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SYNTHESIS OF γ-Fe_2O_3 BY THERMAL DECOMPOSITION OF FERROUS GLUCONATE DIHYDRATE*

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Abstract

Ferrous gluconate dihydrate ($FeC_{12}H_{22}O_{14}\cdot 2H_2O$), was prepared and its thermal decomposition was studied by means of simultaneous thermal analysis, supplemented with a two probe d.c. electrical conductivity measurements under the atmospheres of static air, dynamic air and dynamic nitrogen. Under all the atmospheres final product was found to be α-Fe_2O_3 with FeO, γ-Fe_2O_3, Fe_3O_4 etc. as probable intermediates. γ-Fe_2O_3 was formed under the atmosphere of dynamic air containing water vapour. γ-Fe_2O_3 thus synthesised was characterised for its structure, morphology, thermal and magnetic behaviour.

Keywords: electrical conductivity, γ-Fe_2O_3, magnetic properties, structure, synthesis, thermal analysis

Introduction

Commercially, γ-Fe_2O_3 is prepared by dehydration of synthetic geothite (α-FeO(OH)) to α-Fe_2O_3, its reduction to Fe_3O_4 and finally reoxidation to γ-Fe_2O_3 [1–4].

γ-Fe_2O_3 particles of nanosized dimensions improves many of the required parameters for its effective use as a recording material [3–10]. The study on synthesis of γ-Fe_2O_3 for recording and memory devices is continuously attaining greater significance [1, 3–5]. New synthetic routes for the synthesis of γ-Fe_2O_3 are being continuously investigated, some of them include: the ion exchange reaction of $NaFeO_2$ with benzoic acid [11], thermal decomposition of lepidocracite [12], employing sol-gel techniques [9], decompositions of microemulsions [13], and thermal decompositions of metal carboxylates under controlled conditions [14–15]. The present investigation is a continuation of our ongoing programme on study of the new routes and also em-

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* This paper is dedicated to late Prof. A. J. Mukhedkar.

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ploying new precursors in the synthesis of ultrafine γ-Fe_2O_3 particles and having optimum properties.

In our earlier work [14–18], we have used d.c. electrical conductivity technique as a supplementary tool to thermal analysis in the study of the thermal decomposition reactions for the formation of γ-Fe_2O_3. In the present study we investigate the thermal decomposition of ferrous gluconate dihydrate ($FeC_{12}H_{22}O_{14}\cdot 2H_2O$), by conventional thermal analysis (TG/DTA/DTG) supplemented with electrical conductivity measurements, under different atmospheres.

Experimental

Preparation of $FeC_{12}H_{22}O_{14}\cdot 2H_2O$

Ferrous gluconate dihydrate was prepared by dissolving equal volumes of equimolal solutions of ferrous sulphate and barium gluconate at 60°C, in a flow of dry nitrogen under vigorous stirring. The yellowish grey precipitate of ferrous gluconate dihydrate ($FeC_{12}H_{22}O_{14}\cdot 2H_2O$), thus obtained was washed thoroughly with double distilled water and dried under vacuum. The elemental analysis of the gluconate gave, C: 28.64(29.88), H: 4.97(4.56), Fe: 12.32(11.65), the values in the parenthesis are the calculated values and satisfy the formulae $FeC_{12}H_{22}O_{14}\cdot 2H_2O$.

Thermal analysis

The thermal analysis traces were obtained with Netzsch instrument under the atmosphere of static air, dynamic dry nitrogen, and dynamic dry air (100 mL min^{-1}) from room temperature to 1000°C, with a heating rate of 10°C min^{-1}.

Electrical conductivity

The two-probe method employing a d.c. electrical conductivity method as reported earlier [16–18] was used in the present study.

Infrared studies

The infrared spectra were recorded on a Perkin Elmer model 337 spectrometer using nujol mull.

X-ray diffraction

The powder X-ray diffraction patterns was obtained from a PW 1730 Philips X- ray diffractometer, using CuK_α radiation.

Magnetic hysteresis

The magnetic hysteresis of γ-Fe_2O_3 particles was investigated using a vibrating sample magnetometer-VSM (EG & G Princeton Applied Research Model 4500) magnetometer.

Morphology

The morphology of γ-Fe_2O_3 particles was investigated using Cambridge Stereo Scan 150 instrument.

