in the hydrazine hydrate atmosphere, shows initial dip in conductivity and then increase linearly in 20 hours to 6.96 x 10⁻⁶ ohm⁻¹ cm⁻¹. After 20 hours of exposure to hydrazine atmosphere the conductivity increases slightly and then again steeply upto 50 hours. Thereafter, the conductivity remains constant at 6.86 x 10⁻⁵ ohm⁻¹ cm⁻¹ indicating the equilibration of hydrazine is completed. On exposure to air, after keeping in the hydrazine atmosphere for 120 hours, the conductivity value showed a sudden increase to 2.13 x 10⁻⁴ ohm⁻¹ cm⁻¹ and then started decreasing very fast.
FIG. 3.3 Variations in electrical conductivity of iron oxyhydroxides in Hydrazine atmosphere as a function of time: A) $\gamma$-FeOOH, B) amorphous FeOOH, and C) $\alpha$-FeOOH.
and remained constant at $2.56 \times 10^{-7}$ ohm$^{-1}$ cm$^{-1}$, a three order decrease in the conductivity value is thus observed.

A room temperature conductivity value of $6.1 \times 10^{-8}$ ohm$^{-1}$ cm$^{-1}$ of amorphous FeOOH, which is half an order less than that of $\gamma$-FeOOH, shows no change in the $\sigma$ value for initial 5 hours in the hydrazine atmosphere (curve B) and then it increases, like $\gamma$-FeOOH, steeply in 20 hours to $1.05 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$. But, after that, unlike in $\gamma$-FeOOH, the conductivity here shows a decrease and then remains constant at $\sim 3.53 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$. When the hydrazine equilibrated sample was exposed to air the value increased to $8.92 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ and then it suddenly decreased to $1.7 \times 10^{-7}$ ohm$^{-1}$ cm$^{-1}$ and remained constant at this value.

Both $\gamma$-FeOOH amorphous FeOOH when exposed to air after the hydrazine equilibration fumed and the value of conductivity of the products remained at $\sim 10^{-7}$ ohm$^{-1}$ cm$^{-1}$. The product being $\gamma$-Fe$_2$O$_3$ in both these cases, the conductivity value is now of the oxide.

Thus, $\gamma$-FeOOH amorphous FeOOH undergo electrical conductivity changes on equilibrating with hydrazine. Since the value increase is of 2-3 order, and the oxyhydroxides convert into black coloured magnetic oxide consisting of 41% FeO and the rest Fe$_2$O$_3$ content in it, the increase in conductivity may be due to the presence of Fe$^{2+}$ and Fe$^{3+}$. A Fe$_3$O$_4$ type of black product is thus formed on hydrazine equilibration, which on exposure to air oxidizes into a dull brown coloured $\gamma$-Fe$_2$O$_3$ and since in this oxide only Fe$^{3+}$ ions are present, the conductivity shows a decrease.
On the other hand, the \( \alpha\text{-FeOOH} \) on exposure to hydrazine atmosphere (curve C) shows just a half order change from its room temperature conductivity value in air. Then, the value from \( 1.56 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1} \) decreases to \( 8.93 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1} \) and thereafter, remains constant till it was exposed to air. Unlike in \( \gamma\text{-FeOOH} \) and amorphous FeOOH, here there is no increase in conductivity initially after the exposure of the sample to air. However, the value goes down to \( 1.16 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1} \) and remains constant. The hydrazine equilibration, although, did not show significant change in the conductivity, the sample did fume in air and the product was found to be mixture of \( \gamma\text{-Fe}_2\text{O}_3 \) and \( \alpha\text{-Fe}_2\text{O}_3 \).

c) **Analysis of thermal products of iron oxyhydroxides and hydrazinated iron oxyhydroxides**

i. X-Ray Diffraction Analysis

The thermal products of iron oxyhydroxides in air and different controlled atmospheres and autocatalytic decomposition products of the hydrazinated iron oxyhydroxides were characterized by X-ray diffraction (Table 3.3). \( \gamma\text{-Fe}_2\text{O}_3 \) is the main thermal product of \( \gamma\text{-FeOOH} \) decomposed in all atmospheres. \( \gamma\text{-FeOOH} \) decomposed in atmospheres such as, \( \text{N}_2/\text{MeOH} \) and \( \text{N}_2/\text{IPA} \) at 300°C shows all peak intensities corresponding to those of \( \gamma\text{-Fe}_2\text{O}_3 \). The end product of \( \gamma\text{-FeOOH} \) decomposed in other atmospheres such as, dry \( \text{N}_2 \), \( \text{N}_2/\text{cyclohexane} \), as well as, autocatalytically decomposed hydrazinated \( \gamma\text{-FeOOH} \) complex is \( \gamma\text{-Fe}_2\text{O}_3 \) with the traces of \( \text{Fe}_3\text{O}_4 \). The dehydration of \( \gamma\text{-FeOOH} \) in air gives \( \gamma\text{-Fe}_2\text{O}_3 \) with traces of \( \alpha\text{-Fe}_2\text{O}_3 \), while decomposition in \( \text{N}_2/\text{H}_2\text{O}/\text{air} \) gives \( \gamma\text{-Fe}_2\text{O}_3 \) of better quality.
TABLE 3.3 XRD data of iron oxides obtained by decomposition of iron oxyhydroxides in different atmospheres

