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Studies on ferric oxide hydroxides

Part 1 *Effect of sulfate ions on the formation and physico–chemical properties of ferric oxide hydroxides prepared by a homogeneous precipitation method*

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The effects of sulfate ions on the formation and physico–chemical properties of ferric oxide hydroxides were studied using various techniques. Samples prepared from 0.1 M $Fe(NO_3)_3$ solution without sulfate ions contain mixtures of goethite and hematite, whereas basic sulfates of varying composition were formed from solutions containing sulfate: iron (III) ratio greater than and equal to one. Goethite samples of very narrow particle size range, spherical shape, microporous nature, high surface area, high true density and low packing density and surface acidity, which are very necessary for good catalysts and ferrite making, were obtained at low sulfate: iron (III) ratios (0.25: 0.5).

1. Introduction

Numerous studies have been made on the preparation methods of ferric oxide hydroxides because of their multipurpose uses in pigments, catalysts, coatings, ferrites, magnetic tapes and discs [1–5]. Despite many investigations on the preparation, little is known about the preparation methods of particles which are uniform in both shape and size [6–13]. So development of a simple and novel method of preparation of the monodispersed ferric oxide hydroxide particles of characteristic shape, size and surface properties are very important. On the other hand, the nature of the anion [9–19], the nature of the precipitating agents [20–21], temperature [16–20], pH [20–26], period of ageing [6, 21, 25] and the pH of the solution during ageing [22–26] are all known to influence favourably the formation of a particular form of oxide hydroxides over remaining varieties.

The influence of sulfate ions on the precipitation of ferric oxide hydroxides has been investigated by a number of workers [14–17]. Using ferric sulfate solutions, Arden [15] has obtained basic sulfates or goethite, depending on ageing time and pH. By varying $SO_4^{2-}:Fe^{3+}$ ratios (0:2.4) in acidified iron (III) solutions, Dousma *et al.* [16] have identified the primary product of lower pH as α-Fe_2O_3 and at higher pH as α-FeOOH. Waiter-Levy and Quemeneur [14] have investigated solid phases obtained with different iron (III) concentrations at temperatures ranging from 25 to 200 °C, and concluded that goethite, hematite and a number of basic sulfates formed within this temperature range. Music *et al.* [17] have studied the hydrolysis of ferric sulfate and ferric ammonium sulfate solutions at pH 2.0 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. However, there has been no study of the effects of sulfate ions on both the formation and properties of the products. Therefore, it seems useful to investigate systematically the changes introduced by the addition of sulfate ions in the ferric oxide hydroxide particles. This is interesting not only in the industrial field, but also in colloid chemistry in the preparation of monodispersed particles. The effects of sulfate ions on the formation and properties of ferric oxide hydroxide particles were studied by various techniques and the results are presented in this paper.

2. Experimental procedure

2.1. Sample preparation

Samples of ferric oxide hydroxides were prepared from 0.1 M ferric nitrate solution using homogeneous precipitation (HP) techniques with or without the presence of sulfate ions. Precipitations were carried out in a two necked 2 dm^3 capacity round bottom flask; one neck of which was connected to a condenser and the other neck was used to measure the temperature and pH of the solution. One dm^3 ferric nitrate solution containing 8.37 g of Fe^{3+} and 50 g urea with or without sodium sulfate (as the source of sulfate) was taken in the flask. The pH of the solution was adjusted to a desired value with 0.1 M nitric acid or ammonia and the total volume was made to 1.5 dm^3. The flask containing the solution was heated on a Rota mantle at the desired temperature. During the hydrolysis, the solution was stirred by a magnetic stirrer. When the

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TABLE I Preparation conditions and colour of some ferric oxide hydroxides prepared by homogeneous precipitation method from the 0.1 M $Fe(NO_3)_3$ solution with or without the presence of sulfate ions

