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Studies on the formation of γ-Fe_2O_3 (maghemite) by thermal decomposition of ferrous oxalate dihydrate

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The thermal decomposition of ferrous oxalate dihydrate $FeC_2O_4.2H_2O$, has been investigated using thermogravimetric (TG), differential thermogravimetric (DTG), differential thermal analysis (DTA), X-ray diffraction and infra-red spectroscopic techniques.

The DTA data obtained in air consist of an endothermic dehydration peak at $\sim$ 190° C and two exothermic peaks at $\sim$ 245 and $\sim$ 360° C. The first exotherm corresponds to the primary oxidative decomposition while the second one seems to be due to a structural transformation from a disordered or non-crystalline to a crystalline state of α-Fe_2O_3. Similar experiments carried out using a nitrogen atmosphere show an endothermic peak $\sim$ 190° C followed immediately by an exothermic peak at 240° C. The final product of this decomposition has been identified as Fe_3O_4.

The oxalate dihydrate containing traces of moisture decomposes in air under the ambient of its own gaseous products at $\sim$ 300° C to give γ-Fe_2O_3. This compound has been characterized by X-ray diffraction and magnetic hysteresis measurements.

1. Introduction

The important application of γ-Fe_2O_3 (maghemite) in magnetic recording tapes and ferrite components is well known. It has been found that ferritization is facilitated (occurs at lower temperature, $\leqslant 800°C$) when γ-Fe_2O_3 is used instead of α-Fe_2O_3 as a reactant. Whereas γ-Fe_2O_3 is a vacancy ordered spinel, Fe^{3+} $[\square_{\frac{1}{3}}\ Fe_{5/3}{}^{3+}]\ O_4$, magnetite Fe_3O_4 has an inverse spinel structure, Fe^{3+} $[Fe^{2+}\ Fe^{3+}]\ O_4$. The usual method of preparation of γ-Fe_2O_3 is by the reduction of α-Fe_2O_3 (hematite) to Fe_3O_4 and the re-oxidation of Fe_3O_4 to γ-Fe_2O_3. Tsyrnorechki *et al* [1, 2] prepared γ-Fe_2O_3 by heating $FeC_2O_4.2H_2O$ at 350°C for 24 h in an atmosphere containing 4 to 5% oxygen. Recently, Gopalakrishnan [3] obtained γ-Fe_2O_3 by heating $FeC_2O_4.2H_2O$ in a stream of air around 200°C. However, the data regarding its characterization have not been mentioned. It seems that the infra-red spectra of the metal oxalate and its decomposition products have not been recorded in the literature. With a view to determining the preparative conditions and the process of formation of γ-Fe_2O_3, we followed the thermal decomposition of the dihydrate by TG, DTG DTA, X-ray diffraction, infra-red absorption and magnetic measurements.

2. Experimental

2.1. Preparation of the samples

$FeC_2O_4.2H_2O$ was prepared by the method of Bevan *et al* [4]. It was a fine, yellow crystalline powder. For isothermal decomposition studies in air, a known mass of the oxalate was maintained at selected temperatures (determined from the TG curves) for 6 h in a temperature-controlled air oven while similar studies in nitrogen ambient were made by passing a stream of purified nitrogen over the sample placed in a tube furnace.

2.2. Thermal analyses in air and nitrogen

The thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves in air and nitrogen were recorded on a Mettler thermal analyser. All the experiments were carried out under identical conditions maintaining the following instrumental factors:

TG range, 1 mg (full scale)
DTG, 20 mg min^{-1} (full scale)
DTA, 50 μV (full scale)
heating rate, 8° C min^{-1}
gas flow rate, 150 ml min^{-1}
mass of the sample, $\leqslant$ 10 mg.

2.3. X-ray diffraction studies

The products of the isothermal decomposition of $FeC_2O_4.2H_2O$ were analysed by the X-ray powder diffraction (XRD) method using Mo*Kα* radiation (λ = 0.709 Å, Zr filter) on a Philips instrument (PW 1051). Identifications were made by comparing the experimental "*d*" values and relative intensities with those reported in the ASTM powder data file.

2.4. Infra-red spectroscopy

The infra-red spectra were recorded on a Perkin Elmer model 237 spectrophotometer using nujol mull.

