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Thermal transformation of hydrated ferric oxide gel and preparation of ultrafine oxide

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Hydrated ferric oxide gel has been prepared by addition of a solution of ferric ammonium sulphate to that of sodium hydroxide kept at room temperature. Thermal analysis of the gel shows an endothermic peak at 130° C and three exothermic peaks at 210, 315 and 430° C. The sequence of transformation has also been investigated by thermogravimetry, X-ray diffraction, infra-red spectroscopy and surface-area measurement. The gel is found to consist of α-FeOOH $\cdot n H_2O$ as the primary particle, which crystallizes at around 210° C and subsequently transforms to α-Fe_2O_3 at around 315° C. The initial crystallite size of the oxide formed, is about 700 nm. However, it increases significantly ($\sim$ 3000 nm) accompanied by an exotherm when the oxide is heated beyond 400° C.

1. Introduction

Hydrated ferric oxide gels are normally prepared by the addition of aqueous ammonia or other bases like alkali hydroxides to concentrated aqueous solution of ferric salts. The nature of the primary particles which constitute the gel, depends on the method of preparation and other experimental conditions. Van der Giessen [1] has reported that $FeOOH \cdot nH_2O$ or $Fe_2O_3 \cdot nH_2O$ comprises the primary particles while Towe and Bradley [2], Chukrov *et al.* [3] and recently Saraswat *et al.* [4] have indicated that certain gels consisted of a different primary product, termed protoferrihydrite ($Fe_5HO_8 \cdot 4H_2O$).

Thermal transformation of these gels have been studied extensively by various investigators [1–10]. The rate of transformation, as well as the nature and relative proportion of the products of transformation, are very much dependent on the temperature and pH of the solution during preparation [11–13]. They also depend on the conditions under which the precipitate is aged, especially the temperature of ageing and the presence of anions [14–18] in the solution. It has been reported that in an acidic medium the presence of chloride ions always favours the formation of β-FeOOH and β-Fe_2O_3 [17] whereas, sulphate ions favour the formation of α-FeOOH [19]. A mixture of α- and γ-FeOOH has been reported to be formed when the gel is prepared in the presence of perchlorate ions [15].

Ultrafine ferric oxide particles are reported to be produced under specific experimental conditions [20]. Preparation of such fine particles is important for their application as catalysts in the chemical industries and also for the preparation of different ferrites in the ceramic and electronic industries.

In this paper an attempt has been made to carefully investigate the nature of the primary particles and also the decomposition mechanism of the iron oxide gel prepared under different experimental conditions than those reported earlier.

2. Experimental procedure

Ferric oxide gel was prepared by adding ferric ammonium sulphate (S. Merck – G. R.) solution (0.5 M) to a freshly prepared and continuously stirred 4 N solution of sodium hydroxide (S. Merk – G.R.) kept at room temperature (25° C). The pH, which was measured with a digital pH

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meter, was finally adjusted to 12.5 by further addition of 4 N sodium hydroxide solution. The mixture was kept on a water bath at 100° C for 1 h and then the precipitate was allowed to settle for 2 h at room temperature. It was washed repeatedly with distilled water until free from alkali. A portion of the gel was dried at 50° C for 24 h and the rest was kept at 110° C for 12 h.

To study the thermal decomposition mechanism, samples were prepared by heating the gel at different temperatures between 225 and 500° C for 1 h. These samples were characterized by X-ray diffraction, infra-red spectroscopy, and surface-area measurements.

Thermal analyses were carried out using a Derivatograph (MOM – Hungary) over the temperature range 25–1000° C at a heating rate of 10° C min^{-1}. A suitable weight of sample (200 mg) was taken for each run.

Powder X-ray diffraction measurements were carried out in a Seifert (West Germany) diffractometer using CrKα radiation ($\lambda = 22.91$ nm). A scanning rate of 1.2° min^{-1} was used.

Infra-red spectra were taken with a Perkin-Elmer 273 B spectrophotometer in the range 2000–625 cm^{-1} using nujol as the mull.

Specific surface area measurements were made by the BET method using nitrogen adsorption at – 193° C, after initial degassing of the samples at 150° C for 2 h, with the instrument "Sortptomatic" Model 1800 (Carl Erba, Italy).

3. Results

Thermal analysis results of the hydrated ferric oxide gel are presented in Fig. 1. The DTA of the gel shows a broad endothermic peak around 130° C and three exothermic peaks at 210, 315 and 430° C. Simultaneous occurrence of all these exothermic peaks has not been reported earlier. The thermogravimetry results show that the loss in weight takes place in two steps at temperatures corresponding to the endothermic peak and the second exothermic peak at 315° C. These are confirmed by the appearance of peaks in the DTG plot at corresponding temperatures. Above 315° C practically no loss in weight is observed up to 1000° C.