Results and discussion

Study under static air

Figure 1 shows the thermal analysis trace of ferrous gluconate sample under static air atmosphere. In this figure the dehydration step of $FeC_{12}H_{22}O_{14}\cdot 2H_2O$, is indicated by a broad endothermic peak (~108°C) on the DTA trace. The DTG trace also shows a broad peak (at 108°C). The TG trace shows a mass loss in the temperature range 40–140°C corresponding to the loss of two water molecules. A sample isothermally heated at 160°C shows that the bands due to water molecules were not present in the infrared spectrum. Elemental analysis (C, H and metal estimation) of this sample also agreed with anhydrous gluconate ($FeC_{12}H_{22}O_{14}$).

The oxidative decomposition of the complex $FeC_{12}H_{22}O_{14}$, was indicated by the presence of four exothermic peaks on the DTA trace at 220, 293, 350 and 421°C. Broad peaks on the DTG trace at similar temperatures are noticed. However, the TG trace shows continuous mass loss from 140 to 478°C. The final mass loss corresponds to the formation of α-Fe_2O_3. The samples isothermally heated at 220 and 293°C gave a diffuse X-ray patterns. The X-ray pattern of the sample obtained after heating at 350°C shows mixed phases of Fe_3O_4 and γ-Fe_2O_3, and the sample isothermally heated at 421°C shows to be purely α-Fe_2O_3. Hence it may be understood that the peaks observed on the DTA and DTG traces at 350 and 421°C are due to the transformation to more crystalline forms.

Direct current electrical (d.c.) conductivity of this compound ($FeC_{12}H_{22}O_{14}\cdot 2H_2O$) under this atmosphere could not be studied since the pellet of this sample melted above 200°C.

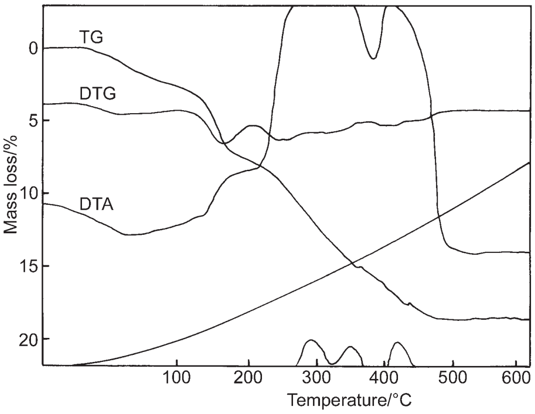

Fig. 1 Thermal trace of $FeC_{12}H_{22}O_{14}\cdot 2H_2O$ under static air atmosphere

When the reaction has been carried out in static air atmosphere, the gaseous product act as a gas buffer for the solid state reaction and some of the reactions will be ill-defined [17]. A study of reaction under dynamic atmospheres viz., dynamic nitrogen and dynamic air has been carried out to compare the data and clarify the results obtained therein.

Study under dynamic nitrogen atmosphere

The thermal analysis traces are shown in Fig. 2. The TG trace shows a mass loss in the temperature range ambient to 160°C, corresponding to loss of two water molecules indicating a dehydration process. The DTA trace shows an endothermic peak at 95 followed by a shoulder at 155°C. The DTG trace shows two peaks at 80 and 185°C, both these traces show the dehydration process for gluconate sample.

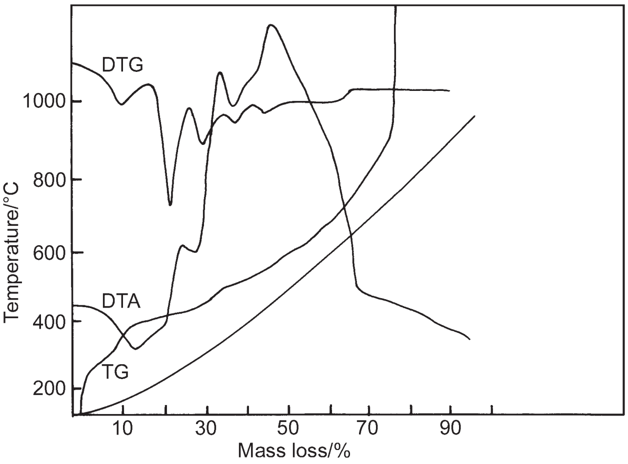

Fig. 2 Thermal trace of $FeC_{12}H_{22}O_{14}\cdot 2H_2O$ under dynamic nitrogen atmosphere