3. Results and discussion

3.1. Thermal studies in air and nitrogen atmospheres

The TG, DTG and DTA curves for $FeC_2O_4.2H_2O$ are shown in Figs. 1 and 2. The results in air (Fig. 1) are in good agreement with those reported by Bevan *et al* [4] and Dollimore *et al* [5]. The TG curve shows a continuous mass loss in the temperature range 170 to 270° C (total loss $\simeq$ 55.5%, corresponding to the formation of Fe_2O_3). The DTA curve consists of an endothermic dehydration peak (at ~ 190° C) and two exothermic peaks (at 245 and 360° C). The first exotherm corresponds to an oxidative decomposition while the second one, which is relatively weak in intensity, appears to be due to a structural transformation. This is further suggested by the fact that there is no mass loss in the TG curve corresponding to this peak.

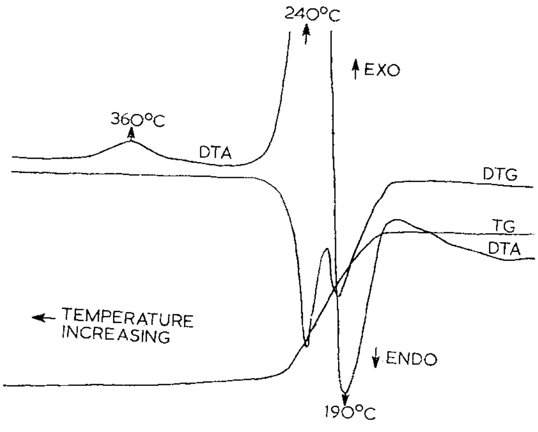

Figure 1 TG, DTG and DTA curves for $FeC_2O_4.2H_2O$ in air.

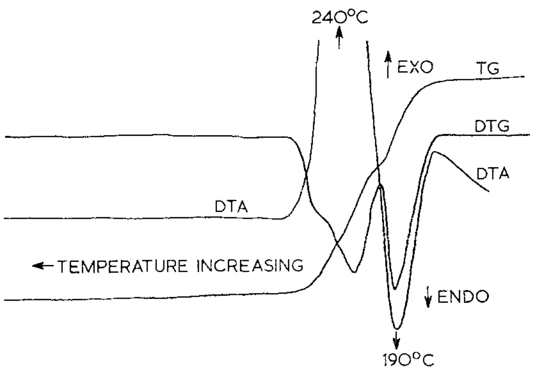

Figure 2 TG, DTG and DTA curves for $FeC_2O_4.2H_2O$ in nitrogen.

The curves using a nitrogen atmosphere (Fig. 2) indicate some difference with those of Bevan *et al* [4] and Dollimore *et al* [5] in that they observed a peak around 340° C, which is not observed in our case. The TG curve shows a continuous mass loss (total loss ~ 60%, corresponding to the formation of FeO) up to about 270° C. There is a small but distinct kink at 210° C indicating the dehydration and decomposition to be two distinguishable reactions.

3.2. Isothermal decomposition, infra-red spectroscopic and X-ray studies

The results of these experiments are presented in Table I.

The decomposition is almost complete even at 200° C (mass loss $\simeq$ 54%) and this is confirmed by the infra-red spectra of the samples heated at 200, 230, 300 and 350° C in which the bands at 3450, 1625 and 810 cm^{-1} characteristic of OH(H_2O), CO and OH(H_2O) groups, respectively (present in the pure oxalate as well as in the sample heated at 150° C) are absent. The sample heated at 170° C indicates a mass loss of 37.4% which is more than that required by dehydration alone (theoretical mass loss $\simeq$ 20%). Thus it is evident that the onset of decomposition starts around 170° C itself. However, the infra-red spectrum of this product shows the band at 1625 cm^{-1} (due to the carbonyl group) indicating that decomposition is incomplete.

TABLE I Isothermal decomposition of $FeC_2O_4.2H_2O$ in air

Temp. (°C)	Time of heating (h)	% mass loss	Infra-red data			X-ray data	Colour of the product
			3450 cm^{-1} OH(H_2O)	1615 cm^{-1} (CO)	810 cm^{-1} OH(H_2O)		
100	6	—	+	+	+	$FeC_2O_4.2H_2O$	Yellow
150	6	3.4	+	+	+	$FeC_2O_4.2H_2O$	Yellow
170	6	37.4	–	+	–	Non-crystalline or disordered material	Dark red-brown
200	6	53.8	–	Weak peak	–	Non-crystalline or disordered material	Dark red-brown
230	6	55.5	–	–	–	Non-crystalline or disordered material	Dark red-brown
300	6	55.5	–	–	–	α-Fe_2O_3	Red-brown
350	6	55.5	–	–	–	α-Fe_2O_3	Red-brown

The starting material, $FeC_2O_4.2H_2O$, gave a sharp pattern in the X-ray diffractogram while the products obtained after heating at 170, 200 and 230°C gave a diffuse-pattern indicating them to be disordered or non-crystalline. The samples heated at 100 and 150°C are found to be $FeC_2O_4.2H_2O$. The final product of decomposition in air is α-Fe_2O_3 while that in nitrogen is Fe_3O_4. The isothermal decomposition studies at 200 and 230°C enable us to interpret the second isotherm at 360°C in the DTA curve in air as being due to the transition from a non-crystalline state of the α-Fe_2O_3 formed to a crystalline form.