<table>
<thead>
<tr>
<th>Iron Oxide</th>
<th>d (Å)</th>
<th>(l/h)</th>
<th>d (Å)</th>
<th>(l/h)</th>
<th>d (Å)</th>
<th>(l/h)</th>
<th>d (Å)</th>
<th>(l/h)</th>
<th>d (Å)</th>
<th>(l/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Fe$_2$O$_3$ (reported)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>2.95</td>
<td>(30)</td>
<td></td>
<td></td>
<td>2.51</td>
<td>(100)</td>
<td>2.086</td>
<td>(15)</td>
<td>1.7</td>
<td>(19)</td>
</tr>
<tr>
<td>Cubic</td>
<td>2.95</td>
<td>(34)</td>
<td>2.78</td>
<td>(19)</td>
<td>2.52</td>
<td>(100)</td>
<td>2.08</td>
<td>(24)</td>
<td>1.7</td>
<td>(12)</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>3.66</td>
<td>(25)</td>
<td>2.69</td>
<td>(100)</td>
<td>2.51</td>
<td>(50)</td>
<td>2.20</td>
<td>(40)</td>
<td>1.838</td>
<td>(40)</td>
</tr>
<tr>
<td>γ-Fe$_2$O$_3$ (reported)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(autocatal.)</td>
<td>2.96</td>
<td>(53)</td>
<td></td>
<td></td>
<td>2.523</td>
<td>(100)</td>
<td>2.09</td>
<td>(33)</td>
<td>1.7</td>
<td>(27)</td>
</tr>
<tr>
<td>γ-FeOOH in N$_2$ + MeOH</td>
<td>2.95</td>
<td>(27)</td>
<td></td>
<td></td>
<td>2.51</td>
<td>(100)</td>
<td></td>
<td></td>
<td>1.7</td>
<td>(10)</td>
</tr>
<tr>
<td>γ-FeOOH in N$_2$ + IPA</td>
<td>2.95</td>
<td>(44)</td>
<td></td>
<td></td>
<td>2.52</td>
<td>(99)</td>
<td>2.09</td>
<td>(43)</td>
<td>1.71</td>
<td>(34)</td>
</tr>
<tr>
<td>γ-FeOOH in N$_2$ + cyclohexane</td>
<td>2.97</td>
<td>(38)</td>
<td></td>
<td></td>
<td>2.54</td>
<td>(100)</td>
<td>2.09</td>
<td>(23)</td>
<td>1.7</td>
<td>(27)</td>
</tr>
<tr>
<td>γ-FeOOH in N$_2$ + H$_2$O + air</td>
<td>2.97</td>
<td>(34)</td>
<td>2.70</td>
<td>(65)</td>
<td>2.52</td>
<td>(100)</td>
<td>2.08</td>
<td>(22)</td>
<td>1.7</td>
<td>(31)</td>
</tr>
<tr>
<td>γ-FeOOH in N$_2$ + IPA</td>
<td>2.97</td>
<td>(71)</td>
<td></td>
<td></td>
<td>2.89</td>
<td>(79)</td>
<td></td>
<td></td>
<td>1.79</td>
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</tr>
<tr>
<td>Amp FeOOH (autocatal.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.51</td>
<td>(99)</td>
<td>2.076</td>
<td>(58)</td>
<td>1.60</td>
<td>(74)</td>
</tr>
<tr>
<td>Amp FeOOH in N$_2$ + MeOH</td>
<td>2.95</td>
<td>(58)</td>
<td></td>
<td></td>
<td>2.51</td>
<td>(99)</td>
<td>2.071</td>
<td>(51)</td>
<td>1.7</td>
<td>(43)</td>
</tr>
<tr>
<td>Amp FeOOH in N$_2$ + IPA</td>
<td>2.95</td>
<td>(100)</td>
<td></td>
<td></td>
<td>2.52</td>
<td>(57)</td>
<td>2.09</td>
<td>(55)</td>
<td>1.7</td>
<td>(55)</td>
</tr>
<tr>
<td>Amp FeOOH in N$_2$ + cyclohexane</td>
<td>2.53</td>
<td>(100)</td>
<td></td>
<td></td>
<td>2.51</td>
<td>(30)</td>
<td>2.1</td>
<td>(30)</td>
<td>1.7</td>
<td>(30)</td>
</tr>
<tr>
<td>Amp FeOOH in N$_2$ + IPA</td>
<td>2.513</td>
<td>(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reported values [408-413]
The end product of amorphous FeOOH decomposed in N₂/H₂O/air, N₂/MeOH, N₂/IPA, and dry N₂ at atmospheres is γ-Fe₂O₃. All the peaks here corresponds to γ-Fe₂O₃, while the decomposition in N₂/cyclohexane gives γ-Fe₂O₃ with traces of Fe₃O₄. Autocatalytic decomposition of hydrazinated amorphous FeOOH complex exclusively gives γ-Fe₂O₃.

α-FeOOH decomposed in N₂/MeOH, N₂/IPA, dry N₂, as well as autocatalytically decomposed hydrazinated α-FeOOH complex gives a mixture of α-Fe₂O₃ and γ-Fe₂O₃ as seen from their xrd data (Table 3.3).

**ii Infra red analysis**

Infrared bands at 558, 400, 395 and 370 cm⁻¹ observed in the thermal products γ-Fe₂O₃ of iron oxyhydroxides, hydrazinated iron oxyhydroxides and iron oxyhydroxides heated in different atmospheres such as N₂/MeOH, N₂/IPA N₂/Cyclohexane etc. are being compiled in Fig 3.4. These band positions agree well with the reported values for γ-Fe₂O₃ [280,333,350]. The thermal product α-Fe₂O₃ that formed from iron oxyhydroxides shows an ir band positions at 650, 525, 440, 390 and 382 cm⁻¹, are also shown in Fig.3.4 and these too agree closely with the reported bands for α-Fe₂O₃ [350,415]. These iron oxyhydroxides and hydrazinated iron oxyhydroxides which give a mixture of γ-Fe₂O₃ and α-Fe₂O₃ show ir bands (Fig 3.4) corresponding to both.

The iron oxyhydraxide and hydrazinated iron oxyhydroxides which gives γ-Fe₂O₃ or α-Fe₂O₃ or mixture of γ-Fe₂O₃ & α-Fe₂O₃ are clearly indicated in the Fig.3.4.
FIG. 3.4  Infra red spectra of the end products of iron oxyhydroxides decomposed in different atmospheres

Auto cat, N₂/MoOH, N₂/IPA, N₂/cyclohexane

\[ \begin{align*}
\text{γ-FeOOH} & : \gamma F_0, \gamma F_1, \gamma F_2, \gamma F_{12} \\
\text{α-FeOOH} & : N F_6, N F_4, N F_5, N F_{10} \\
\text{Amp. FeOOH} & : A M_5, A F_2, A F_3, A M_7
\end{align*} \]
These observations and also the phase identification done by XRD, allow us to confirm the formation of the oxides.

iii. Magnetic characterization

The saturation magnetization of the thermal products of iron oxyhydroxides in air and different controlled atmospheres and autocatalytic decomposition products of the hydrazinated iron oxyhydroxides were measured [417] by using a low field hysteresis loop tracer. In fig 3.5 the saturation magnetization value, $\sigma_s$, in emu/g, of the product is indicated at the end of the arrow, for each atmospheric decomposition.

A least value of 19.20 emu/g was observed for air decomposed product and a maximum of 71.65 emu/g for autocatalytically decomposed hydrazinated $\gamma$-FeOOH.0.3H$_2$O which is close to the expected and reported value for $\gamma$-Fe$_2$O$_3$ of 71-74 emu/g [416]. $\gamma$-Fe$_2$O$_3$ obtained in dry N$_2$ atmospheric decomposition of $\gamma$-FeOOH showed a $\sigma_s$ of 43.69 emu/g. The dry nitrogen containing a known partial pressure of methanol when provided during the thermal decomposition of $\gamma$-FeOOH, the product $\gamma$-Fe$_2$O$_3$ showed an improvement in the $\sigma_s$ value of 59.70 emu/g. The decomposition of the $\gamma$-FeOOH in N$_2$/IPA and N$_2$/cyclohexane did not improve further the $\sigma_s$ value and remained at 58.5 and 56.11 emu/g, respectively. The N$_2$/H$_2$O/air atmospheric decomposition of the $\gamma$-FeOOH lead to the end product of smaller $\sigma_s$ value of 26.6 emu/g.

The amorphous FeOOH.0.8H$_2$O in air decompose to $\alpha$-Fe$_2$O$_3$ with lowest $\sigma_s$ value of 2.46 emu/g. In dry N$_2$ the decomposition product is highly magnetic
FIG. 3.5 Saturation magnetization, $\sigma_s$, in emu/g of decomposed end products of iron oxyhydroxides and their hydrazinated complexes
with $\sigma s$ of 61.24 emu/g and found to be $\gamma$-Fe$_2$O$_3$. When the amorphous FeOOH was decomposed in N$_2$/Methanol, N$_2$/IPA and N$_2$/cyclohexane, the products obtained are mainly $\gamma$-Fe$_2$O$_3$ and the $\sigma s$ values are, respectively, 47.81, 30.34 and 41 emu/g. The hydrazine equilibrated sample of amorphous FeOOH on autocatalytic decomposition gave $\gamma$-Fe$_2$O$_3$ of $\sigma s$ value 60.14 emu/g. The least value of $\sigma s$ of 2.46 emu/g that observed in the air decomposed product of amorphous FeOOH improved to a value of 22.51 emu/g on decomposing it in N$_2$/H$_2$O/air, suggesting the influence of water in the decomposition.