The d.c. electrical conductivity results for the sample $FeC_{12}H_{22}O_{14}\cdot 2H_2O$ are shown in Fig. 3, by a plot of $\log\sigma$ *vs.* $1/T$, where σ is the electrical conductivity (ohm cm^{-1}) and T is the temperature in absolute scale. The σ value shows a peak in the region from ambient temperature to 180°C. This peak can be understood as dehydration step [16]. Figure 4(a) shows the X-ray diffraction pattern for ferrous gluconate dihydrate and Fig. 4(b) shows the X-ray diffraction pattern for dehydrated ferrous gluconate. It is seen from these two traces that the crystalline form is lost when dehydration takes place. The infrared spectrum of the sample isothermally heated at 160°C, did not show any bands corresponding to ν_{OH}. Elemental analysis also agreed with the composition of the anhydrous formulae, $FeC_{12}H_{22}O_{14}$. This anhydrous sample was found to be amorphous in nature with X-ray study. The transition from crystalline to amorphous gluconate would possibly indicate the formation of better γ-Fe_2O_3, having nanosized particles with high density when carried out under controlled conditions. This transition from amorphous to crystalline phase results in better properties for ferrites that are prepared by sol-gel techniques [19]. Hence γ-Fe_2O_3 formed from the thermal decomposition of ferrous gluconate may have better thermal and structural properties when compared to those prepared from thermal decomposition of carboxylates studied earlier by us [16–18]. This is also evident from the saturation magnetisation and coercive force measurements, which are discussed later.

In Fig. 2, after the dehydration peaks the DTA trace shows exothermic peaks at 210, 320, 395 (shoulder) and 440°C. The peaks on the DTG trace were observed at 275, 360, and 415°C. The TG trace shows a two-step mass loss. The first step of mass loss occurred between 160 and 220°C corresponding to the formation of a mixture of FeO and anhydrous gluconate. The electrical conductivity plot shows the presence of a peak in the temperature region 180 to 225°C. A sample isothermally heated in this region (200°C, for 2 h) indicated the presence of FeO in the X-ray diffractogram (Table 1). The infrared spectrum shows a broad band at 550 cm^{-1}, which is assigned to Fe–O stretching frequency [16]. In the electrical conductivity trace (Fig. 3) a steady increase in σ-value is noticed with a shoulder around 280°C, later a steep increase in σ-value is noticed upto 460°C thereafter the conductivity trace remained almost constant, which is a typical behaviour for the Fe_3O_4 [16]. On further heating the final conversion to α-Fe_2O_3 takes place. The X-ray diffraction of the sample isothermally heated at 280°C, shows a mixture of FeO and Fe_3O_4. The X-ray pattern of the sample isothermally heated at 500°C (2 h), shows the sample to be Fe_3O_4 (Table 2).

Table 1 Comparison of X-ray diffraction data of FeO obtained from $FeC_{12}H_{22}O_{14}\cdot 2H_2O$ by heating under dynamic nitrogen at 200°C (2 h)

Observed *d*-spacing values (μm), present study	Reported [23] *d*-spacing values μm
4676(40)	
3180(25)	
2889(22)	
2493(75)	2490(80)
2304(20)	
2154(100)	2153(100)
2089(25)	
2058(45)	
1612(10)	
1605(22)	
1524(40)	1523(60)
1300(22)	1299(25)
1134(10)	
1075(9)	1077(15)

Figures in parenthesis show the relative line intensities normalised to the strongest intensity line (given by 100)

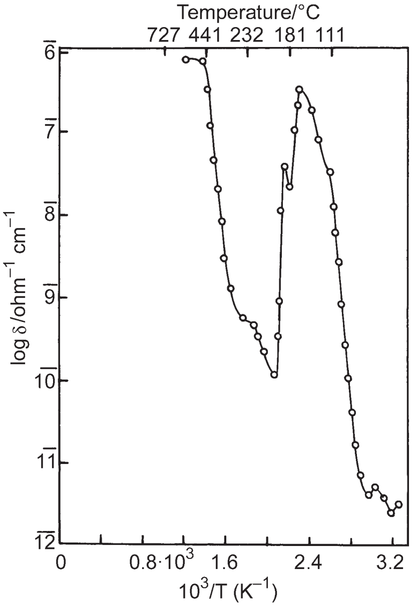

Fig. 3 d.c. electrical conductivity trace for $FeC_{12}H_{22}O_{14}\cdot 2H_2O$ under nitrogen atmosphere

Table 2 X-ray data of Fe_3O_4, obtained from $FeC_{12}H_{22}O_{14}\cdot 2H_2O$, by heating under nitrogen atmosphere at 500°C (2 h)