Fig. 2 shows the infra-red spectra of the hydrated ferric oxide gel heated to different temperatures (A, 50° C; B, 110° C; C, 225° C; D, 350° C). Samples A and B show a broad peak in the range 1700–1600 cm^{-1} and another peak at 1740 cm^{-1}. Both these peaks have completely disappeared in samples C and D. Samples A and B show two more peaks at 900 and 800 cm^{-1} which are also present in sample C. However, both these peaks have disappeared when the sample is heated above 350° C. It is well known that the absorbed water has a bending mode around 1650 cm^{-1} and therefore the peaks which are present in samples A and B between 1600 and 1750 cm^{-1} may be due to the adsorbed water. Kauffman and Hazel [14] have discussed in detail the various types of iron oxyhydroxides and have reported that the region from 600 to 1100 cm^{-1} corresponds to bending vibrations of FeOOH; 900 and 800 cm^{-1} for α-FeOOH; 1020 and 745 cm^{-1} for γ-FeOOH and a weak peak at 840 cm^{-1} for β-FeOOH.

Powder X-ray diffraction analyses were performed for the samples heated at different temperatures. The sample dried at 50° C is completely amorphous to X-rays and that dried at 110° C shows a partial crystallization indicated by the appearance of broad X-ray peaks corresponding to α-FeOOH. X-ray diffraction patterns for the samples heated at higher temperatures are shown in Fig. 3. The sample heated at 225° C shows well-defined α-FeOOH peaks. With further increase in temperature (300° C) the α-Fe_2O_3 peaks also appear, in addition to those of α-FeOOH. In the gels, which are heated to 350 and 500° C, the α-FeOOH peaks have completely disappeared and only α-Fe_2O_3 peaks are present. It may be noted that there is no significant variation in the intensity and half-width of the α-Fe_2O_3 peaks when the samples are heated to temperatures up to 350° C. However, a marked decrease in half-width and nearly four to five-fold increase in intensity are observed when the sample is heated to 500° C.

4. Discussion

The first endothermic peak around 130° C in DTA of Fig. 1 is due to the removal of loosely bound water and possibly the partial removal of consitutional water. Calculations based on TG results show the presence of FeOOH and Fe_2O_3 above 210 and 315° C, respectively. Normally, only an endothermic peak has been reported for the formation of iron oxyhydroxide from hydrated ferric oxide gel [9] but in the present investigation we find a broad endothermic peak immediately followed by an exotherm at 210° C. This exotherm may be due to the complete

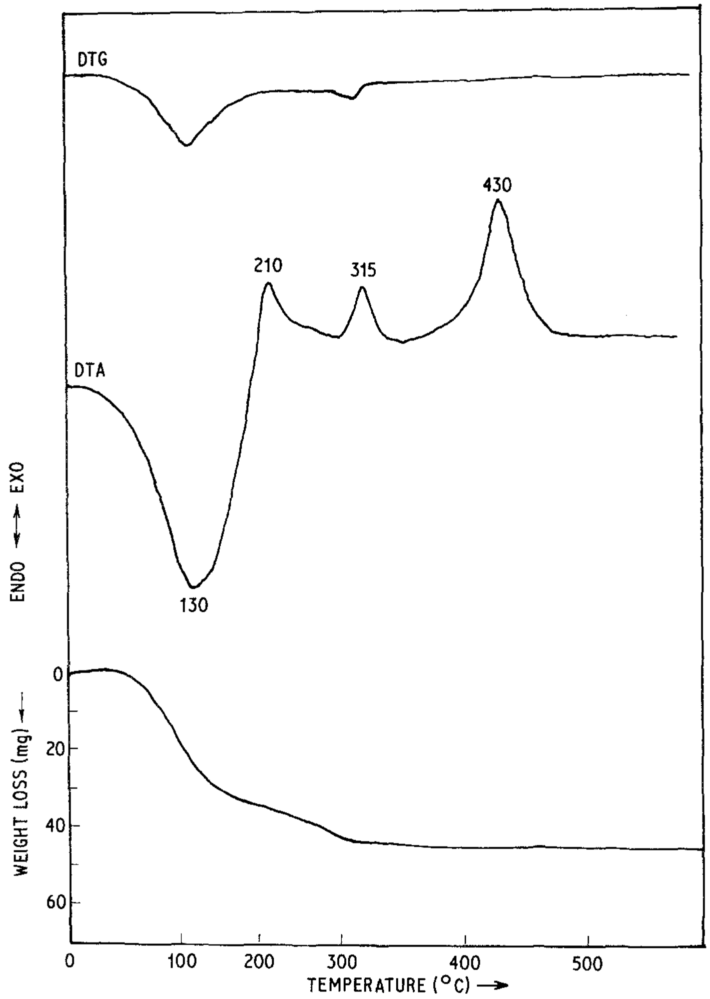

Figure 1 DTG, DTA and TG of hydrated ferric oxide gel.

crystallization of FeOOH which might have formed during the endothermic process, or the gel itself may have consistuted the FeOOH·nH$_2$O as the primary particle [1]. The infra-red spectrum of the gel which was dried at 50° C for 24 h, shows the α-FeOOH peaks at 800 and 900 cm^{-1} (Fig. 2). This clearly suggests that α-FeOOH·nH$_2$O is the primary particle of the gel.

