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Crystallization phenomenon in defective goethites

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Abstract

Samples of iron oxihydroxides were synthesized from $Fe_2(SO_4)_3$ and NaOH at room temperature followed by steam treatment in 1 M KOH for several intervals of time. The crystallinity variation of the goethite in function of ageing was studied by means of Infrared Spectroscopy, XRD and DTA. The product of dehydration, Fe_2O_3, maintains the defect structure up to a temperature between 580 to 725°C where an exothermic effect is observed in the DTA due to stress relief and recrystallization.

Key words: Crystallization; defects; DTA; goethites.

El fenómeno de la cristalización en goethitas con defectos

Resumen

Se sintetizaron muestras de oxihidróxidos de hierro a partir de $Fe_2(SO_4)_3$ y NaOH a temperatura ambiente con un tratamiento posterior con vapor de agua en KOH 1 M a varios intervalos de tiempo. Se estudió la variación de la cristalinidad de la goethita en función del envejecimiento mediante IR, DRX y DTA. El Fe_2O_3 producto de la deshidratación mantiene la estructura de defectos hasta una temperatura entre 580 y 725°C donde se observa la aparición de un efecto exotérmico en DTA debido a la liberación de tensiones y recristalización.

Palabras clave: DTA; cristalización; defectos; goethitas.

Introduction

Many properties of the iron oxides depend, in high extent, on the chemical composition (purity) as well as on the particle morphology, and thus, on the way of preparation. For these reasons the methods of preparation and characterization of iron oxides are widely investigated.

The hydrolysis of ferric salts originates any of three varieties of iron(III) oxihydroxides crystalline as a final product: , or -FeOOH (1, 2) and although it occurs with different relationship of base/Fe(III) (3), it could remain for an induction period that could be relatively long. The abrupt increase of pH immediately provokes the precipitation of iron(III) hydroxide poorly ordered (4). The nature of the hydrolysis and the behav-

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ior of the precipitation starting from hydrolyzed solutions of iron(III) nitrate, chloride and perchlorate demonstrate that the anion plays a very important role in the crystal growth process.

The presence of sulphate ion influences the iron(III) hydrolysis in a different way with respect to the rest of the anions, in spite of this, few experiments have been carried out to explain these particularities. Starting from pH measurements and absorbance, Dousma *et al.* (5) found that, at room temperature, the iron(III) sulphate hydrolysis originates a mixture of phases (-FeOOH, -Fe_2O_3 and amorphous precipitate), but at high pH values the goethite is the favored phase. On the other hand, Music *et al.* (6) found that iron(III) sulphate and iron(III) ammonium sulphate hydrolysis at 90°C differ from the rest of the ions in forming $Fe(OH)SO_4$ which transform into basic iron(III) sulphate of complex composition, that avoids or suppresses the transformation to iron(III) oxides and oxihydroxides.

A particular characteristic of the iron hydroxide system in solution is the variety of interconversions that take place between them. One of the more studied transformations is the conversion from ferrihydrite (5 Fe_2O_3 $9H_2O$) to goethite and/or hematite (7). This phenomenon occurs by two competitive mechanisms, which contain the redissolution and the reprecipitation of the aggregation. The latter conduces, additionally, to the formation of hematite (1-10). Cornell and Giovanoli have well established the conditions by which the formation of hematite-free goethite is favored as well as the morphology of the growing particles (4). From the proportion phase point of view they observed that, at 70°C, the hematite disappears between pH 11.3-14.1 but at 90°C the total disappearance of -Fe_2O_3 only occurs at pH 13.4.

Heating of the goethite between 230-270°C leads to -Fe_2O_3 formation with heat absorption. Goethites were classified from the point of view of the thermoanalytical characteristics in three types: type I, which has a sharp exothermic peak at 400°C, type II with an endothermic effect at 350°C followed by an other exothermic; and type III which is characterized by an endothermic effect at 350°C. The well crystallized samples present in the DTA only an endothermic peak in this interval. Normally, a thermal treatment of the goethite to temperatures between 200-600°C results in a crystalline form of the hematite of bad quality, which is defined as protohematite. At higher temperatures, protohematite is converted into the more orderly crystalline variety of -Fe_2O_3 (11, 12).