In air and N$_2$/H$_2$O/air, the $\alpha$-FeOOH.0.2H$_2$O decomposed to give $\alpha$-Fe$_2$O$_3$ with a very small value of $\sigma s$ of ~ 2.45. In dry N$_2$, N$_2$/Methanol and N$_2$/IPA, the thermal products of $\alpha$-FeOOH show $\sigma s$ values ~ 12.18 emu/g. This higher values of $\sigma s$ is due to the presence of $\gamma$-Fe$_2$O$_3$ along with $\alpha$-Fe$_2$O$_3$ as the end product. Hydrazinated sample of $\alpha$-FeOOH, however, on autocatalytic decomposition yielded fairly good magnetic material with $\sigma s$ value of 16.03 emu/g. The xrd revealed the presence of mixture of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ in the product.

iv. Mössbauer spectroscopy

The iron oxides synthesized by the thermal decomposition of amorphous FeOOH under different controlled atmospheres at 300°C were investigated by us[418], using 57 Fe Mössbauer spectroscopy. The Mössbauer spectra were taken at 90 and 300 K using a constant acceleration spectrometer and a $^{57}$Co/Rh source. The isomer shifts are quoted with reference to $\alpha$-Fe. Typical Mössbauer spectra recorded at 27 and −183 °C are shown in Fig. 3.6a,b,c.
FIG. 3.6a) Mossbauer spectra of 1) amorphous FeOOH and 2) amorphous FeOOH decomposed autocatalytically
3.6 b) Mossbauer spectra of decomposed end products of amorphous FeOOH at 300°C in 1) dry N₂ + MeOH atmosphere and 2) dry N₂ + IPA atmosphere.
3.6 c) Mossbauer spectra of decomposed end products of amorphous FeOOH at 300°C in 1) N₂ + H₂O + air atmosphere and 2) dry N₂ atmosphere
Amorphous FeOOH decomposes in air to non-magnetic $\alpha$-Fe$_2$O$_3$. However, by heating this material under controlled atmosphere of N$_2$/H$_2$O/air at 300°C gives a mixture of magnetic and non-magnetic iron oxide. The room temperature Mössbauer spectrum of this oxide consists of a paramagnetic doublet ($\delta = 0.33 \pm 0.02$ mm/s; $\Delta = 0.69 \pm 0.02$ mm/s). No further magnetic ordering was observed at $-183$ °C. The relevant parameters are similar to those reported in the literature for superparamagnetic $\gamma$-Fe$_2$O$_3$.

A superparamagnetic doublet was also observed by Liaw et al [419] in their study of the products obtained from amorphous FeOOH, under the almost similar preparative conditions. They have attributed this to undecomposed FeOOH and consider it to be responsible for increasing activity in oxidative dehydrogenation of butene with steam. The fact that this end product is magnetic while the parent material is not, clearly indicates that the decomposition of the precursor has occurred. These results rule out the presence of any undecomposed FeOOH in our run. The increasing catalytic activity, as reported by Liaw and Coworkers probably arises from the in situ formation of active $\gamma$-Fe$_2$O$_3$.

The room temperature Mössbauer spectrum of autocatalytically decomposed hydrazinated amorphous FeOOH is characterized by asymmetrically broadened ($\Gamma = 0.83 \pm 0.02$ mm/s) lines, as well as, an intensity distribution, suggesting an uneven distribution of the particle sizes, and/or a poor crystallinity. As a result, the measured hyperfine field ($H_{av} = 31$ T, $H_{max} = 37$ T) are fairly low as compared to the values reported in the literature for $\gamma$-Fe$_2$O$_3$ [420]. No substantial
split was observed at $-183^\circ \text{C}$ apart from increasing average ($H_{av} = 41 \text{ T}$) and maximum ($H_{max} = 46 \text{ T}$) hyperfine fields.

The Mössbauer spectra recorded at $27^\circ \text{C}$, of the end product of decomposition of amorphous FeOOH at $300^\circ \text{C}$ in dry $\text{N}_2$, $\text{N}_2$/MeOH and $\text{N}_2$/IPA, are nearly symmetrical patterns, similar in appearance and typical for intermediate grain-sized (+60nm) species. $H_{av}$ falls in the range 41-43 T and $H_{max}$ in the range 45-47 T [418] and no substantial changes are observed at $-183^\circ \text{C}$ apart from increasing $H_{av}$ and $H_{max}$ to the range 45-47 T and 48-50 T respectively.

The distribution of hyperfine fields show a prevalent $\gamma$-$\text{Fe}_2\text{O}_3$ phase. The broadening of the line widths ($\Gamma = 0.57 \pm 0.02 \text{ mm/s}$) is ascribed to the overlapping of the hyperfine fields or a distribution of particle sizes. The slight difference observed in the parameters can be regarded as due to a gradual rearrangement in the Fe ions environment, or as a result of a mixture of structures (cubic and tetragonal) depending on the conditions of the preparation.

d) Decomposition of Fe(OH)$_3$ and hydrazinated Fe(OH)$_3$ of iron ore

The Fe(OH)$_3$ precipitated from acid extract of iron ore (section 3.2.1.a) on thermal decomposition yielded oxide and x-ray characterization revealed $\alpha$-$\text{Fe}_2\text{O}_3$ formation. The hydrazinated Fe(OH)$_3$, after equilibration in hydrazine hydrate, on exposure to air fumed to magnetic oxide. And the x-ray characterization indicated the presence of mainly $\gamma$-$\text{Fe}_2\text{O}_3$.

e) Mechanism of $\gamma$-$\text{Fe}_2\text{O}_3$ formation.
The results that have been discussed so far can be summed up as follows.

a) $\alpha$-FeOOH decomposes in air to $\alpha$-Fe$_2$O$_3$ but the hydrazine method yields a mixture of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$.

b) $\gamma$-FeOOH thermally and the hydrazinated $\gamma$-FeOOH autocatalytically decompose giving mainly $\gamma$-Fe$_2$O$_3$. Hydrazine method, however, gives better quality oxide of $\sigma$s 71.65 emu/g, while air decomposition product shows $\sigma$s of mere 19.20 emu/g.

c) Amorphous FeOOH dehydrates in air to $\alpha$-Fe$_2$O$_3$ but the hydrazine method produces $\gamma$-Fe$_2$O$_3$ of better quality.

d) Decomposition of these iron oxyhydroxides in different controlled atmospheres, however, gives some mixed results whose analyses require additional investigations to make any conclusion, as regarding the influence of water vapour in stabilizing the $\gamma$-Fe$_2$O$_3$. However, the different atmospheric decomposition of $\gamma$-FeOOH and amorphous FeOOH did indicate an improvement in the quality of $\gamma$-Fe$_2$O$_3$ that formed over that of simple air, as well as, N$_2$/H$_2$O/air atmospheres. The $\gamma$-Fe$_2$O$_3$ obtained in N$_2$/H$_2$O/air also found to show higher saturation magnetization value than that formed in ordinary air decomposition of $\gamma$-FeOOH and amorphous FeOOH.

Thus, the hydrazine method seems to be easily giving $\gamma$-Fe$_2$O$_3$ from iron hydroxides or oxyhydroxides.

$\gamma$-FeOOH consists of corrugated sheets of edge and corner shared octahedra of FeO$_4$X$_2$ (where X = OH). The layered structured $\gamma$-FeOOH with the hydrogen bonds in between the layers transform topotactically into $\gamma$-Fe$_2$O$_3$. Here,
the [100], [010] and [001] axes of \( \gamma \)-FeOOH become [001], [110] and [1\bar{1}0] of \( \gamma \)-Fe\(_2\)O\(_3\) [342].

The topotactic change consists of two parts, geometrical and chemical. The geometrical part classifies the way in which one lattice can be transformed into another, while retaining the original network of the structure. The chemical part, on the other hand, accounts for the possibility of replacing one kind of atom by another and also the increase or lowering the total number of atoms per unit of lattice. Thus, in general, topotactic changes involving the loss or gain of atoms will leave the main symmetry directions of the crystals unchanged. But, it also seems possible that an asymmetrical crystals may, by loss of its atoms, transform into a form of higher symmetry.