Sample No.	$SO_4^{2-}:Fe^{3+}$ in solution	Initial pH of solution	Temperature of hydrolysis (°C)	Period of hydrolysis (h)	Final pH of solution	Colour of precipitate (dired at 120 °C)
1	0.00	1.0	90	10.5	6.13	Orange
2	0.25	1.0	90	9.5	6.37	Yellow
3	0.50	1.0	90	9.0	6.23	Brown
4	1.00	1.0	90	8.5	6.34	Reddish brown
5	1.50	1.0	90	8.0	6.40	Pale yellow
6	2.00	1.0	90	7.5	6.40	Grey
7	1.00	1.5	90	7.5	6.32	Brown
8	0.50	1.5	90	6.5	6.48	Pale yellow
9	1.00	0.5	90	20.0	6.21	Pale brown
10	0.50	0.5	90	35.0	6.26	Brown
11	1.00	1.0	100	5.0	6.75	Brick red
12	0.50	1.0	100	5.5	6.47	Pale brown
13	1.00	1.0	80	26.0	6.15	Pale brown
14	0.50	1.0	80	28.5	6.17	Pale brown
15[a]	1.00	1.0	90	11.0	6.11	Yellowish brown
16[b]	0.50	1.0	90	10.0	6.28	Yellowish brown

[a] Prepared without stirring

[b] $(NH_4)_2SO_4$ as the source of sulfate ions.

TABLE II Particle size distribution analysis data of some ferric oxide hydroxides prepared by homogeneous precipitation method from 0.1 M $Fe(NO_3)_3$ solution with or without the presence of sulfate ions

Sample No.	Particle size distribution (%)			
	188–37.6	37.6–16.7	16.7–4.83	– 4.83
1	–	–	–	100
2	–	25.8	53.9	20.3
3	3.3	73.9	17.8	5.0
4	10.4	73.8	11.8	4.0
5	17.8	61.1	19.3	1.8
6	27.5	30.7	22.0	19.8
7	13.8	47.8	27.1	11.3
8	0.1	63.5	23.9	12.6
9	34.1	20.9	19.2	25.8
10	–	47.4	43.6	9.0
11	–	31.3	35.4	33.3
12	–	1.5	59.2	39.3
13	9.4	68.1	13.2	9.3
14	2.3	38.8	29.1	29.8
15	0.2	34.1	53.6	12.1
16	1.0	72.5	24.2	2.3

pH of the solution reached 6.5 ± 0.4, heating was stopped and the solution was cooled to room temperature. The precipitate was filtered, washed thoroughly until the washings were free from sulfate and nitrate ions and then dried at 120 °C in an air oven for 20 h. A number of samples were prepared by this method by varying $SO_4^{2-}:Fe^{3+}$ ratios, source of SO_4^{2-} ion, initial pH of the solution and temperature of precipitation. All the conditions of the precipitation are presented in Table I.

2.2. Physical measurements

X-ray diffraction (XRD) patterns of the powdered samples were taken using a Philips semi-automatic X-ray diffractometer with an autodivergent slit and a graphite monochromator using CuK_α radiation, operated at 40 kV and 20 mA. The characteristic reflection peaks (*d*-values) were matched with the JCPDS data files and different phases were identified. The particle sizes of the samples were analysed by laser induced Malvern particle sizer, type 3600E, and the distribution of different sizes in wt % were presented (cf. Table II). The particle morphology of the samples was examined by scanning electron microscopy (SEM). The secondary electron images were recorded on an SEM (Cameca), operated at 25.0 kV.

The specific surface area of the powders was measured using the Brunauer–Emmett–Teller (BET) nitrogen method in a Micromeritics high speed surface area analyser (Model No. 2202). Packing density was measured by packing a known amount of the sample in a 5 ml measuring cylinder and applying 50–60 gentle taps within which minimum packing volume was reached [27]. The packing volume was noted with an accuracy of ± 0.1 ml. True density was determined by the pycnometric method by displacement of pure toluene at 26–27 °C (density of toluene was 0.8604 g cm^{-3} at 27 °C).