Observed *d*-spacing values (μm), present study	Fe_3O_4, *d*-spacing in μm [24]
4820(5)	4850(8)
2980(25)	2967(30)
2535(100)	2532(100)
2420(5)	2424(8)
2092(20)	2099(20)
1716(5)	1715(10)
1620(25)	1616(30)
1482(35)	1485(40)
1312(5)	1419(2)
1288(9)	1328(4)
1220(9)	1281(10)
1098(4)	1266(4)
1060(3)	1212(2)
	1122(4)
	1093(12)
	1050(6)

Figures in parenthesis show the relative intensities normalised to that of the strongest line (given by 100)

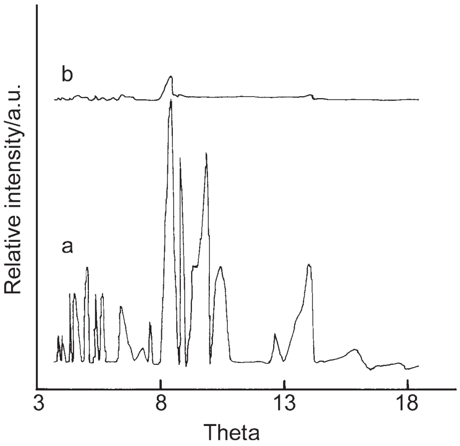

Fig. 4 XRD pattern for a – $FeC_{12}H_{22}O_{14}$·$2H_2O$; b – dehydrated $FeC_{12}H_{22}O_{14}$·$2H_2O$

Study under dynamic air atmosphere

The thermal analysis trace for $FeC_{12}H_{22}O_{14}$·$2H_2O$ is shown in Fig. 5. The TG trace shows a two-step mass loss. The first step of mass loss occurred in the range from ambient temperature to 160°C, corresponding to partial dehydration of the gluconate. The DTA and DTG traces show peaks at 160 and 178°C. The complete dehydration of the gluconate complex occurs around 230°C, which is noticed on the TG trace, and by an endothermic peak on DTA trace at 220°C.

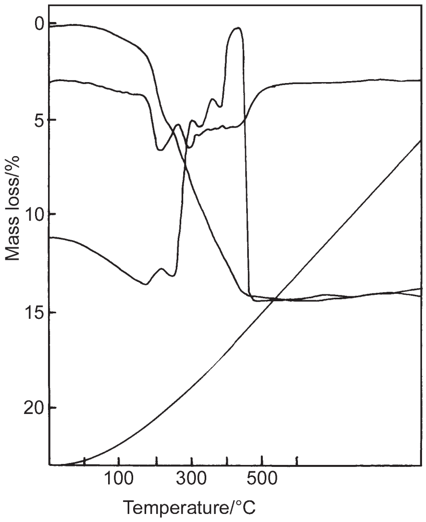

Fig. 5 Thermal trace of $FeC_{12}H_{22}O_{14}$·$2H_2O$ under dynamic air atmosphere

The oxidative decomposition of the complex was indicated by the presence of three exothermic peaks on the DTA trace at 282, 336 and 402°C respectively. The DTG trace also shows peaks at 178 and 265°C. The TG trace shows a continuous mass loss upto 460°C, where a final formation to α-Fe_2O_3, took place. The isothermal heat treatments were given at 290, 340, and 410°C respectively. The X-ray diffraction shows that the sample obtained on isothermal heating at 290°C was a mixture of FeO with some gluconate complex (presence of broad peaks, showing conversion from amorphous to crystalline nature were observed), at 340°C it was a mixture of Fe_3O_4 and γ-Fe_2O_3, and at 410°C the formation of α-Fe_2O_3 was complete. Though the amorphous → crystalline transition took place in this atmosphere, from the anhydrous gluconate to formation of different iron oxides, including γ-Fe_2O_3, it is observed that the stabilisation of this γ-Fe_2O_3 was not completely possible on isothermal heating. It is reported in our earlier studies [18] that moisture plays an important role in formation and stabilisation of γ-Fe_2O_3, phase formed so. The mechanism for the stabilisation of γ-Fe_2O_3 phase is understood with the formation of hydrogen ferrite phase with the possible reaction of γ-Fe_2O_3 and water vapour [12, 18]. The role of water vapour and its subsequent decomposition with the formation of hydrogen ferrite is very important in understanding the doping features of γ-Fe_2O_3 [12]. Hence, we have carried out our experiments under the influence of dry air containing water vapour to investigate the feasibility of formation of γ-Fe_2O_3 and its subsequent stabilisation.

