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The hydrolysis product of ferric nitrate in sodium hydroxide

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The hydrolysis product of ferric nitrate is obtained by adding ferric nitrate solution to a boiling solution of 2.5 N sodium hydroxide. The sample is amorphous to X-rays when heated below 600° C, but it shows X-ray lines of α-Fe_2O_3 at 650° C. Thermal analysis of the sample gives an endothermic peak at 80° C and two small exothermic peaks at 280° C and 700° C. Transmission electron microscopy and infrared spectroscopy confirm the primary particles as a defect form of $FeOOH \cdot H_2O$. The defect FeOOH form of the sample converts to the disordered form of Fe_2O_3 on further heating around 700° C. The drastic fall in the surface area of the sample beyond 600° C suggests sudden growth of particle size, which is confirmed by a small endothermic peak at 700° C.

1. Introduction

The investigation and understanding of the nature of the primary particles present in iron oxide gel and its thermal transformation to its respective oxides are very important because of its utilization in industry as catalysts, pigments, coatings, etc.

In general, gels consist of a network of macromolecules or are built up of chains of loosely aggregated sol particles held together by van der Waals forces [1, 2]. Iron oxide gel belongs to the latter class [3]. This gel, when left in contact with mother liquor for a long enough time, recrystallizes with the formation of either α-Fe_2O_3 or α-FeOOH or a mixture of both the particles of submicroscopic dimension. The formation of particles with different shapes, sizes and even different stoichiometry depending on the different conditions of precipitation and ageing, has been reported by Matijevic [4]. Music *et al.* [5] studied the effect of ageing of ferric nitrate without the addition of a base and obtained ferric hydroxy polycations of the formula $[Fe(OH)_x(NO_3)_{3-x}]_n$ as the primary particles. Wolska and Szajada [6] and Wolska [7] reported the formation of hydrohaematite by ageing ferric nitrate with sodium hydroxide solution at pH 10 to 11 while Kriger *et al.* [8] obtained amorphous iron (III) hydroxide from ferric nitrate with sodium hydroxide in the pH range 7.5 to 12.0. The atomic arrangement of this amorphous iron (III) hydroxide is typical of α-FeOOH.

Many investigators applied different experimental techniques such as differential thermal analysis (DTA), thermogravimetry (TG), X-ray diffraction, electron microscopy, etc., to follow the sequence of the thermal transformation of gels. Bhattacharyya and Ramachandran [9] observed the presence of an exothermic effect at 420° C due to the crystallization of amorphous ferric oxide together with an endotherm at lower temperatures. Similar results have also been reported by many investigators [10, 11] with a slight difference of temperature. Lodding and Hammel [12] explained this exotherm as due to the conversion of amorphous ferric oxide to α-Fe_2O_3. Pechkovskii *et al.* [13] reported that thermal stability of the gel containing amorphous ferric oxide changes on addition of certain chemicals like urea, phosphoric acid, etc., during its preparation.

In the present investigation, ferric oxide gel was prepared by adding ferric nitrate solution to a boiling solution of sodium hydroxide. This gel is found to remain amorphous to X-rays up to a temperature which is relatively higher than those reported by earlier workers. The nature of the primary particles of the gel and the mechanism of its thermal transformation have been investigated.

2. Experimental details

Hydrated ferric oxide gel was prepared by slowly adding (0.1 M) ferric nitrate solution (GR) to a boiling solution of 2.5 N sodium hydroxide (GR) solution. The pH of the reaction mixture was maintained constant. The precipitate was then washed repeatedly with distilled water until the washings were free from adsorbed impurity ions. The residue was then dried in air. The air-dried (30° C) samples of hydrated ferric oxide were heated at 100, 200, 250, 400, 500, 600, 650 and 800° C, and the specimens were characterized by different techniques.