The surface acidity of the samples was determined on the basis of the irreversible adsorption of non-interacting amine (2,6-dimethyl pyridine, *p*Ka = 6.90) by a spectrophotometric method [29]. In each experiment about 0.2 g of accurately weighed dried sample was taken in a 25 ml ground glass stoppered conical flask. A freshly prepared 0.01 M 2,6-dimethyl pyridine (10 ml) was pipetted into the flask. The flask was fitted with a ground glass stopper, shaken for 2 h at constant temperature and filtered. The concentration of the substrate was determined spectrophotometrically. The acid sites were calculated from the amount of substrate adsorbed on the surface.

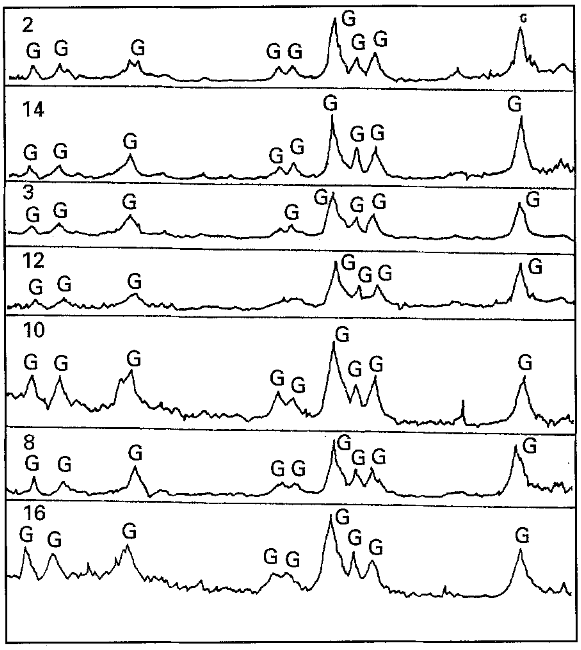
2.3. Chemical analysis

About 1 g of accurately weighed sample was dissolved in 30 ml of 1 : 1 HCl and made up to 100 ml in a conical flask. Total Fe^{3+} in an aliquot was estimated by reduction with stannous chloride and titrated with dichromate using barium diphenylamine sulfonate as indicator and sulfate content was determined gravimetrically as barium sulfate [30]. Sodium content was measured using an atomic absorption spectrophotometer (Varian, Model 1475).

3. Results and discussion

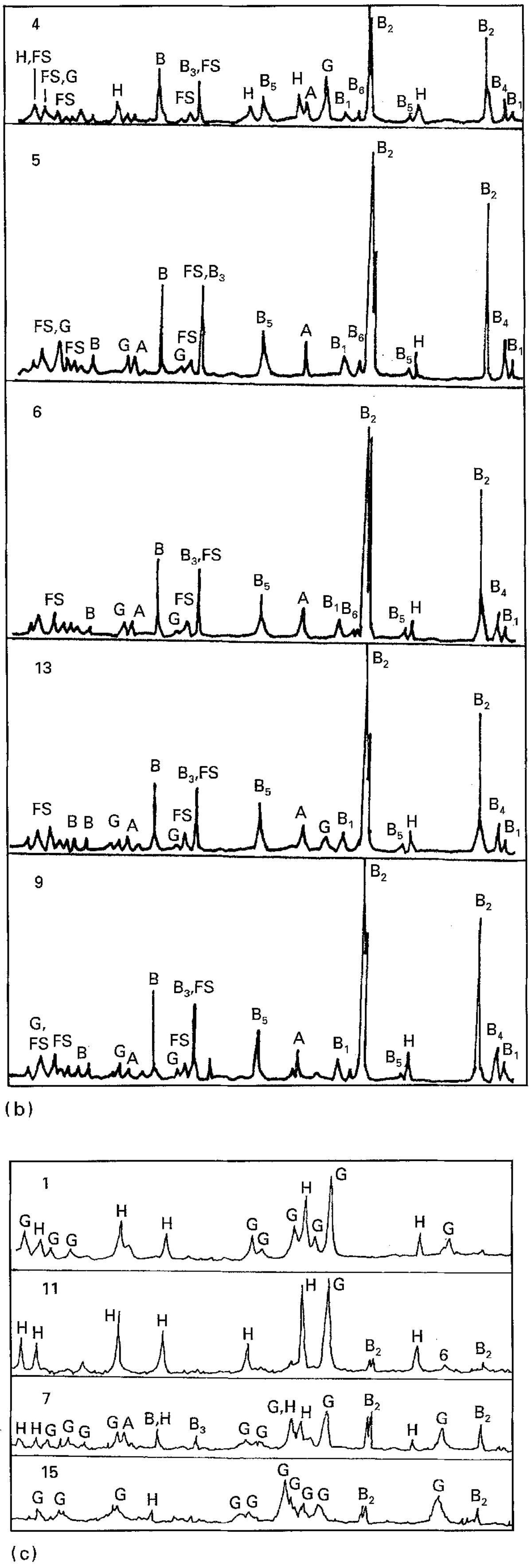
3.1. Effect of sulfate ions on the formation of ferric oxide hydroxides