\( \gamma \)-FeOOH on hydrazination, however, found to turn black in colour and the product is magnetic in nature containing 41.0 % of FeO in it (Table 3.2) and the rest being Fe\(_2\)O\(_3\). A ferrous-ferric oxide is, thus, formed from \( \gamma \)-FeOOH in hydrazine atmosphere which on exposure to air fumed giving \( \gamma \)-Fe\(_2\)O\(_3\). Thus, a ferrous-ferric oxide of Fe\(_3\)O\(_4\) type is the intermediate phase in the hydrazine method of preparation of \( \gamma \)-Fe\(_2\)O\(_3\) from \( \gamma \)-FeOOH.

Amorphous FeOOH too turns black on hydrazine equilibration and fumes when exposed to air giving a dull brown \( \gamma \)-Fe\(_2\)O\(_3\). But the intermediate powder had 1.2 % FeO. Here, Fe\(_3\)O\(_4\) type of phase that formed might have transformed immediately into \( \gamma \)-Fe\(_2\)O\(_3\). \( \alpha \)-FeOOH, on the other hand, did not show any change in colour on hydrazination, but it too fumed when exposed to air forming a mixture of \( \alpha \)-Fe\(_2\)O\(_3\) and \( \gamma \)-Fe\(_2\)O\(_3\).
Electrical conductivity studies too indicate the possibility of formation of Fe₃O₄ type of phase during hydrazine equilibration of the iron oxyhydroxide and the subsequent decomposition of it to γ-Fe₂O₃ on exposure to air.

Hydrazine is a reducing agent and x-ray diffraction done on the product of hydrazine decomposition on Fe₂O₃ found [53] to convert it into magnetite, Fe₃O₄. Hydrazine sulphate decomposition in an alkaline medium on Fe₂O₃ also converted the oxide into magnetite and here the hydrazine sulphate first dissociates [421-422] into hydrazine,

\[(N₂H₄)_2 · H₂SO₄ = 2N₂H₅⁺ + SO₄²⁻ = 2N₂H₄ + 2H⁺ + SO₄²⁻\]

The reduction of Fe₂O₃ is then a coupled reaction, as given below,

\[N₂H₅⁺ = N₂ + 5H⁺ + 4e\]

\[3 Fe₂O₃ + 2H⁺ + 2e = 2 Fe₃O₄ + H₂O\]

Similarly a hydrous ferric oxide decomposes hydrazine sulphate and transforms the oxide into magnetite [423] as follows,

\[3 Fe₂O₃-x/2(OH)ₓ + 2H⁺ + 2e = 2 Fe₃O₄ + (1 + 3/2 x)H₂O\]

The ferrous-ferric intermediate that formed as intermediate in the decomposition of hydrazinated γ-FeOOH in the present studies finally transform into γ-Fe₂O₃. Thus, a Fe₃O₄ type of spinel is the intermediate product of hydrazination of γ-FeOOH and amorphous FeOOH which easily yields spinel γ-Fe₂O₃.

Thus, there are different mechanisms that occur in the transformation of γ-FeOOH and hydrazine modified γ-FeOOH into γ-Fe₂O₃. Simple topotactic thermal dehydration of γ-FeOOH directly yields γ-Fe₂O₃, while hydrazine method produces the oxide through on intermediate phase Fe₃O₄. However, the oxidation of
Fe$_3$O$_4$ is initiated just on exposure of the hydrazinated $\gamma$-FeOOH in air. Commercial preparation of $\gamma$-Fe$_2$O$_3$ from $\alpha$-FeOOH is a multistage process and every step requires a laborious control of atmosphere. In this regard, the hydrazine method of the synthesis of $\gamma$-Fe$_2$O$_3$ is simple and the quality of the oxide is also comparable with the oxide obtained by the cumbersome commercial process.

3.3.2 Conclusions

1. $\gamma$-FeOOH, $\alpha$-FeOOH and amorphous FeOOH synthesized by solution method from reported procedures are found to contain water of hydration in their structure and accordingly formulas, $\gamma$-FeOOH.0.3H$_2$O, $\alpha$-FeOOH. 0.2H$_2$O and amorphous FeOOH.0.8H$_2$O respectively, are fixed for these oxyhydroxides.

2. Both $\alpha$-FeOOH and amorphous FeOOH dehydrate in air to $\alpha$-Fe$_2$O$_3$ at 300$^\circ$C, while $\gamma$-FeOOH topotactically transforms mainly into $\gamma$-Fe$_2$O$_3$.

3. Hydrazine equilibrated $\gamma$-FeOOH and amorphous FeOOH found to uptake 10% hydrazine and autocatalytically decompose to $\gamma$-Fe$_2$O$_3$. On the other hand, $\alpha$-FeOOH take up just 1% hydrazine when equilibrated in a desiccator containing hydrazine hydrate, but on exposure to air it fumes and yields a mixture of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$.

4. The topotactic dehydration of $\gamma$-FeOOH directly yields $\gamma$-Fe$_2$O$_3$, while the hydrazine equilibrated $\gamma$-FeOOH autocatalytically decomposes and forms $\gamma$-Fe$_2$O$_3$ through an intermediate phase Fe$_3$O$_4$. 
5. The saturation magnetization value of the $\gamma$-Fe$_2$O$_3$ obtained by hydrazine method from $\gamma$-FeOOH is close to the reported value of $\sigma$, 71-74 emu/g. The simple dehydration of $\gamma$-FeOOH yields the oxide of $\sigma$ value of just 19.20 emu/g.

6. Commercial preparation of $\gamma$-Fe$_2$O$_3$ from $\alpha$-FeOOH is a multistep reaction requiring a rigid control of atmosphere in every step, while hydrazine method to prepare the oxide is simple and single step from $\gamma$-FeOOH. Commercial method too adopts the formation of $\gamma$-Fe$_2$O$_3$ via Fe$_3$O$_4$. An intermediate phase Fe$_3$O$_4$ is essential in the formation of better quality $\gamma$-Fe$_2$O$_3$.

7. Iron hydroxide, Fe(OH)$_3$ precipitated by NaOH from acid extract of iron ore decomposes to $\alpha$-Fe$_2$O$_3$ in air, while the hydrazinated Fe(OH)$_3$ yields mainly $\gamma$-Fe$_2$O$_3$ on autocatalytic decomposition in ordinary atmosphere.
Synthesis of $\gamma$-Fe$_2$O$_3$ from iron (II) carboxylato-hydrazinates
Synthesis of $\gamma$-Fe$_2$O$_3$ from iron (II) carboxylato-hydrazinates

Metal carboxylates are widely studied precursors in the synthesis of metal oxides. Mixed metal carboxylates by controlling methods of synthesis are further giving scope for preparing, by simple thermal decomposition, a wide variety mixed metal oxides of different crystal structure such as, spinels of different magnetic properties and, perovskites with diversent properties like dielectric, semi conducting, magnetic and super conducting of technological importance. Simple iron oxalate, ferrous oxalate dihydrate, FeC$_2$O$_4$.2H$_2$O, has been investigated by many researchers and the results of this is taken as model in understanding the preparation, characterization and thermal decomposition of other iron carboxylates : Mono or dicarboxylates or higher carboxylates.
However, in our present investigations we are aiming at an easy synthesis of \( \gamma \)-Fe\(_2\)O\(_3\). We have selected iron carboxylates which have been systematically synthesized by research group in our laboratory and others. During the very first attempt to prepare \( \gamma \)-Fe\(_2\)O\(_3\) from, ferrous oxalate dihydrate, by Rane et al [264], they considered the various aspects in controlling the preparation of this oxide. Especially, a controlled atmosphere of water vapour transforms the FeC\(_2\)O\(_4\).2H\(_2\)O to mainly \( \gamma \)-Fe\(_2\)O\(_3\), while simple air decomposition yields the thermodynamically more stable iron oxide, \( \alpha \)-Fe\(_2\)O\(_3\). The control of water vapour during decomposition of other iron (II) carboxylates [272 - 277] such as, ferrous fumarate, ferrous succinate, ferrous malonate, ferrous tartrate, ferrous maleate and ferrous malate, also yielded \( \gamma \)-Fe\(_2\)O\(_3\), on the other hand, air decomposition of all carboxylates ended into \( \alpha \)-Fe\(_2\)O\(_3\).