Infra-red and X-ray diffraction studies show that no α-FeOOH is present in the sample heated at 350° C and only α-Fe$_2$O$_3$ is present above this temperature. This indicates that the second exotherm at 315° C corresponds to the conversion of α-FeOOH to α-Fe$_2$O$_3$. It has been reported in the literature that this type of conversion need not always be associated with an endotherm. Kelly [21] has classified naturally occurring goethite into three types based on the thermal decomposition of α-FeOOH to α-Fe$_2$O$_3$. The first type had a sharp exotherm at about 400° C, type two had an endotherm followed by an exotherm and the third type had only endotherm at 350° C. These results support our conclusion of the conversion of α-FeOOH to α-Fe$_2$O$_3$ accompanied by an exotherm at 315° C.

The crystallite size of the samples has been determined by X-ray line broadening. The crystallite sizes are 670 and 3000 nm for the gels heated at 350 and 500° C, respectively. This is also supported by measurement of specific surface area of the samples, the results of which are presented in Table I.

The slight increase in specific surface area between 225 and 300° C may be due to the formation of micropores which are normally formed by the removal of water molecules from iron oxyhydroxides. The decrease in surface area between 300 and 350° C is due to the formation of crystalline α-Fe$_2$O$_3$ above 315° C. The meagre change between 350 and 400° C and the sudden

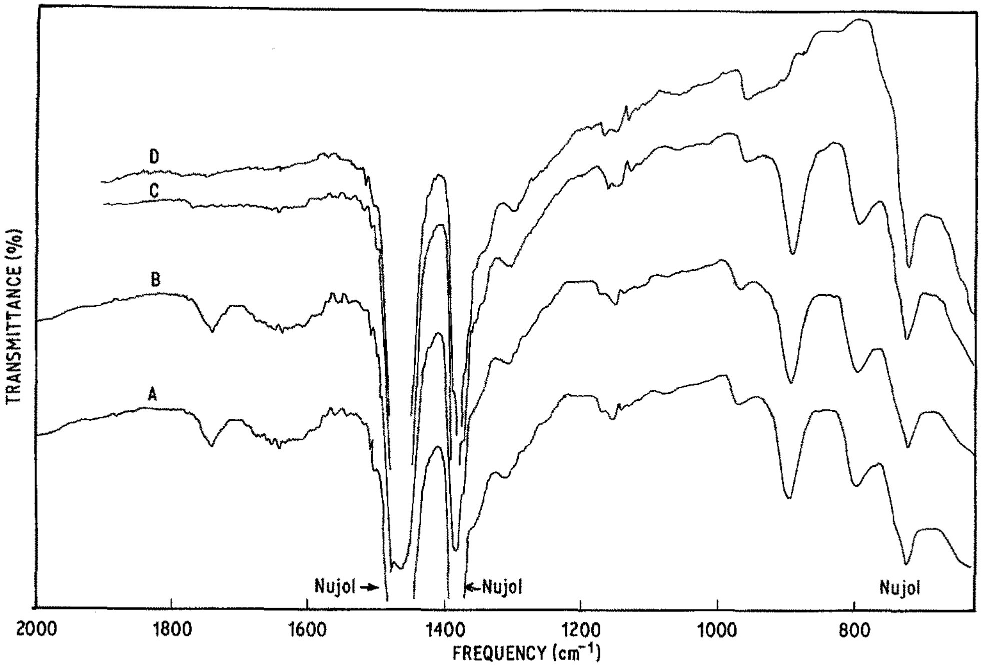

Figure 2 Infra-red spectra at room temperature of hydrated ferric oxide gel heated at (A) 50° C; (B) 110° C; (C) 225° C and (D) 350° C.

drop between 400 and 500° C in the surface area of the gel clearly indicate that there is a significant increase of the particle size only when the sample is heated beyond 400° C. As it has been confirmed by the X-ray diffraction pattern that there is no crystallographic transformation in the temperature range 350–500° C the change in particle size is mainly responsible for the exotherm observed at 430° C. This may be compared with the reported "glow phenomenon" observed in certain samples which has also been explained on the basis of large variation in particle size [7].