The XRD patterns of the samples are shown in Fig. 1a–c. The peaks of samples 2, 3, 8, 10, 12, 14 and 16 (Fig. 1a) coincide with those of α-FeOOH indicating that these are pure goethite particles [31]. The broad peaks indicate that the precipitates are fine crystallites. SEM photographs of goethite samples prepared in the presence of sulfate ions indicate that the precipitates are fine crystallites and tend to achieve spherical shape (Fig. 2b–h). Fig. 2e–h shows that the fineness of the crystallites increases with increasing temperature of hydrolysis and initial pH of solution. It is observed from Fig. 1b that samples 4, 5, 6, 9 and 13, prepared in the presence of SO_4^{2-} possess characteristic peaks of basic sulfates of different compositions, such as $Fe(OH)SO_4$, $Fe(OH)SO_4 \cdot 2H_2O$, $Fe_3(SO_4)_2 \cdot (OH)_5 \cdot 2H_2O$, $H_2OFe_3(SO_4)_2(OH)_5H_2O$, $4Fe_2(SO_4)_3$-$5Fe_2O_3 \cdot 27H_2O$; oxysulfates, $Fe_2O(SO_4)_2$; ferric sulfates, $Fe_2(SO_4)_3$; hematite, (α-Fe_2O_3); akaganeite, β-FeOOH); and goethite (α-FeOOH), Fig. 1c shows that samples (11 and 15) prepared at



(a)

Figure 1 XRD patterns of (a) α-FeOOH (goethite) samples prepared by homogeneous precipitation method in presence of sulfate ions, and (b–c) ferric oxide hydroxides showing the formation of basic sulfates. B, $Fe(OH)SO_4$; B_1, $Fe(OH)SO_4 \cdot 2H_2O$, B_2, $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$, B_3, $H_2OFe_3(SO_4)_2(OH)_5H_2O$; B_4, $4Fe_2(SO_4)_3 \cdot 5Fe_2O_3 \cdot 27H_2O$; B_5, $Fe_2O(SO_4)_2$; B_6, $Fe(OH)SO_4 \cdot 5H_5O$; H, hematite (α-Fe_2O_3); A, akaganeite (β – FeOOH); FS-ferric sulfate); G, goethite.