Study under dynamic air containing water vapour

A complete study of direct current electrical conductivity under the atmosphere of dynamic air containing water vapour could not be carried out as the ferrous gluconate pellet melted on heating. The formation of pure γ-Fe_2O_3 and its stabilisation was possible by isothermally heating the gluconate sample at 360°C for an h in a rotating

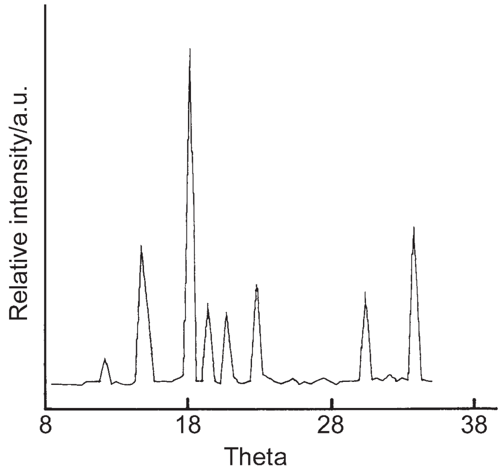

Fig. 6 XRD pattern of γ-Fe_2O_3 synthesised by thermal decomposition of $FeC_{12}H_{22}O_{14}\cdot 2H_2O$ under dynamic air containing water vapour atmosphere

flask, under this atmosphere. The X-ray diffraction pattern fitted well for this sample with that of γ-Fe_2O_3 [20] having a cubic structure as shown in Fig. 6. It is observed that the gluconate complex under this atmosphere of dynamic air containing water vapour first melts, forming froth and than decomposes to give pure γ-Fe_2O_3 at 360°C. Hence the earlier discussion on formation and stabilisation of γ-Fe_2O_3 is in concurrence with the present results.

Particle morphology

Figure 7 shows the scanning electron micrograph (SEM) of γ-Fe_2O_3, prepared from the gluconate precursor, it is observed from this figure that the particles are nanosized (<100 nm). The particles are mainly rectangular and mostly uniformed sized. However, large agglomerates are also seen.

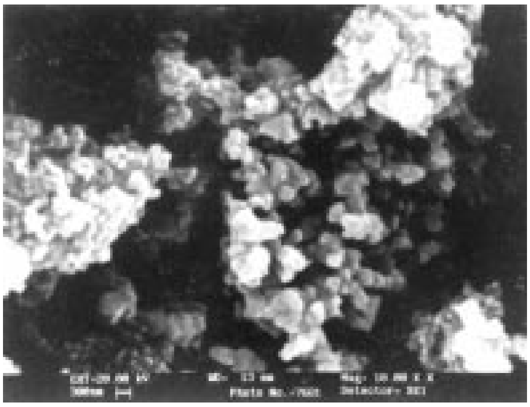

Fig. 7 Scanning electron micrograph of γ-Fe_2O_3 synthesised in the present study

Magnetic properties

To test the feasibility of the above synthesised γ-Fe_2O_3, as a recording material, the results of coercive force (H_c), saturation magnetisation (M_s), and Curie temperature (T_c) are obtained and shown in Table 3. These values are compared with that of the commercially available results. It is reported that the aciculate shape of γ-Fe_2O_3 particle plays a major role in achieving, desired magnetic properties for use in magnetic recording [4]. Slightly lower values of the magnetic parameters in the present study, may be due to the particle shape criterion (not acicular, in the present study). The rectangular nature of the particles indicates that γ-Fe_2O_3, prepared from ferrous gluconate may also find use as a heterogeneous catalyst, gas sensors and for other technological purposes, apart from its use as a magnetic tape recording material [17, 21, 22].

Table 3 Magnetic hysteresis results for γ-Fe_2O_3

Magnetic property	γ-Fe_2O_3, obtained in the present study	γ-Fe_2O_3 results from literature [4]
Coercive force/Oe	200	250
Saturation magnetisation/emu g^{-1}	59	60
Remanance ratio	0.5	0.6

Conclusions

- γ-Fe_2O_3 as nanomaterial with required magnetic properties, from the ferrous gluconate precursor, under the atmosphere containing water vapour is obtained.
- It was observed that the water vapour atmosphere stabilises the formation of γ-Fe_2O_3, which is in concurrence with earlier studies.
- Under all the atmospheres it was observed that the anhydrous gluconate formed by dehydration of ferrous gluconate dihydrate is amorphous, i.e., a change from crystalline to amorphous phase. This anhydrous ferrous gluconate later converts to crystalline iron oxide. The γ-Fe_2O_3 obtained from this process, has a cubic structure as revealed from X-ray data.
- γ-Fe_2O_3 obtained in the present study may find application for magnetic recording, heterogeneous catalyst, sensor and for other technological applications.

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