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Thermal transformation of iron (III) oxide hydrate gel

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Iron(III) oxide hydrate gel, prepared from ferric ammonium sulphate and sodium hydroxide at pH 10.5 and 60° C, is characterized to be ferrihydrite, and its thermal analyses showed two endotherms at 110 and 380° C and two exotherms at 230 and 420° C, respectively. X-ray diffraction and infrared spectroscopic studies have been used to identify the different products formed at different temperatures. Based on these techniques, a scheme for the decomposition of ferrihydrite to α-Fe_2O_3 is presented.

1. Introduction

The large scale occurrence, catalytically active nature and the capacity of forming a variety of products are essentially the reasons why iron is precipitated time and again in the various forms of oxide hydrate, all of which ultimately yield the alpha ferric oxide around 400° C. The nature of the anion [1–13], the nature of the reagent [6, 14], the temperature [6, 15–18], the pH [6, 15–18], the period of ageing [8–10, 12, 13, 15–20] and the pH of the solution during ageing [13, 15–19] are all known to influence favourably the formation of a particular form of oxide hydrate over the remaining varieties. Normally goethite formation is favoured at higher pH and lower temperature, while haematite is the product at lower pH and higher temperatures [15]. But there are instances in which goethite is formed at a lower pH also [21]. As pointed out by Matijevic [22], any small change in a given set of experimental conditions will completely alter the nature of the products formed.

Using ferric sulphate solutions, Arden [23] has obtained basic sulphates or goethite, depending on ageing time and pH. Dousma *et al.* [24] have studied the influence of sulphate ions on the formation of an iron(III) oxide phase and concluded that the role of sulphate ions is rather complex. They have identified the primary product at a lower pH as α-Fe_2O_3 and at a higher pH as α-FeOOH with the help of Mössbauer spectroscopic study. Recently Music *et al.* [1] have studied the hydrolysis of 0.1 M ferric sulphate and 0.1 M ferric ammonium sulphate solutions at $pH < 2$ and at a temperature of 90° C and concluded that the presence of $FeSO_4^+$ complex suppresses the formation of iron(III) hydroxy polymers and subsequent production of iron(III) oxyhydroxides and oxides.

During the preparation of the mixed oxides of copper and iron for studying their catalytic activity, we noticed the formation of ferrihydrite as the primary product from ferric ammonium sulphate and sodium hydroxide. A detailed survey of literature on the preparation conditions of ferrihydrite indicated that it was prepared either by the addition of an alkali to a 0.1 to 0.5 M ferric nitrate solution around a pH of 7.0 [25–30] or by hydrolysis of a 0.06 M ferric nitrate solution at 85 to 95° C [28, 31, 32], or by heating around 200° C the precipitate obtained from ferric chloride and ammonium hydroxide at a pH of 8 to 9 [33]. Further, the transformation of ferrihydrite to haematite or goethite is also reported to be mainly dependent on the activity of water during the preparation [30] and also on the cations and anions present in the solution [34].

Thermal analyses of this sample of ferrihydrite gave results which are quite different from the earlier reported ones of ferrihydrite of both mineral origin [21, 26–28] and that prepared in the laboratory [25, 31, 33, 35, 36]. Hence the present work was undertaken. This paper presents the characterization of the oxyhydrate of iron formed under

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a different set of experimental conditions and its thermal transformation to different products as identified by X-ray diffraction studies and infrared spectroscopy.

2. Experimental procedure

Ferric oxide hydrate is precipitated at a pH of 10.5 and a temperature of 60° C by the addition of ferric ammonium sulphate (SM GR) solution (0.5 M) to a solution of 2 N sodium hydroxide (SM GR). The precipitate is allowed to settle overnight at room temperature and then washed with distilled water until the washings are completely free from isolated hydroxide and sulphate ions. The gel is dried in air at 30° C (sample S_0) and then heated for 2 h at different temperatures.

Thermal analyses are carried out with 200 mg samples using a Derivatograph (MOM, Hungary) in the temperature range of 30 to 1000° C at a heating rate of $10^\circ\,\mathrm{C\,min^{-1}}$.

X-ray diffraction data are obtained using an X-ray diffractometer type DRON-I (USSR) operated at 30 kV and 10 mA. The filtered X-ray sources used are Fe$K\alpha$ and Mo$K\alpha$. Average crystallite sizes of the samples heated to different temperatures are determined by X-ray diffraction line broadening technique using the relation $\beta_{1/2} = 0.94\lambda/D\cos\theta$, where λ is the wave length of the X-ray used, D is the average diameter of the crystallite and $\beta_{1/2}$ is obtained by the relation

$$\beta_{1/2} = [(\beta_m - \beta_i)(\beta_m^2 - \beta_i^2)^{1/2}]^{1/2}$$

where β_m is the width measured at half height of a peak of the sample and β_i is the instrumental broadening. The instrumental broadening is determined using α-Fe_2O_3 powder sintered at 1000° C for 2 h.