X-ray diffraction patterns of these samples were obtained by using an X-ray diffractometer type

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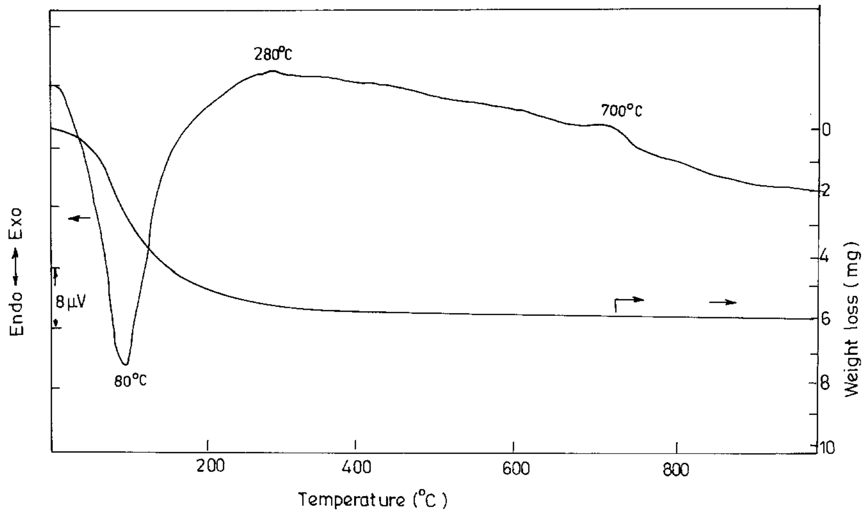

Figure 1 DTA and TG of hydrated ferric oxide gel.

JDX-8P (Jeol) operated at 30 kV and 15 mA. CuK_α filtered radiation was used as the X-ray source.

Thermal analysis of the air-dried sample was carried out in a Stanton Rederoft, STA-780 simultaneous thermal analyser using a suitable quantity of the sample (20 to 25 mg).

A Perkin Elmer 983 model infrared spectrophotometer was used for recording infrared spectra of the samples in the range 200 to 4000 cm^{-1} by using either potassium chloride or polythene pellets.

Electron micrographs and the electron diffraction patterns of the samples were taken on Jem-200 CX (Jeol) model electron microscope with a power rating of 100 kV and 42 cm camera length. The magnification of the microscope was adjusted to × 48 000.

Specific surface areas of the samples were measured by the BET method using Quantasorb surface area analyser.

3. Results and discussion

Results of thermal analysis of the precipitate obtained from the ferric nitrate solution are presented in Fig. 1. The DTA of the air-dried sample shows a large endothermic peak around 80° C and two small exothermic peaks at 280 and 700° C. The endothermic peak at 80° C is due to the removal of water. TG results show that the major loss in weight takes place within 200° C but the weight loss continues up to about 400° C, beyond which, practically, there is no further loss in weight. Assuming the final product to be Fe_2O_3, from a knowledge of total weight loss, the formula of the primary particles is found to be either $Fe_2O_3 \cdot 3H_2O$ or $FeOOH \cdot H_2O$. Infrared spectra (IR) of the precipitate heated to 200° C (Fig. 2) show one broad absorption peak around 3400 cm^{-1} and four more peaks around 1630, 1515, 1340 and 940 cm^{-1}, but all these peaks almost disappear when the sample is heated to 400° C and above. It is well-known that OH stretching vibration causes a strong absorption band at 3400 cm^{-1}. The bending vibration around 1600 cm^{-1} has a lower absorbance compared to that of the stretching vibration. The strong absorption band around 940 cm^{-1} is due to OH deformation vibration [3]. Therefore, IR peaks at 3400, 1630 are due to the absorbed water