It may be noted in Fig. 3 that there is a non-uniform variation in the intensity and half-width of the (1 1 0) and (1 0 4) peaks of α-Fe_2O_3 as a function of temperature. At 350° C the (1 0 4) peak has slightly lower intensity than that of the (1 1 0) peak while the reverse is true at 500° C. Naona and Fujiwara [22] made a similar observation in their samples in which the slit-shaped micropores were converted to regular macropores when the samples were heated at higher temperatures. It may be possible that on heating our samples beyond 400° C the change in particle size is also associated with a variation in the pore structure.

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

Temperature (° C)	225	300	350	400	500
Surface area ($m^2 g^{-1}$)	146	156	112	106	33

5. Conclusions

The results presented in this paper indicate the presence of α-$FeOOH \cdot nH_2O$ as the primary particle. This α-FeOOH completely crystallizes above 210° C and transforms to α-Fe_2O_3 above 315° C. This α-Fe_2O_3 has a particle size of around 670 nm and therefore the method is suitable for the preparation of ultrafine particles of α-Fe_2O_3. However, the crystallite size increases significantly accompanied by an exotherm when the sample is heated beyond 400° C. The thermal tranformation of the gel can, therefore, be represented as:

$$\underset{\text{(amorphous)}}{\alpha\text{-FeOOH}\cdot n\text{H}_2\text{O}} \xrightarrow{210^\circ\text{C}} \underset{\text{(crystalline)}}{\alpha\text{-FeOOH}}$$

$$\alpha\text{-FeOOH} \xrightarrow{315^\circ\text{C}} \alpha\text{-Fe}_2\text{O}_3$$

$$\alpha\text{-Fe}_2\text{O}_3 \xrightarrow[\text{Change in crystallite size}]{430^\circ\text{C}} \alpha\text{-Fe}_2\text{O}_3.$$

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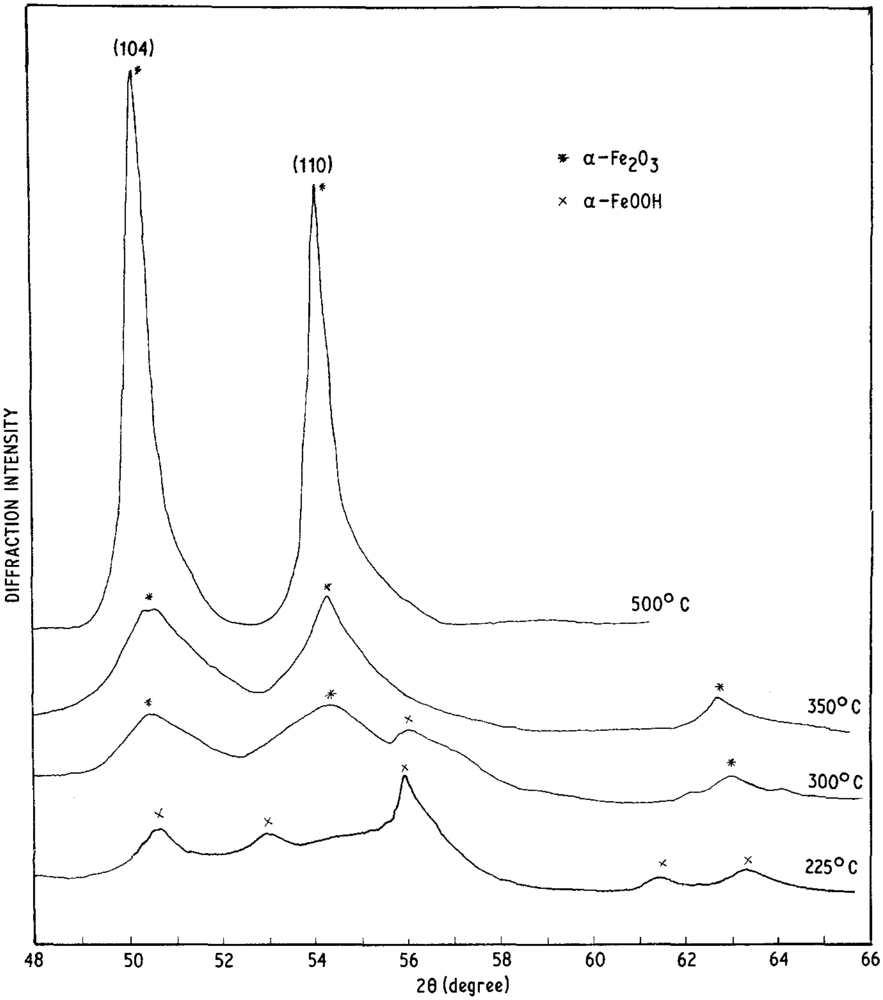

Figure 3 X-ray diffraction powder patterns of hydrated ferric oxide gel heated at the temperatures indicated.

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