Infrared spectra are recorded on a Perkin–Elmer Model 577 grating spectrophotometer in the range of 4000 to 200 $\mathrm{cm^{-1}}$ using caesium iodide films.

3. Results and discussion

The X-ray diffraction pattern of the air dried gel (S_0) is shown in Fig. 1. Broad diffraction lines are observed at 0.254, 0.224, 0.197, 0.172 and 0.150 nm. The infrared spectrum of S_0 (Fig. 2) exhibits a broad absorption band around 3400 $\mathrm{cm^{-1}}$ and another at 1630 $\mathrm{cm^{-1}}$, while the region of 1100 to 600 $\mathrm{cm^{-1}}$, characteristic of OH or O–H . . . O bending vibrations, is almost featureless and a rather broad absorption band is noticed in the 600 to 400 $\mathrm{cm^{-1}}$ region.

A thorough comparison of the X-ray diffraction data and the infrared spectrum of S_0 with the standard XRD patterns [25–32, 34, 37, 38] and infrared spectra [25, 33, 39] of the different phases of iron oxide hydrate indicates that the sample S_0 is ferrihydrite.

Calculation of the lattice parameters of the air dried sample gives a hexagonal unit cell with $a_0 = 0.5086$ and $c_0 = 0.9347$ nm. These values agree very well with those of ferrihydrite [38]. From a consideration of all these facts, namely, the characteristic XRD line at 0.197 nm, unit cell values of a_0 and c_0, the infrared spectra, the paramagnetic nature of the sample S_0 and the method of preparation adopted here, it is concluded unequivocally that the sample S_0 is ferrihydrite.

The differential thermal analysis (DTA), thermogravimetric (TG) and differential thermogravimetric (DTG) analyses curves of S_0 are shown in Fig. 3. The DTA curve shows a strong endotherm at 110° C and an exotherm at 230° C. This is followed by a second endotherm at 380° C and a small exotherm at 420° C. The TG loss is 11.5 to 12% from 30 to 230° C, 3.5 to 4% from 230 to 400° C, no detectable loss between 400 and 450° C, $<1\%$ from 450 to 600° C and practically no loss beyond 600° C. The total TG loss is 16%. The DTG curve indicates two distinct peaks, one around 110° C and the other at 380° C.

It is interesting at this stage to look into the thermal analysis data of other workers. DTA curves for ferrihydrite generally showed an endotherm around 100° C and an exotherm at 300 to 350° C [21, 25–28, 31, 33, 35, 36]. Studying in an inert atmosphere of nitrogen, Towe and Bradley [31] obtained an endotherm at 100° C and an exotherm at 425° C, which they attributed to evolution of abundant molecular water and to final development of haematite character, respectively. Van der Giessen [25] observed a rather broad endothermic peak between 20 and 200° C with a minimum at 150° C, due to dehydration of ferrihydrite, and a sharp exotherm between 350 and 450° C due to recrystallization. Towe and Bradley obtained the ferrihydrite sample by the hydrolysis of 0.06 M ferric nitrate solution at 85° C and van der Giessen prepared ferrihydrite by treating ferric nitrate solution with a concentrated solution of ammonium hydroxide.

For a natural sample, Schwertmann and Fischer [21] noticed an endothermic peak at about 100° C due to the loss of adsorbed water