(b)

(c)

Figure 1 Continued

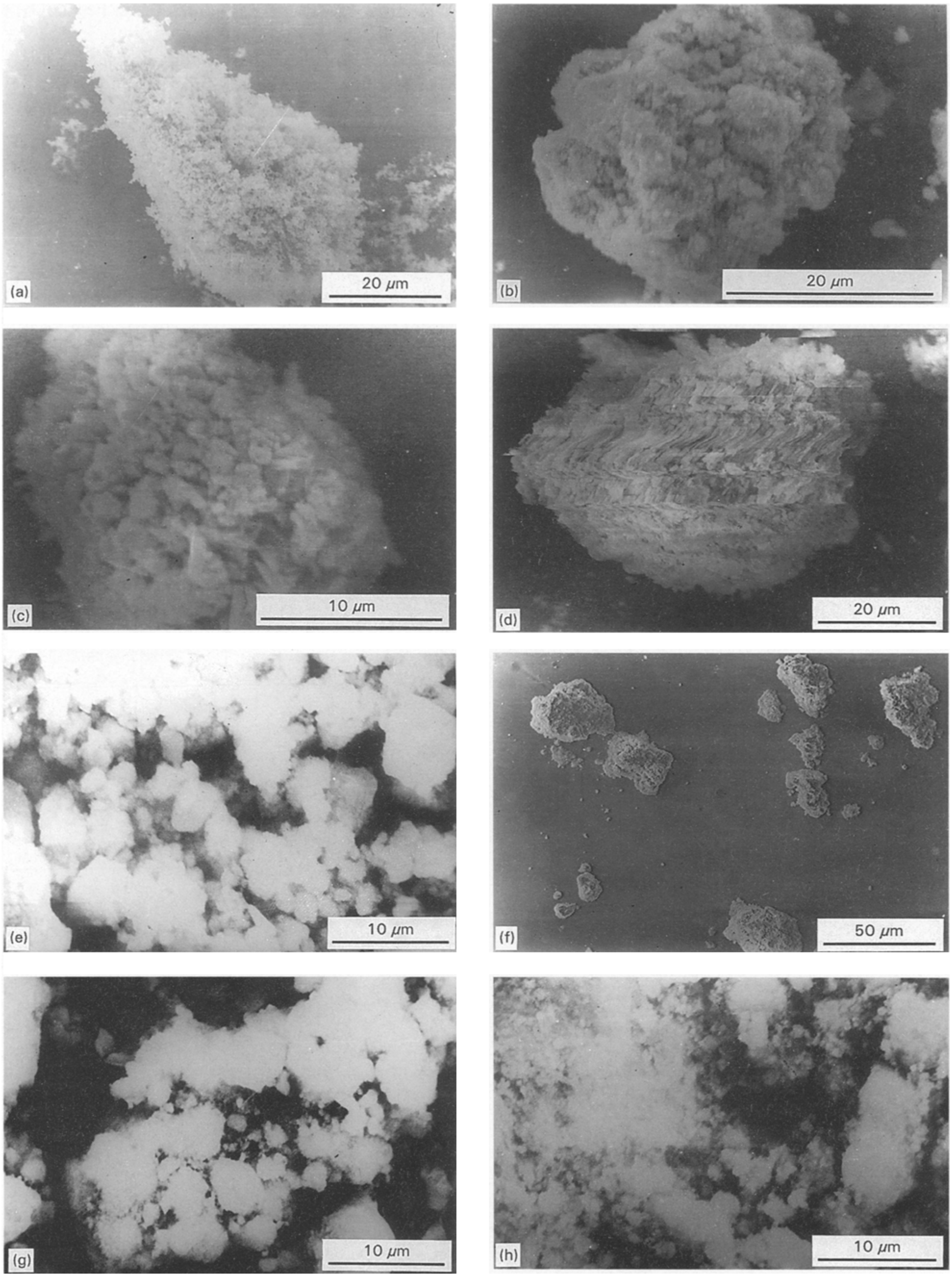


Figure 2 The effect of the (a–d) sulfate ions on the morphology of ferric oxide hydroxides (reaction conditions: temperature 90°C pH = 1.0. (a) Sample 1, SO_4^{2-}:Fe^{3+} = Nil; (b) Sample 3 SO_4^{2-}: Fe^{3+} = 0.5; (c) sample 4, SO_4^{2-}: Fe^{3+} = 1.0; (d) sample 6, SO_4^{2-}: Fe^{3+} = 2.0), and (e–h) temperature of hydrolysis and starting pH on the morphology of ferric oxide hydroxides (reaction conditions: for SO_4^{2-}/Fe^{3+} = 0.5; pH = 1.0; (e) sample 14, 80 °C; (f) sample 12, 100 °C; for SO_2^{4-}:Fe^{3+} = 0.5; 90 °C; (g) sample 10, pH = 0.5, (h) sample 8, 1.5.

higher temperatures (100 and 90 °C) with SO_4^{2-} : Fe^{3+} ratio of 1.0 and initial pH = 1.0 contain only one form of basic sulfate, i.e. $Fe_3(SO_4)_2 \cdot (OH)_5 \cdot 2H_2O$, along with goethite and hematite; whereas sample seven which is prepared at pH = 1.5, temperature 90 °C and at the same SO_4^{2-}: Fe^{3+} ratio contain $Fe(OH)SO_4$, $H_2OFe_3(SO_4)_2$ $(OH)_5H_2O$, and $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$, along with goethite, hematite and akaganeite.

The figure also shows that samples prepared by urea hydrolysis without sulfate ions contain mixtures of hematite and goethite. It is also interesting to observe that the diffraction peaks characteristic of α-FeOOH depicted in Fig. 1a diminished and characteristic peaks of basic sulfates appeared and became stronger and sharper as the $SO_4^{2-}:Fe^{3+}$ ratio increased from 0.5 to 2.0, temperature of hydrolysis decreased from 90 to 80 °C and initial pH of the solution reduced to 0.5 from 1.0 (Fig. 1b). Fig. 1c shows that the formation of basic sulfates is suppressed and goethite and hematite is enhanced