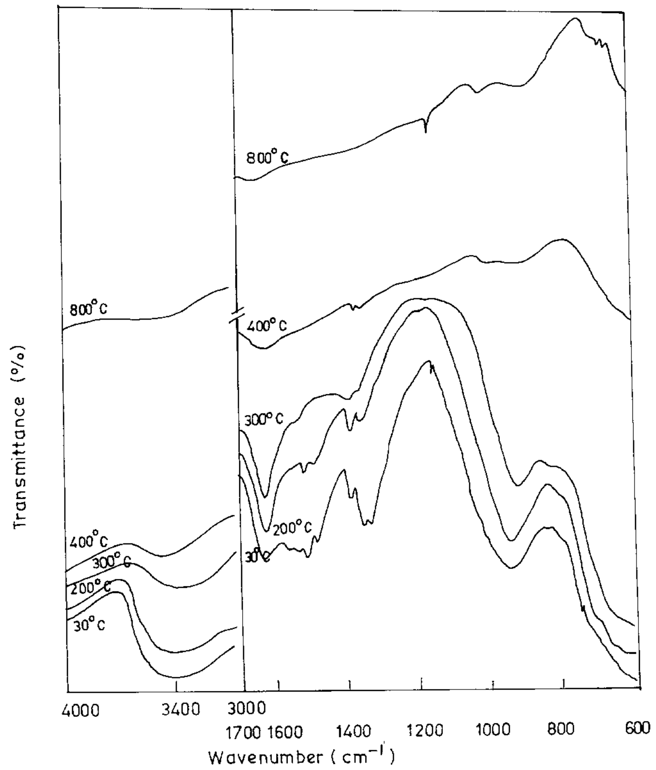

Figure 2 Infrared spectra of hydrated ferric oxide gel heated at different temperatures.

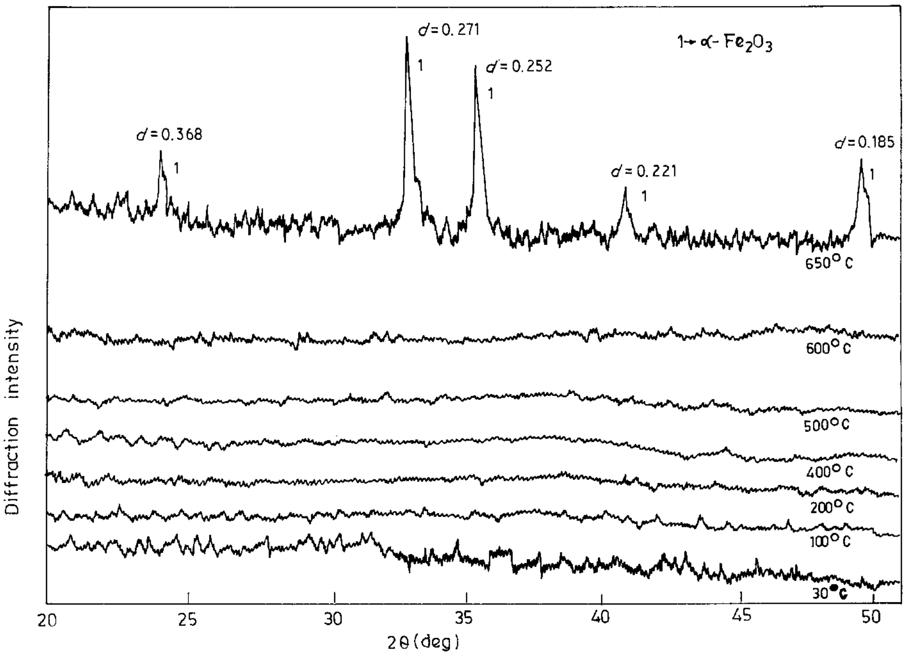

Figure 3 X-ray diffraction patterns of hydrated ferric oxide gel, heated at the temperatures indicated.

present in the sample. However, the peak at 940 cm^{-1} strongly suggests the presence of OH group only. Hence, the primary particles in the precipitate are possibly of the form of FeOOH · H_2O.

X-ray diffraction analysis of the samples heated at different temperatures (Fig. 3) shows their amorphous nature up to 600° C, beyond which a definite pattern corresponding to α-Fe_2O_3 is observed. On the other hand, electron diffraction pattern of the air-dried sample (Fig. 4a) shows four distinct diffraction rings corresponding to the *d* values of 0.385, 0.230, 0.190 and 0.135 nm, indicating that although the precipitates after drying are amorphous to X-rays, they are not so to the electron beam and exist in a microcrystalline form. The *d* values do not exactly coincide with those reported for FeOOH but are quite close to them. On the other hand, they are very different from those of Fe_2O_3. It is known that the *d* values of FeOOH vary to some extent depending on the preparation conditions. This variation may be due to the presence of various structural defects normally incorporated into the lattice during preparation. Deviation may also be due to the presence of either nitrate or/and carbonate ion impurities, which are adsorbed by the particles during precipitation. The possible presence of these type of impurities is indicated by the observation of two IR bands at 1515 and 1340 cm^{-1} in the air-dried sample [14].