But, then, a simple modification of FeC\(_2\)O\(_4\).2H\(_2\)O in our laboratory by Moye, Rane & Kamat Dalai [278] on hydrazination yielded FeC\(_2\)O\(_4\).N\(_2\)H\(_4\) and FeC\(_2\)O\(_4\).2N\(_2\)H\(_4\) and their decomposition in ordinary atmosphere easily produced \( \gamma \)-Fe\(_2\)O\(_3\). Such hydrazine methods of synthesis of metal oxides and mixed metal oxides of technological importance [424,-430] are attracting attention of many researchers. As we were looking for a simple method to synthesize \( \gamma \)-Fe\(_2\)O\(_3\) useful in ferrites synthesis, the hydrazine method seems to be a way out. Already we have used such method in easy synthesis of \( \gamma \)-Fe\(_2\)O\(_3\) from iron hydroxides from iron ore rejects and iron oxyhydroxides again obtained from iron hydroxides from iron ore rejects in part I of this chapter.
To explore the importance of $\gamma$-$\text{Fe}_2\text{O}_3$ in ferrites synthesis it is better to consider different sources for $\gamma$-$\text{Fe}_2\text{O}_3$ and hence, we decided to prepare $\gamma$-$\text{Fe}_2\text{O}_3$ from iron (II) carboxylates, by hydrazine method. In this chapter we are presenting our results on the synthesis, characterization and decomposition of iron (II) carboxylato-hydrazinates: ferrous fumarato-hydrazinates, ferrous succinato-hydrazinates, ferrous malonato-hydrazinates, ferrous tartrato-hydrazinates, ferrous maleato-hydrazinates and ferrous malato-hydrazinates. No such hydrazinate complexes of the iron (II) carboxylates are observed in the literature.

3.4 Experimental : Preparation, characterization and decomposition

3.4.1 Synthesis of Iron (II) Carboxylato-hydrazinates

Both solution and equilibration methods similar to the one used for ferrous oxalato-hydrazinates [268] have been adopted to synthesize iron (II) carboxylato-hydrazinates.

Ferrous fumarato-hydrazinates, ferrous succinato-hydrazinates, ferrous malonato-hydrazinates, ferrous maleato-hydrazinates and ferrous malato-hydrazinates were all prepared by taking the required quantities of the sodium salts of their respective carboxylic acids in hydrazine hydrate, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (99 - 100 %). The mixture were stirred well in an inert atmosphere for 2-3 hours. To the well stirred solution a freshly prepared ferrous chloride solution, obtained from pure iron (99.99%), was added slowly and the stirring was continued further for an hour.
Caution: Hydrazine and hydrazine derivatives are carcinogens. Handle them carefully.

a) Solution method

i. Ferrous fumarate - hydrazinate (FFH)

0.5 M Sodium fumarate was mixed with hydrazine hydrate (99-100%) in the molar ratio of 1:4 and stirred on a magnetic stirrer for one and half hour in the presence of nitrogen atmosphere, bubbling at the rate of 10-15 bubbles/min. The use of N₂ atmosphere was to avoid the atmospheric CO₂ from reacting with hydrazine and forming carbazic acid [279] as per the equation,

\[ N₂H₄ + CO₂ \rightarrow H₂NNHCOOH \]  

To this solution of sodium fumarate and hydrazine hydrate, a freshly prepared 0.5 M FeCl₂ solution was slowly added with vigorous stirring, in presence of N₂ atmosphere. Yellow coloured ferrous fumarate - hydrazinate slowly starts precipitating. The precipitate was then extracted with alcohol and carefully filtered on the suction pump and dried with ether.

It has been reported [170] that if a strong suction is applied for longer duration, precursors may catch fire. During the stirring of sodium fumarate and hydrazine hydrate, some fumes of hydrazine were present in the upper part of the container and on addition of FeCl₂ solution, it reacted directly with hydrazine fumes forming a dark blue coloured complex. This complex gets mixed with the yellow precipitate of FFH, thus, contaminating it. In order to avoid this contamination, N₂ gas was bubbled at a faster rate before chloride solution was added.
ii. Ferrous succinato - hydrazinate (FSII)

An aqueous solution of sodium succinate and hydrazine hydrate in the molar ratio of 1:4 was stirred for $1\frac{1}{2}$ h. in N$_2$ atmosphere at room temperature and then a freshly prepared ferrous chloride solution was run down into the mixture and continued stirring in N$_2$ atmosphere for half an hour more. Pale yellow coloured precipitate obtained was filtered, washed with alcohol and dried with ether.

iii. Ferrous malonato - hydrazinate (FMII)

0.5 M Malonic acid was stirred with hydrazine hydrate in the molar ratio of 1:4, in N$_2$ atmosphere. Freshly prepared ferrous chloride solution was then added slowly to the mixture with constant stirring. The pale yellow coloured precipitate was extracted in alcohol, filtered, washed with alcohol and dried with ether.

iv. Ferrous maleato - hydrazinate (FMIII)

Sodium maleate (0.5M) and hydrazine hydrate in the molar ratio of 1:4, were stirred for $1\frac{1}{2}$ h. in N$_2$ atmosphere. To this, a freshly prepared 0.5M ferrous chloride solution was added, drop by drop, with constant stirring in N$_2$ atmosphere. The yellow coloured precipitate obtained was filtered, washed with alcohol and dried with ether.

v. Ferrous malato - hydrazinate (FLII)

Sodium malate solution was mixed with hydrazine hydrate in the molar ratio of 1:4 and stirred for $1\frac{1}{2}$ h in an inert atmosphere of N$_2$. Freshly prepared solution of ferrous chloride was then run down into the mixture. The stirring was continued
in N₂ atmosphere for half an hour more. The yellow coloured precipitate formed, was extracted with alcohol, filtered and dried with ether.

b) Equilibration method

i. Ferrous tartrato - hydrazinate (FTH)

Ferrous tartrato - hydrazinate was prepared by hydrazine equilibration method. First ferrous tartrate one and half hydrate was prepared by adding sodium tartrate to an aqueous ferrous ammonium sulphate in an inert atmosphere, with constant stirring. Pale greenish yellow precipitate that formed was filtered, washed with little warm water and then dried.

The dry hydrated ferrous tartrate was then placed in a petridish and kept in a desiccator containing hydrazine hydrate (99-100%). Hydrazine hydrate vapours got equilibrated on the ferrous tartrate thus forming ferrous tartrato - hydrazinate complex.

All these iron carboxylato - hydrazinate complexes were filled in the air tight sample tubes and stored in a vacuum desiccator.

3.4.2 Characterization.

a) Chemical analysis

I. Hydrazine estimation

Hydrazine content of all the complexes was analyzed titrimetrically using KIO₃ as titrant [299].

ii. C, H, N analysis
The percentages of carbon and hydrogen was estimated by a standard technique.

iii. Analysis of iron content

The percentage of iron was determined by the standard potassium dichromate method [299].

b) Infra red analysis

The infra red spectra of all the complexes and their thermal products were taken soon after the preparation of the sample on Shimadzu FTIR, model 8101 A.

c) Density measurement

The density of the complexes and their final thermal products was determined at room temperature using carbon tetrachloride as the medium.