with increasing temperature of precipitation and initial pH of the solution. So, it can be concluded that formation and crystallization of α-FeOOH particles are accelerated in the presence of sulfate ions up to $SO_4^{2-}:Fe^{3+}$ ratio of 0.5, while they are suppressed as the ratio exceeds 0.5 in the solution.

Table 1 shows that the degree of hydrolysis and coagulation or coalescence of particles increased as the sulfate concentration in the solution increased. As a result, the period of hydrolysis for increasing the pH from 1.0 to 6.3 ± 0.2 reduced with increased sulfate ion concentration. Nagai *et al.* also reported similar observations in the case of aluminium hydroxide prepared by the homogeneous precipitation method in the presence of sulfate ions [1]. Chemical analysis data of samples 4, 5, 6, 9 and 13 show the presence of sulfate and Na content more than 22.95 and 0.29%, respectively, and show the formation of basic sulfates as indicated in the XRD patterns (Fig. 1b). Table III also shows the fall in sulfate content from 22.95 to 4.14% in samples where XRD shows the presence of goethite and hematite, rather than the basic sulfates which are suppressed. On the other hand, a mixture of hematite and goethite are present in sulfate-free ferric oxide hydroxide samples.

A number of authors [6, 7, 32] have proposed the following scheme to account for the formation of ferric oxide hydroxides from acidified aqueous solutions

$$\text{Monomers} \longrightarrow \text{Polymers} \xrightarrow[\text{growth}]{\text{Nucleation}} Fe(OH)_3$$

$$\text{dimers} \xleftarrow[\text{Polymerization}]{}$$

$$\begin{tikzcd} Fe(OH)_3 \arrow[r, "\text{Growth +}", "\text{Oxylation}"'] \arrow[dr, "\text{Growth}"'] & FeOOH \\ & Fe_2O_3 \end{tikzcd}$$