An electronmicrograph of the air-dried specimen (Fig. 5a) shows very fine crystals, most of which are clustered together; some of them have needle-like morphology which is typical of FeOOH crystals. On the basis of all these observations (the strong IR band at 940 cm^{-1}, weight loss during the thermogravimetric analysis, electron micrograph and diffraction data) it can definitely be concluded that the primary particles in the precipitate are microfine FeOOH · H_2O particles which are amorphous to X-rays. The exact crystalline form (α, β or γ) of the microcrystals, however, could not be ascertained due to the possible presence of unidentified crystalline defects. The electron diffraction pattern of the sample heated to 500° C (Fig. 4b) shows fine well-defined rings corresponding to *d* values of 0.273, 0.232, 0.164, 0.118 and 0.095 nm. All the values coincide exactly with those reported (JCPBS) for α-Fe_2O_3. By comparing the electron micrograph of the air-dried sample with that of the sample heated at 500° C (Figs 5a and b), it is noticed that the needle-shape morphology changes to much finer equi-angular grains. From this observation it can

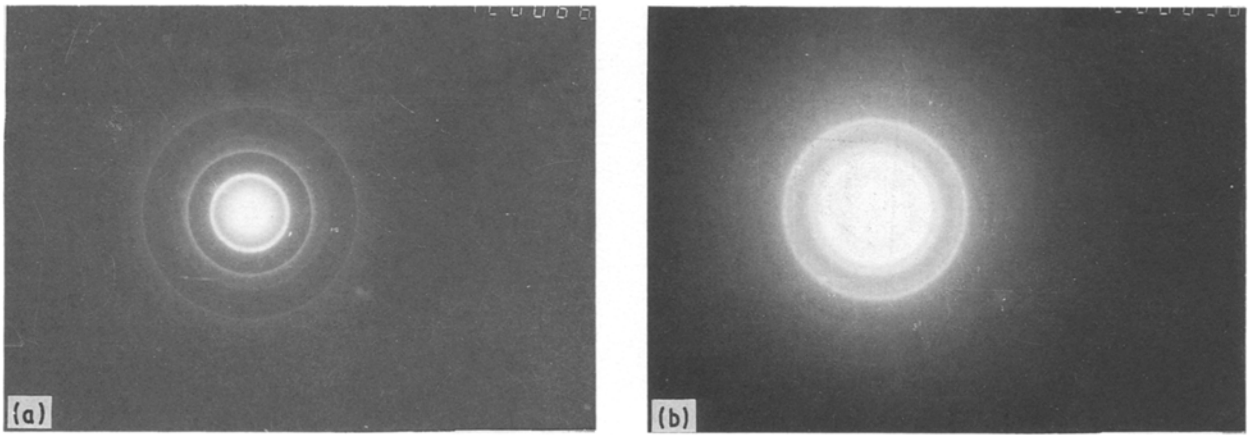

Figure 4 Electron diffraction patterns of hydrated ferric oxide gel, heated at (a) 30° C and (b) 500° C.