3.4.3 Thermal decomposition studies

a) Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA)

Simultaneous TG and DTA in air was carried out on STA 1500 instrument from RT to 600°C of all the complexes. The heating rate of 10 -15°C/min. was maintained.

b) Isothermal weight loss studies

Isothermal weight loss studies were carried out at various predetermined temperatures, based on TGA and DTA traces, by using a platinum crucible. The
isothermal products obtained at different interval of temperature were chemically analysed for the hydrazine content.

c) **Autocatalytic decomposition**

All these iron (II) carboxylato-hydrazinates decompose autocatalytically. Here, the dry samples were spread over a petridish and a burning splinter was brought near to it when the small portion of it caught fire. A red glow that formed immediately spreads over the entire bulk, completing the decomposition in an ordinary atmosphere.

3.4.4 Phase identification and magnetic studies of the thermal products

a) **X-ray analysis**

X-ray powder diffraction (XRD) studies were carried on Rigaku D MAX II, X-ray diffractometer, using Cu and Fe targets on all the iron (II) carboxylato-hydrazinate complexes. Autocatalytically decomposed products of the complexes were also studied by XRD and the phase identification was done by comparing the observed d-values with the JCPDS files [408-413].

b) **Magnetic Characterization**

Saturation magnetization values of the autocatalytically decomposed end products of the complexes were measured on a high field hysteresis loop tracer that described by Likhite et al [304], using Ni as the standard substance.
3.4.5 Microstructure analysis

Microstructure of the autocatalytically decomposed end product of the complexes were studied using scanning electron microscope (SEM). SEM micrographs were taken using a well polished pellet surface and were used to compute average grain size.

3.5 Results and Discussion

a) Fixation of chemical formulas of iron (II) carboxylato-hydrazinates

All the precursors were characterised by chemical analysis, IR analysis and density measurements. The characterisation was supported by thermal studies and the formula for each complex was identified.

i. Infra red analysis

The IR spectra of FeII, FeIII, FeII and FeIII are given in fig 3.7 a &b, while that of FMH and FTH are given in fig. 3.7 c. The asymmetric and symmetric stretching frequencies of carboxylate ions [Table 3.4] in all the complexes are seen in the range of 1610-1624 cm\(^{-1}\) and 1377-1410 cm\(^{-1}\), respectively, with \(\Delta v (v_{asy} - v_{sym})\) separation of ~ 210-240 cm\(^{-1}\), indicating the monodentate linkage of both carboxylate groups in the dianions [384-387]. Thus the fumarate, succinate, malonate, tartrate, maleate and malate dianions in these complexes coordinate to the metal as bidentate ligand via both the carboxylate groups.

The observed N-N stretching frequencies in the range of 960-980 cm\(^{-1}\) for all these complexes except ferrous tartrato-hydrazinate (FTH) reveal clearly that the
FIG. 3.7 a) Infra red spectra of 1) FFH and 2) FSH
FIG. 3.7 b) Infra red spectra of 1) FEII and 2) FLI
FIG. 3.7 c) Infra red spectra of 1) FMH and 2) FTH
hydrazine moieties are present as bridging bidentate ligands [278,384-386]. A monodentate link of hydrazine with iron is seen \( v(\text{N-N}) \sim 930 \text{ cm}^{-1} \) for FFH. Ferrous malonato-hydrazinate (FMH), however, has both monodentate and bidentate linkage of hydrazine with the metal [Table 3.4]. These results suggest that the carboxylato-hydrazinate complexes of iron(II) carboxylato-hydrazinate complexes of iron(II) are formed.

ii. Chemical analysis

The percentages of hydrazine, iron, carbon and hydrogen of all the iron (II) carboxylato-hydrazinates are given in Table 3.4

The ferrous fumarato-hydrazinate was found to contain 27.16% hydrazine, 24.0% iron, 19.30% carbon and 3.96% Hydrogen, while in ferrous succinato-hydrazinate the percentages of \( \text{N}_2\text{H}_4, \text{Fe}, \text{C} \) and \( \text{H} \) are 27.52, 23.87, 20.3 and 3.67, respectively. The percentage of \( \text{N}_2\text{H}_4, \text{Fe}, \text{C} \) and \( \text{H} \) was found to be 20.43, 24.25, 17.90 and 3.73, respectively, in ferrous malonato-hydrazinate. The observed percentages of hydrazine, iron, carbon and Hydrogen in ferrous tartrato-hydrazinate are 12.41, 25.5, 17.22 and 3.53, respectively. Ferrous maleato-hydrazinate and ferrous malato-hydrazinate was found to contain 26.74 and 25.12 percent of \( \text{N}_2\text{H}_4 \) and 24.67 and 22.80 percent of Fe, respectively.

iii. Total weight loss

The observed total weight loss for FFH, FSII, FMII, FFII, FEII and FLH are 65.86, 65.94, 64.30, 68.54, 65.85 and 65.5 percent, respectively (Table 3.4). Thus, from the data of observed on the total weight loss and chemical analyses (section 3.8.1), the following chemical formula are fixed for the iron (II) carboxylato-hydrazinate complexes of iron(II) carboxylato-hydrazinate complexes of iron(II) are formed.
<table>
<thead>
<tr>
<th>Hydrazinates</th>
<th>Chemical analysis in %</th>
<th>Density</th>
<th>Infrared data, cm⁻¹</th>
<th>Total Weight Loss, %</th>
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</thead>
<tbody>
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<td>Obsd.</td>
<td>Calcd.</td>
<td>g cm⁻³</td>
<td>δ(o-c-o)</td>
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<td>2N₂H₄ (FFH)</td>
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<td>23.88</td>
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<td>C</td>
<td>19.30</td>
<td>20.52</td>
<td></td>
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<td></td>
<td>H</td>
<td>3.96</td>
<td>4.27</td>
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<tr>
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<td>27.11</td>
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<td>23.87</td>
<td>23.68</td>
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<td>Fe</td>
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<td>24.95</td>
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<td>H</td>
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<td>4.46</td>
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<tr>
<td>FeC₄H₂O₅</td>
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</tr>
</tbody>
</table>
lato-hydrazinates.

(1) **Ferrous fumarato-hydrazinate (FFH) - FeC₄H₂O₄.2N₂H₄**

A chemical formula, FeC₄H₂O₄.2N₂H₄, is fixed for ferrous-fumarato-hydrazinate. The hydrazine content experimentally observed (Table 3.4) is 27.16% and the calculated value, based on the above formula, is 27.35%. The experimental iron, carbon and hydrogen percentages too match closely with the calculated ones, 24.00 (23.88), 19.30 (20.52) and 3.96 (4.27), respectively. The values in bracket are the calculated ones and, hereafter, the calculated values will be given in the bracket, soon after the experimentally observed values, for ready reference. The total mass loss of 65.86% observed is close to the calculated value of 65.81%, based on the above formula fixed for ferrous fumarato-hydrazinate (FFH).

(2) **Ferrous succinato-hydrazinate (FSH)-FeC₄H₄O₄.2N₂H₄**

A formula of FeC₄H₄O₄.2N₂H₄ for ferrous succinato-hydrazinate is arrived at from the percentage values of hydrazine, 27.52 (27.11), carbon 20.30 (20.35); hydrogen 3.67 (5.0), total mass loss, 65.94 (64.10).