Based upon the results it can be mentioned here that sulfate ions at lower pH in the presence of some free Fe(III) cations catalyse the growth + oxylation reaction and help in the formation of α-FeOOH nuclei, which subsequently monitor the formation of goethite particles. At higher $SO_4^{2-}:Fe^{3+}$ ratios (1.0) the formation of a number of ferric sulfate complex species [33], such as $(FeSO_4)^+$, $(FeHSO_4)^{2+}$ and $Fe(SO_4)_2^-$ takes place at all temperatures and pH. In addition to that, there is no free Fe(III) in the solution. So the formation of goethite (oxylation reaction) is suppressed and samples containing various forms of basic sulfates precipitate irrespective of initial pH and temperature of hydrolysis. Similar observations were also made by Dousma *et al.* [16]. Matijevic *et al.* [12] observed that positively charged basic sulfate is formed below pH 6.2 and the morphology was dependent on the $SO_4^{2-}:Fe^{3+}$ ratio and the presence of foreign cations.

3.2. Effect of sulfate ions on the particle sizes

To develop a better understanding of the effect of sulfate ions on the formation and particle sizes of the

TABLE III Phase composition and chemical analysis data of some ferric oxide hydroxides prepared by homogeneous precipitation method from 0.1 M $Fe(NO_3)_3$ solution with or without the presence of sulfate ions

Sample No.	Total iron (%)	SO_4^{2-} (%)	Na (%)	Crystalline phases present[a]
1	61.55	0.00	0.000	H, G
2	58.96	0.62	0.004	G
3	57.94	1.26	0.008	G
4	47.70	22.95	0.320	H, G, A, B, B_1, B_2, B_3, B_4, B_5, B_6, FS
5	35.69	38.58	0.596	H, G, A, B, B_1, B_2, B_3, B_4, B_5, B_6, FS
6	34.82	39.13	0.740	H, G, A, B, B_1, B_2, B_3, B_4, B_5, B_6, FS
7	58.74	10.05	0.130	G, H, B_2, B_3, A, B
8	59.00	0.76	0.003	G
9	37.86	34.74	0.290	H, G, A, B, B_1, B_2, B_3, B_4, B_5, B_6
10	58.40	1.55	0.008	G
11	57.02	4.14	0.060	H, B_2, G
12	58.06	0.72	0.004	G
13	40.03	34.31	0.496	H, G, A, B, B_1, B_2, B_3, B_4, B_5, B_6, FS
14	57.83	1.23	0.008	G
15[b]	59.85	5.35	0.053	G, B_2, H
16[c]	57.22	1.92	–	G

[a] H, hematite; G, goethite; A, akaganeite; B, $Fe(OH)SO_4$; B_1, $Fe(OH)SO_4 \cdot 2H_2O$; B_2, $Fe_3(SO_4)_2OH_5 \cdot 2H_2O$; B_3, $H_2OFe_3(SO_4)_2(OH)_5 \cdot H_2O$; B_4, $4Fe_2(SO_4)_3 \cdot 5Fe_2O_3 \cdot 27H_2O$; B_5, $Fe_2O(SO_4)_2$; B_6, $Fe(OH)SO_4 \cdot 5H_2O$, FS, $Fe_2(SO_4)_3$

[b] Prepared without stirring.

[c] $(NH_4)_2SO_4$ as the source of sulfate ion.