In none of the above experiments performed in air could we confirm the formation of γ-Fe_2O_3 as stated by Gopalakrishnan [3]. However, γ-Fe_2O_3 was obtained in a separate set of experiments, the details of which are given in following Sections.

4. Formation and characterization of γ-Fe_2O_3

About 50 g $FeC_2O_4.2H_2O$ (slightly moist) were placed in a large porcelain dish and kept in a furnace maintained at 300°C for 15 to 20 min when a red glow was seen to appear on the surface of the sample. The dish was taken out and its contents were thoroughly mixed producing dull red-brown coarse product. The colour of the sample itself gave an indication of the formation of γ-Fe_2O_3.

The product was X-ray characterized and identified as γ-Fe_2O_3 with traces of α-Fe_2O_3 (Table II). Further confirmation was obtained from magnetic hysteresis measurements made on an a.c. electromagnetic hysteresis loop tracer [6]. The sample was found to give a large coercive force (~ 250 Oe). It may be noted that although the starting material ($FeC_2O_4.2H_2O$) was a fine powder, the product (γ-Fe_2O_3) was

TABLE II X-ray and magnetic data for γ-Fe_2O_3

X-ray data				Magnetic data		
Reported "*d*" value	Intensity	Present investigation "*d*" value	Intensity	Property	Reported	Present investigation
2.94	S	2.94	S	Coercive force	250 to 300 Oe	250 Oe
2.51	VS	2.69 (α-Fe_2O_3)	W	Saturation magnetization	74 emu g^{-1}	70 emu g^{-1}
2.08	S	2.50	VS	Ratio of remanence to saturation (M_R/M_S)	0.67	0.6
1.82	S	2.07	MS			
1.70	MS	1.87 (α-Fe_2O_3)	W			
1.60	S	1.70	MS			
1.47	S					

quite coarse. This is perhaps associated with the ferrimagnetic property of the compound.

5. A possible explanation for the formation of γ-Fe_2O_3

In general, γ-Fe_2O_3 is formed by the following reaction route:

$$FeO \text{ (wüstite)} \rightarrow Fe_3O_4 \text{ (magnetite)} \rightarrow \gamma\text{-}Fe_2O_3 \text{ (maghemite)}.$$

This γ-Fe_2O_3 transforms at high temperatures (> 400°C) into α-Fe_2O_3 (corundum structure) which is antiferromagnetic. The formation of magnetite phase is an essential step in the preparation of γ-Fe_2O_3. In order that Fe_3O_4 is formed as an intermediate during the ferrous oxalate decomposition, it is necessary that the ambient atmosphere over the sample produces a low partial pressure of oxygen or even a slightly reducing atmosphere. This is perhaps realized in the present experiment if one considers the following reactions which are expected to occur during the decomposition

$$FeC_2O_4.2HO \rightarrow FeC_2O_4 + 2H_2O$$
$$FeC_2O_4 \rightarrow FeO + CO + CO_2$$
$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 .$$

These gaseous reaction products, therefore, produce gas buffers like CO-CO_2, H_2-H_2O which produce low oxygen partial pressures. Hence, an intimate mixing of the oxalate during its decomposition (i.e. when the red glow occurs on the surface of the sample) provides the decomposing species with an environment of low oxygen partial pressure. This enables the formation of Fe_3O_4 and its transformation to γ-Fe_2O_3.

6. Conclusions

The present study leads us to the following conclusions:

(a) γ-Fe_2O_3 cannot be obtained by heating $FeC_2O_4.2H_2O$ in a stream of air at 210°C as reported earlier [3]. γ-Fe_2O_3 can be obtained by heating $FeC_2O_4.2H_2O$ in air at 300°C under the ambient of its own gaseous products;

(b) the presence of traces of moisture in the starting oxalate seems to be necessary. It was found that poor yields of γ-Fe_2O_3 were obtained when the starting material was completely dry;

(c) γ-Fe_2O_3, prepared as described above, possesses good magnetic properties ($H_c \sim 250$ Oe) and, hence, may be useful in the manufacture of such materials as magnetic tapes and ferrite materials.

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