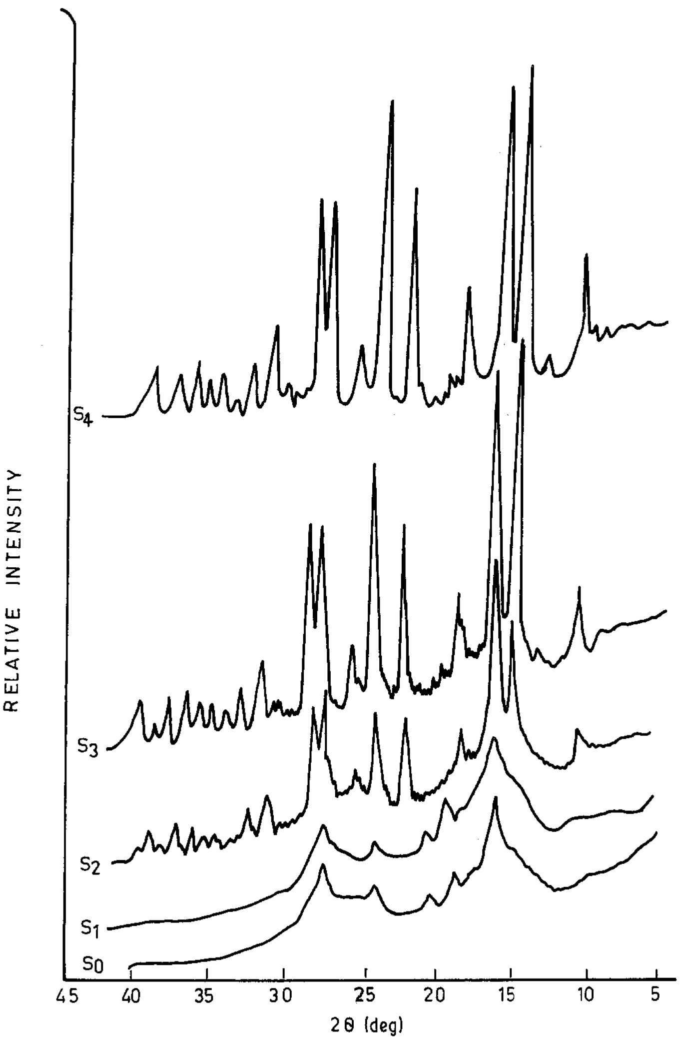

Figure 1 X-ray diffraction patterns of iron oxide hydrate heated to different temperatures: S_0–30° C; S_1–110° C; S_2–200° C; S_3–300° C; S_4–400° C (S_4 – reduced to half the size).

followed by an exotherm between 200 and 300° C, which they attributed to the organic matter present in their samples. Saraswat *et al.* [33] observed an endothermic peak at 180° C (range 80 to 350° C) and an exothermic peak at 410° C due to crystallization of haematite.

Results of thermal analysis in the present case are considerably different from the earlier reported ones, presumably because of the method of preparation adopted in this study.

The X-ray diffraction data of the sample heated at 110° C is almost identical to that of

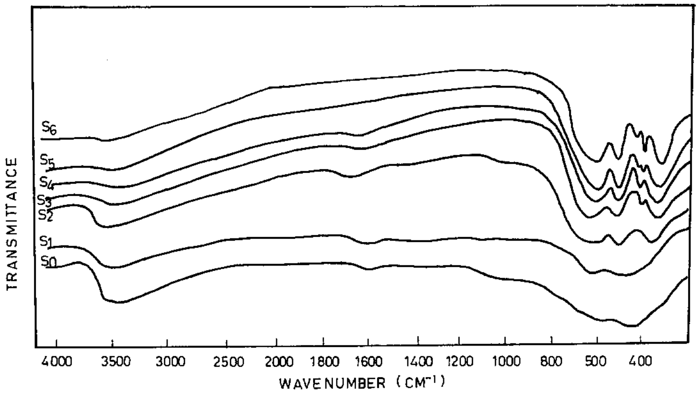

Figure 2 Infrared spectra of iron oxide hydrate heated to different temperatures: S_0–30° C; S_1–110° C; S_2–200° C; S_3–300° C; S_4–400° C; S_5–500° C; S_6–600° C.

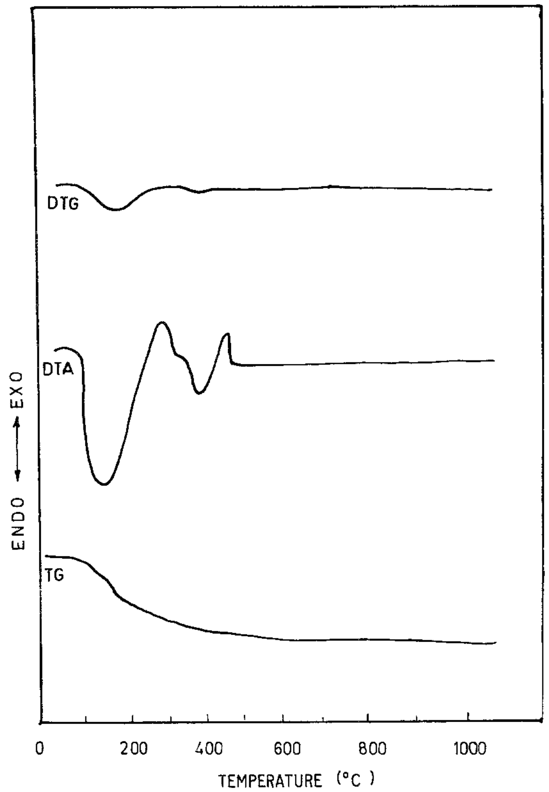

Figure 3 DTA, TG and DTG curves of iron oxide hydrate.

the air-dried sample S_0, thus showing that no chemical change took place during the heating process. But the infrared spectrum of the sample heated at 110° C (Fig. 2) shows a decrease in the areas of 3400 and $1630\,cm^{-1}$ peaks compared to those of the air-dried sample. This observation, along with TG data, reveals that the first endotherm at 110° C is due to the elimination of loosely bound water molecules.