product, the particle size distribution in weight percentage determined using a Malvern particle sizer is presented in Table II. It is very interesting to observe that very fine particles (100 wt % finer than 5 µm and irregular shape) are obtained in the absence of sulfate and the size of the particles becomes coarser and the shape becomes spherical with increasing sulfate concentration in the solution as well as in the precipitates (Fig. 2a, b). The particle size distribution in weight percentage in the range 37.6–4.83 µm virtually remains 90 wt % at the $SO_4^{2-}:Fe^{3+}$ ratio of 0.25 to 0.5 and then decreases to 85.6, 80.4 and 52.7 wt % as the ratio increases from 0.5 to 2.0. It is worth mentioning here that 90 wt % of particles remain in a narrow range of 37.6–4.83 µm when precipitation takes place at 90 °C, pH = 1.0 and the $SO_4^{2-}:Fe^{3+}$ ratio is 0.25, and virtually monosize particles (> 96 wt %) are formed when ammonium sulfate is used as the source of sulfate ions. Hence, it is evident that both $SO_4^{2-}:Fe^{3+}$ ratio and source of sulfate ions are controlling factors for the formation and growth of monosize particles. The influence of sulfate ions in increasing the particle size of the precipitates is, perhaps, due to

1. adsorption of these anions on the oxide hydroxides surfaces, and
2. formation of basic sulfates.

Similarly, Kandori *et al.* [19] have also observed that the phosphate ion is an important controlling factor on the size and crystallinity of α-FeOOH particles. As others have observed [1–10], Table II also shows that the particle size distribution in the case of the precipitates depends on the starting pH of the solution, speed of agitation and temperature of hydrolysis.

TABLE IV Surface properties of some ferric oxide hydroxides prepared by homogeneous precipitation method from $Fe(NO_3)_3$ solution with or without the presence of sulfate ions

Sample No.	Packing density (ρ_p) ($g\,ml^{-1}$)	True density (ρ_t) ($g\,ml^{-1}$)	Surface area ($m^2\,g^{-1}$)	Surface acid sites ($\mu mol\,g^{-1}$)
1	0.67	3.50	69.84	30
2	0.40	4.48	110.44	15
3	1.21	3.98	96.17	25
4	0.90	3.02	31.05	25
5	0.93	2.69	6.16	20
6	1.08	2.60	6.08	15
7	0.82	3.17	53.18	30
8	0.69	4.42	133.55	65
9	1.30	2.61	5.33	25
10	1.03	3.85	112.12	55
11	0.82	3.66	31.05	30
12	1.21	3.96	89.46	40
13	1.29	2.67	15.36	20
14	1.28	4.29	90.67	40
15[a]	0.79	3.12	90.86	15
16[b]	0.78	4.21	84.17	35

[a] Prepared without stirring.

[b] $(NH_4)_2SO_4$ as the source of sulfate ion.

3.3. Effect of sulfate ions on surface properties

The surface properties, such as specific surface area and surface acidity, of the products are presented in Table IV. The specific surface area and surface acidity of the precipitates decrease with increase in $SO_4^{2-}:Fe^{3+}$ ratio in the solution. The particle morphology of the samples (prepared under varying SO_4^{2-} concentrations) presented in Fig. 2 shows that the samples are porous and the microporosity decreases with increasing SO_4^{2-} content in the precipitates. The decrease in specific surface area at higher $SO_4^{2-}:Fe^{3+}$ ratios also attributes to the decrease in the microporous nature of the particles and the particles become mesoporous. This decrease in microporosity is, perhaps, due to adsorption and/or formation of basic sulfates, while precipitation takes place in the presence of high concentrations of sulfate ions. Increase in the starting pH of the solution in the case of an $SO_4^{2-}:Fe^{3+}$ ratio of 0.5–1.0 influences favourably the surface area and true density of the products. Table IV also shows that the concentration of sulfate ions in the precipitate controls the surface acidity and as a result, increases although not considerably with increasing initial pH of the solution and temperature of hydrolysis at $SO_4^{2-}:Fe^{3+}$ ratio of 0.5–1.0. It is also interesting to observe that the sample prepared from 0.1 M $Fe(NO_3)_3$ solution containing $SO_4^{2-}:Fe^{3+}$ ratio of 0.25 possesses lowest packing density and highest true density. The packing density of samples prepared at $SO_4^{2-}:Fe^{3+}$ ratio of 0.5–1.0 shows a decreasing trend with increasing initial pH of the solution and hydrolysis temperature.

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