(3) **Ferrous malonato-hydrazinate (FMH) - FeC₃H₂O₄.1 1/2N₂H₄.H₂O**

A chemical formula of FeC₃H₂O₄.1 1/2N₂H₄.H₂O is assigned to ferrous malonato-hydrazinate, based on the different constituents, observed and calculated: hydrazine, 20.43 (21.46); iron, 24.25 (24.95); carbon, 17.90 (16.08); hydrogen, 3.73 (4.46) and total mass loss of 64.30 (64.35).

4. **Ferrous tartrato-hydrazinate (FTII) - FeC₄H₄O₆. N₂H₄.H₂O**
A chemical formula of $\text{FeC}_4\text{H}_4\text{O}_6\cdot \text{N}_2\text{H}_4\cdot \text{H}_2\text{O}$ is fixed for ferrous tartrato-hydrazinate. The observed and calculated percentages of the different constituents show a close values: hydrazine, 12.41 (12.61); iron, 25.5 (25.17); carbon, 17.22 (18.90); hydrogen, 3.53 (3.94). The total mass loss of 68.54% is also close to the calculated value of 68.56% suggesting that the formula is correct.

5. Ferrous maleato-hydrazinate (FEH) - $\text{FeC}_4\text{H}_2\text{O}_4\cdot 2\text{N}_2\text{H}_4$

The observed contents of $\text{N}_2\text{H}_4$ - 26.74%, Fe - 24.67% and a total mass loss of 65.85%, match well with the calculated values of 27.88% for $\text{N}_2\text{H}_4$, 23.88% for Fe and total weight loss 65.85%, using the formula for ferrous maleato-hydrazinate as $\text{FeC}_4\text{H}_2\text{O}_4\cdot 2\text{N}_2\text{H}_4$.

6. Ferrous malato-hydrazinate (FLH) - $\text{FeC}_4\text{H}_4\text{O}_5\cdot 2\text{N}_2\text{H}_4$

From the observed contents of $\text{N}_2\text{H}_4$ - 25.12%, Fe - 22.80% and a total mass loss of 68. a formula $\text{FeC}_4\text{H}_4\text{O}_5\cdot 2\text{N}_2\text{H}_4$ is assigned to ferrous malato-hydrazinate. The calculated values for these constituents compare well (Table 3.4) with the observed ones, indicating the correctness of the formula fixed by us.

Among all these complexes the FMH and FLH show a water of crystallization in them.

iv. Pycnometric Density

The densities of all the complexes are given in the table 3.4. The densities of FFH, FSH, FMH, FTH, FEH and FLH are 1.38, 1.18, 1.51, 1.22, 1.9 and 1.86, respectively.
b) Formation of $\gamma$-Fe$_2$O$_3$ from iron (II) carboxylato-hydrazinates

i. Thermal analysis and hydrazine estimation of thermal products

All iron (II) carboxylato-hydrazinates decompose in air, thermally and auto-catalytically, to iron oxide of magnetic in nature. XRD patterns of these products match well with the pattern of the standard commercial $\gamma$-Fe$_2$O$_3$ and $d_{hkl}$ values of these compare closely with the values of JCPDS files [410 - 411] for $\gamma$-Fe$_2$O$_3$.

All iron (II) carboxylato-hydrazinates lose weight continuously in air when heated from room temperature (RT) to $700^\circ$C, showing no definite steps on the TG trace. DTA, however, indicates a few intense exothermic peaks in this temperature range, thereby, suggesting a step wise thermal decomposition. (Fig 3.8) In order to correspond these DTA peaks with the TG values, a rough weight loss steps were marked in certain temperature ranges and the results are compiled in Table 3.5. An electrothermal analysis (ETA) done on FFH, FSH, FMH and FTH too gave us [300,303] some information on the step wise thermal decomposition of these complexes. To investigate thoroughly the thermal path, isothermal weight loss measurements at different predetermined temperatures were carried out and hydrazine contents were also estimated on these thermal products. The results of such studies are tabulated in Table 3.5.

**FFH, FSH, FEH and FLH**

Ferrous fumarato-hydrazinates (FFH), FeC_4H_4O_4.2N_2H_4, on heating in air $\sim 300^\circ$C loses 65.86% of its weight yielding iron oxide, $\gamma$-Fe$_2$O$_3$. DTA shows exothermic peaks around $178^\circ$, $217^\circ$ and $293^\circ$C followed by a small exothermic hump $\sim 353^\circ$C.
FIG. 3.8 a) TG/DTA traces of 1) FFH and 2) FSH
FIG. 3.8 b) TG/DTA traces of 1) FMH and 2) FTH
FIG. 3.8 c) TG/DTA traces of 1) FEH and 2) FLH
TABLE 3.5 Isothermal weight loss. DTA/TG analysis of iron (ii) carboxylato-hydrazinates

<table>
<thead>
<tr>
<th>Hydrazinates</th>
<th>TG wt. loss/DTA peaks</th>
<th>Isothermal / Chemical analysis</th>
<th>Remarks</th>
<th>Saturation magnetization emu g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature range, °C</td>
<td>Wt. loss in %</td>
<td>Exo/Endo peaks</td>
<td>Temp °C</td>
</tr>
<tr>
<td>Ferrous</td>
<td>RT-182</td>
<td>23.63</td>
<td>178 exo</td>
<td>RT</td>
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<tr>
<td>Fumarato-hydrazinate (FFH)</td>
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<td>178 exo</td>
<td>70</td>
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<td>FeC₄H₂O₄.2N₂H₄</td>
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<td>23.63</td>
<td>217 exo</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>222-308</td>
<td>23.63</td>
<td>310 exo</td>
<td>110</td>
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<td></td>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>Succinato-hydrazinate (FSH)</td>
<td>RT-194</td>
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<td>RT</td>
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<tr>
<td>FeC₄H₄O₄.2N₂H₄</td>
<td>194-240</td>
<td>0.3</td>
<td>226 exo</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>240-312</td>
<td>0.3</td>
<td>242 exo</td>
<td>90</td>
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<td></td>
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TABLE 3.5 (Continued)

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<th>Saturation magnetization emu g⁻¹</th>
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<td>Wt. loss in %</td>
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<td>Temp °C</td>
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<td>(FMH)</td>
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<td></td>
<td>216-246</td>
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<td>Remarks</td>
<td>Saturation magnetization emu g⁻¹</td>
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Ferrous succinato-hydrazinate (FSH), FeC₄H₄O₄.2N₂H₄, decomposes to γ-Fe₂O₃ ~ 300⁰C losing 65.94% of its weight. DTA indicates exothermic peaks around 161⁰, 226⁰ and 242⁰C followed by an exothermic hump ~ 312⁰C.

Ferrous maleato-hydrazinate (FEH), FeC₄H₂O₄.2N₂H₄ decomposes to γ-Fe₂O₃ by losing 65.85% of its weight. Exothermic peaks around 175⁰, 272⁰, 297⁰, 331⁰C are followed by an exothermic hump ~ 341⁰C.

Ferrous malato-hydrazinate (FLH), FeC₄H₄O₅.2N₂H₄, yields γ-Fe₂O₃ by losing 68.5% of its weight ~ 300⁰C. An exothermic hump ~ 324⁰C is preceded by several exothermic peaks : 154⁰, 184⁰, 264⁰, 285⁰, and 289⁰C.

Hydrazine content estimation done on the thermal products of all these iron (II) carboxylato-hydrazinates indicated that the hydrazine present in them is found to be released ~ 110⁰ in FFH, ~ 90⁰ in FSH, ~ 156⁰ in FEH, and ~ 150⁰C in FLH (Table 3.5). The total weight loss of all these unhydrazinated products then completed ~ 300⁰C, yielding poorly magnetic Fe₂O₃. Only FLH showed an exothermic peak ~ 154⁰C corresponding to the removal of hydrazine around this temperature. The other three, however, indicated the first exothermic reaction well above the dehydrazination temperatures. And, all these complexes undergo multistep exothermic reactions to give mainly γ-Fe₂O₃. The intense exothermic process ~ 300⁰C is then followed by an exothermic hump in all complexes. This event is considered here due to the crystallization of the oxide that formed in all these complexes, after the intense exotherm, ~ 300⁰C.