α-Fe_2O_3 is first discernible from the characteristic XRD lines [$d_{104} = 0.269$ nm ($I/I_0 = 65.0$); $d_{110} = 0.251$ nm ($I/I_0 = 100$); $d_{116} = 0.169$ nm ($I/I_0 = 35$); $d_{214} = 0.1484$ nm ($I/I_0 = 0.60$)] of the sample heated at 200° C. The sample heated at 300° C also shows the same lines, but their intensity ratios [$d_{104} = 0.269$ nm ($I/I_0 = 100$); $d_{110} = 0.251$ nm ($I/I_0 = 62$); $d_{116} = 0.169$ nm ($I/I_0 = 70$); $d_{214} = 0.1484$ nm ($I/I_0 = 40$)] are found to be different.

In order to distinguish between these two samples, the infrared spectra are taken (Fig. 2). A marked difference is noticed between the spectra of the samples heated at 200 (S_2) and 300° C (S_3), especially in the areas of the peaks at 3400 and $1630\,cm^{-1}$ and the appearance of a new peak in S_3 at $375\,cm^{-1}$. It can be inferred from X-ray diffraction and infrared spectroscopy that both ferrihydrite and α-Fe_2O_3 are present at 200° C, while only α-Fe_2O_3 is present at 300° C. Hence the exotherm at 230° C in the DTA of S_0 may be attributed to the conversion of ferrihydrite to α-Fe_2O_3.

The X-ray diffraction patterns as well as the infrared spectra of the samples heated at 400° C and at higher temperatures all show lines of α-Fe_2O_3 only. Preparation of iron oxyhydroxide in the presence of sulphate ion is reported to give an impurity of sulphate in the products [40]. So the small endotherm observed at 380° C in DTA may be considered to be due to either elimination of water or sulphur dioxide. Chemical analysis indicates the absence of sulphate ion in the samples. Infrared spectra do not show any noticeable peak in the range of 1200 to $1040\,cm^{-1}$, where SO_4^{2-} is expected to show absorption maxima [41]. The DTA curve also has no observable minima beyond 400° C, where sulphate generally gets decomposed. In view of the above and the decrease in the areas of peaks at 3400 and $1630\,cm^{-1}$ in infrared spectra when the sample is heated from 300 to 400° C, the endotherm at 380° C must correspond to the removal of constitutional water. This is also supported by appropriate losses in TG and the corresponding peak in DTG.

Crystallite sizes of the samples as determined by the X-ray line broadening technique are found to be 9.5 nm at 200° C, 12.0 nm at 300° C, 14.0 nm at 400° C, 26.0 nm at 500° C and 26.5 nm at 600° C. It is seen that there is a large increase in crystallite size, when the sample is heated at 500° C compared to the same heated at 400° C. Hence the small exotherm in the DTA at 420° C is attributed to crystallization of α-Fe_2O_3. The TG results show that there is no loss in weight between 400 and 450° C and the DTG curve confirms the same. Hence the exothermic effect in DTA between 410 and 430° C can be explained on the basis of crystallization of α-Fe_2O_3 in this temperature range.

Calculation from the TG data leads to the formula for S_0 as $Fe_2O_3 \cdot 1.8\,H_2O$. As S_0 is confirmed to be ferrihydrite, it can be better represented by the formula $Fe_2O_3 \cdot 2FeOOH \cdot 2.6\,H_2O$ [39]. The scheme of decomposition of ferrihydrite on the basis of the studies of thermal analyses, X-ray diffraction and infrared spectroscopy can be represented as

$$Fe_2O_3{\cdot}2FeOOH{\cdot}2.6\ H_2O \xrightarrow{30\ \text{to}\ 220^\circ C} 2Fe_2O_3{\cdot}H_2O \xrightarrow{220\ \text{to}\ 400^\circ C} 6Fe_2O_3{\cdot}H_2O \xrightarrow{400\ \text{to}\ 450^\circ C} 6Fe_2O_3{\cdot}H_2O \xrightarrow{450\ \text{to}\ 600^\circ C} \alpha\text{-}Fe_2O_3.$$

In conclusion it may be mentioned that ferrihydrite formed under the conditions adopted in this study shows two endotherms in DTA due to elimination of adsorbed water and constitutional water, respectively, and two exotherms, one due to the conversion of ferrihydrite to α-Fe_2O_3 and the other due to the crystallization of α-Fe_2O_3.

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