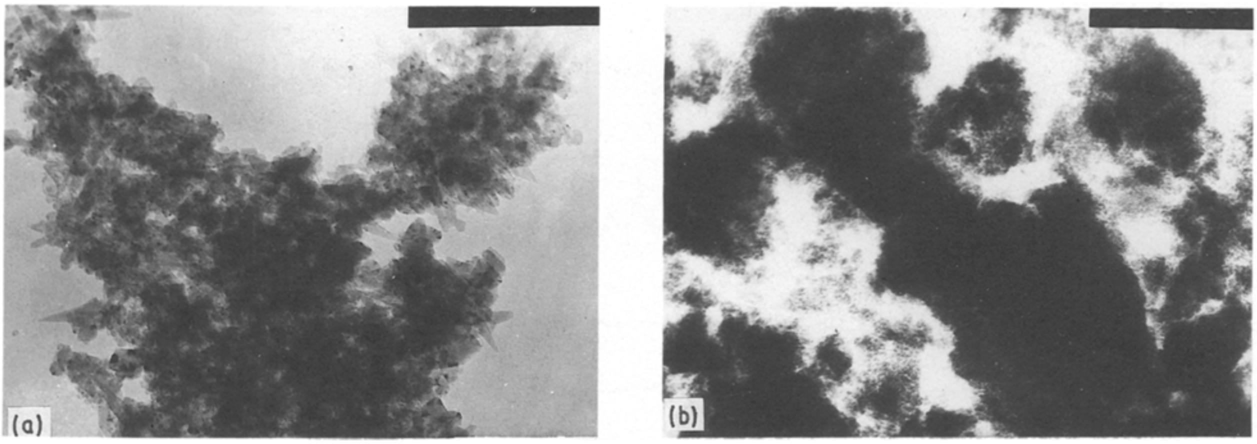

Figure 5 Electron micrographs of hydrated ferric oxide gel heated at (a) 30° C and (b) 500° C.

be concluded that, on heating the sample, needle-shaped crystals decompose with the removal of the hydroxyl ion and with a loss of crystallinity. This results in the formation of much finer structure as shown in Fig. 5b.

This conclusion is also supported by the measurement of surface area of the specimens heated to different temperatures (Table I). The surface area of the sample initially increases with temperature up to 250° C and then decreases gradually as the temperature is raised to 600° C, followed by a sudden drop between 600 and 800° C. The increase of surface area is due to the gradual conversion of micropores, initially present in FeOOH particles to either meso or macropores upon heating to higher temperatures [15]. It is also assumed that with a change of pore size, the FeOOH structure gradually converts to Fe_2O_3 structure. This conversion of defect FeOOH to the disordered form of Fe_2O_3 can be depicted by the presence of an exothermic peak at 280° C in the DTA plot (Fig. 1). The disordered form of Fe_2O_3 slowly changes to an ordered form with increasing temperature as confirmed by X-ray lines of sample heated at 650° C (Fig. 3). The drastic fall in the surface area beyond 600° C suggests a sudden growth of particle size which is also indicated by a small exothermic peak at 700° C in the DTA plot [15].

TABLE I Surface area of the hydrated ferric oxide gel heated to different temperatures

	Temperature ° C				
	100	250	400	600	800
Surface area ($m^2\,g^{-1}$)	96.5	216.2	112.4	81.5	0.5

References

1. I. S. RAJENDRAN, PhD thesis, IIT, Kharagpur, India (1983).
2. H. R. KRUYT, (ed) "Colloid Science", Vol. 2 (Elsevier, Amsterdam, 1949) p. 483.
3. A. A. VAN DER GIESSEN, *Phillips Res. Repts, Suppl.* No. 12 (1968).
4. E. MATIJEVIC, *Pure Appl.Chem.* **50** (1978) 1193.
5. S. MUSIC, A. VERTES, G. W. SIMMENS, I. EZAKANOGY and H. LEIDHEISER, *J. Colloid Interface Sci.* **85** (1982) 256.
6. E. WOLSKA and W. SZAJADA, *J. Mater. Sci.* **20** (1985) 4407.
7. E. WOLSKA, *Z. Kristallogr.* **154** (1981) 69.
8. T. A. KRIGER, O. P. KNINORUCHKE and R. A. BUYANEV, *React. Kinet. Cat. Lett.* **24** (1984) 401.
9. S. K. BATTACHARYYA and V. S. RAMACHANDRAN, *J. Sci. Ind Res.* **138** (1954) 882.
10. C. S. SWAMY, *Curr. Sci.* **35** (1966) 253.
11. R. C. MACKENZIE and G. BERGGREN, in "Differential Thermal Analysis" (Academic Press, London, New York, 1970) p. 272.
12. W. LODDING and L. HAMMEL, *Anal. Chem.* **32** (1960) 657.
13. V. V. PECHKOVSKII, L. S. ESHCHENKA, N. V. GREBENKA, N. B. MILITSIVA and I. E. PRODEN, *Otkrytiya Irabrel* **18** (1985) 86.
14. J. B. HARRISON and V. E. BERKHEISER, *Clays Clay Minerals* **30** (1982) 97.
15. S. RAJENDRAN, V. SITAKARA RAO and H. S. MAITI, *J. Mater. Sci.* **17** (1982) 2709.

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