FMII and FTII
Ferrous malonato-hydrazinate (FMH), FeC₃H₂O₄ 1 1/2N₂H₄.H₂O, loses 64.30% of its weight to give mainly γ-Fe₂O₃. DTA trace shows one intense exothermic peak ~ 242°C followed by an exothermic hump ~ 298°C.

Ferrous tartrato-hydrazinate (FTH), FeC₄H₄O₆.N₂H₄.H₂O, yields magnetic iron oxide by losing 68.54% of its mass. DTA here too indicates one intense exothermic peak ~ 329°C which is then followed by an exothermic hump.

The exothermic hump following the intense exothermic peak is due to the crystallization of the gamma ferric oxide that formed at the end of the intense exothermic reaction.

The hydrazine content estimation done on the thermal products of these complexes, however, shows some different behavior than that observed in FFH, FSH, FEH and FLH.

On heating FMH to 50°C, the hydrazine content of 20.43% that present in it goes down to 16.42%, but the weight loss observed at this temperature, however, is 7.85% (Table 3.5). At 70°C the product obtained retains the hydrazine percentage to 16.18, while the total mass amounts to 9.5%. Further heating to 95°C indicates weight loss of 12.25% and the hydrazine content in it now shows an increase to 17.38%. The thermal product at 170°C still shows 5.68% hydrazine in it and the total hydrazine loss and a almost total mass loss are found to occur ~ 180°C. DTA shows one intense peak ~ 242°C yielding mainly γ-Fe₂O₃. Thus, these results indicate that the dehydrazination begins above 110°C and the weight loss observed below this temperature, hence, is due to the dehydration.
Similar observations were also made on the FTH (Table 3.5). Here, too the dehydration precedes the dehydrazination which is then followed by oxidative decomposition yielding mainly $\gamma$-Fe$_2$O$_3$.

The FMH and FTH are carboxylato-hydrazinate complexes of iron with water of crystallization, thus, undergo dehydration before dehydrazination, which is then followed by oxidative decomposition. The other complexes, FFH, FSH, FEH and FLH, on the other hand, have no water of hydration in them. Here dehydrazination is then immediately followed by oxidative decomposition. A single intense exothermic peak observed in FMH and FTH suggests that the total decomposition is reactive process, while the multistep reactions in the other four complexes indicate the decomposition process is less reactive. A bis-hydrazine malonate, succinate, and maleate and fumarate complexes of metals, Co, Ni and Zn [384-386] are also found to show single and multistep decomposition reactions, suggesting reactive and less reactive processes yielding the respective metal oxides as an end products.

ii. X-ray characterization

The XRD patterns of the autocatalytically decomposed end product of the iron (II) carboxylato-hydrazinates are shown in Fig. 3.9. The end products are found to be magnetic in nature. XRD patterns of these end products match with the pattern of the standard commercial $\gamma$-Fe$_2$O$_3$ and $d_{hkl}$ values of these compare well with the values of JCPDS files [410-411] for $\gamma$-Fe$_2$O$_3$. An extra peak at $d = 2.7$ is found in these XRD spectra which corresponds to the strongest line of $\alpha$-Fe$_2$O$_3$. 

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FIG. 3.9  XRD patterns of the autocatalytically decomposed end products of Iron(II) carboxylato-hydrazinates
The traces of α-Fe₂O₃ that are found are due to the intense heating taking place during the autocatalytic decomposition converting few particles of γ-Fe₂O₃ to α-Fe₂O₃.

iii. Infra red analysis

The IR spectra of autocatalytically decomposed end products of the iron (II) carboxylato-hydrazinates (Fig 3.7.d) reveal that the end products of all the complexes are mainly, γ-Fe₂O₃ with some admixture of α-Fe₂O₃. The band position observed for γ-Fe₂O₃ are 558, 463, 450 and that observed for α-Fe₂O₃ are 542, 440, 382 which match well with the reported values [280, 333, 350, 415] and these values are close to those γ-Fe₂O₃ synthesized from iron oxy hydroxides as described in part I of this chapter.

c) Magnetic characterization and microstructure analysis.

A saturation magnetization value, Mr, in the range of 18 to 43 emu/g, (Table 3.5) is observed for γ-Fe₂O₃ obtained from autocatalytically decomposed products of all these iron (II) carboxylato-hydrazinates. A standard commercial sample of γ-Fe₂O₃ with a Js value of 71 emu/g suggests that the values obtained for the oxide, synthesized in the present investigations, are not close to the reported values [416] of 71-74 emu/g. However, the values in the range of 35-60 emu/g are also observed in the literature [431] for γ-Fe₂O₃. One explanation for such low values in our gamma ferric oxide samples may be due to some admixture of α-Fe₂O₃. XRD and IR data reveals such admixture in our samples. This may be due to the fact that the hydrazinated complexes decompose almost explosively to gamma ferric oxide.
FIG. 3.7 d) Infra red spectra of the end products of iron(II) carboxylato-hydrazinates
And, the local temperature reaches to such a high temperature that the formed oxide transforms partially into a thermodynamically more stable $\alpha$-$\text{Fe}_2\text{O}_3$.

Another reason for the low saturation magnetization value is the small particle size and large surface area. The SEM micrographs reveals that the average particle size of the autocatalytically decomposed end products of iron (II) carboxylato-hydrazinate ranges from 0.1-0.3 $\mu$m. The particles of the oxide end products are spherical in shape. All the SEM micrographs (Fig. 3.10) show the aggregation of the particles at some places, which is due to the excessive burning of some of the particles during decomposition of the complexes, which results in agglomeration.

**3.6 CONCLUSIONS**

1. Iron (II) carboxylato-hydrazinates: Ferrous fumarato-hydrazinate, $\text{FeC}_4\text{H}_2\text{O}_4\cdot2\text{N}_2\text{H}_6$; ferrous succinato-hydrazinate, $\text{FeC}_4\text{H}_4\text{O}_4\cdot2\text{N}_2\text{H}_6$; ferrous malonato-hydrazinate, $\text{FeC}_3\text{H}_2\text{O}_4\cdot1\text{/2N}_2\text{H}_4\cdot\text{H}_2\text{O}$; ferrous tartrato-hydrazinate, $\text{FeC}_4\text{H}_4\text{O}_6\cdot2\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$; ferrous maleato-hydrazinate, $\text{FeC}_4\text{H}_4\text{O}_5\cdot2\text{N}_2\text{H}_4$ and ferrous malato-hydrazinate, $\text{FeC}_4\text{H}_4\text{O}_5\cdot2\text{N}_2\text{H}_4$, are being synthesized easily from the respective sodium salts of carboxylic acids, ferrous chloride and hydrazine hydrate in an inert atmosphere.

2. All iron (II) carboxylato-hydrazinates decompose autocatalytically in an ordinary atmosphere yielding mainly $\gamma$-$\text{Fe}_2\text{O}_3$.

3. The easy synthesis of $\gamma$-$\text{Fe}_2\text{O}_3$ from iron (II) carboxylato-hydrazinates, thus, avoids a cumbersome control of water vapor partial pressure that required in arresting the thermal decomposition path of iron (II) carboxylates at $\gamma$-$\text{Fe}_2\text{O}_3$ step.
FIG. 3.10 SEM micrographs of the autocatalytically decomposed end products of iron (II) carboxylato-hydrazinates