In a previous work, Cordeiro *et al.* (13) have pointed out the dependence of the band frequency and intensities in the IR spectra; the XDR peaks intensities and the DTA profiles on the nickel content of synthetic goethites. These authors correlated the above properties with the crystalline content of the final products.

The main objective of the present work was the synthesis of -FeOOH with several grades of crystallinity and structural disorder and their characterization by X-ray Diffraction, DTA and Infrared Spectroscopy.

Experimental

Amorphous hydroxide was prepared by dropwise addition, with a flow of 4.6 mL/min under vigorous stirring at 15.9 rad/min, of 1 mol/L sodium hydroxide to 700 mL of 0.6 mol/L iron(III) sulphate at 20°C up to pH 13. All the reagents used were of analytical grade. The resulting precipitate was left to rest for 4 h and shaken in a plastic recipient for 140 h at 50°C, then filtered and washed with distilled water until the filtrate indicated the absent of sulphate ions when tested with barium chloride. This product was then dried at 80°C for 2 h in a stove and denoted as sample F.

Table 1
Conditions of DTA records and TG

Sample	Mass(mg)	S_{DTA}
F	497	500 V
F2H	427	1 mV
F4H	466	1 mV
F8H	494	1 mV
F16H	502	1 mV

S: Sensibility.

The transformation of sample F to a more crystalline precipitate was carried out by steam treatment in alkaline media. Four portions of 5 g of sample F were mixed with 50 mL of 1 M KOH in a beaker and then treated with water vapor stream for 2; 4; 8 and 16 h respectively, these samples are then referred as: F2H; F4H; F8H and F16H. Later they were filtered and washed with distilled hot water until the solution pH drops to 7. Thus, the materials obtained were dried at 50 and 80°C for 2 h at each temperature.

The thermal decomposition of sample F8H was performed at two different temperatures (505 and 775°C) during two hours in a furnace with automatic control. The samples were denoted as F8HA and F8HB, respectively.

Differential thermal analysis and thermogravimetry

A Derivatograph Q-1500D of the system Paulik-Paulik-Erdey was used. The experimental conditions were: heating rate 20°C.min^{-1}, maximum temperature 1000°C, TG sensitivity 500 mg, DTG sensitivity 2.5 mV; empty crucible as reference and dynamic air atmosphere. The other conditions are specified in Table 1 for each sample.

IR spectroscopy

The infrared spectra were registered in a 75 IR Specord from 4000 to 400 cm^{-1}. Pellets were made mixing 2 mg of the hydroxide with 98 mg of KBr in an agate mortar.

X-ray diffraction

XRD profiles were recorded using Co-K on a DROM 3 diffractometer with monochromator operating at 36 kV and 36 mA. For the crystallite size determination the Bartram method was applied (14).

Results and Discussion

The IR spectrum of sample F (Figure 1b) shows no sharp peaks in the zone where the typical bands of crystallinity of the goethite appear (FeOH: 890-790 cm^{-1}; FeO: 630 cm^{-1}; FeO of the net: 450; 425 and 405 cm^{-1}) which agrees with those reported by Subrt (15) for the ferrihydrite (Figure 1 a). In the 3700-2600 cm^{-1} region several bands (related to structure water) are observed, with a peak at 3450 cm^{-1} and two shoulders at 3300 and 3000 cm^{-1}. Their rate of intensities is similar to the disordered hydroxide.

The resulting spectra of the samples derived from F, for the interval between 1300 to 400 cm^{-1}, are shown in Figure 2. As can be seen from the figure, there is an increase in the intensity of the characteristic bands of the goethite after two hours of steam treatment, but after four hours there is no significant variation of these bands.

The X-ray diffraction pattern of sample F presents some of the principal goethite lines with very low intensity, while samples F2H to F16H those lines that initially were not present or were very weak appear, increasing the intensity gradually. From Figure 3, the enhancement of the 110; 130; 021 and 111 lines is proportional to the increase in treatment time. The iron oxihydroxide crystallite size grows, as can be seen, upon comparing the intensities of these lines. This parameter was calculated around 300-350 Å, which agrees with that, reported by Dousma *et al.* (5). The XRD results for the sample treated for 16 hours are listed in Table 2.

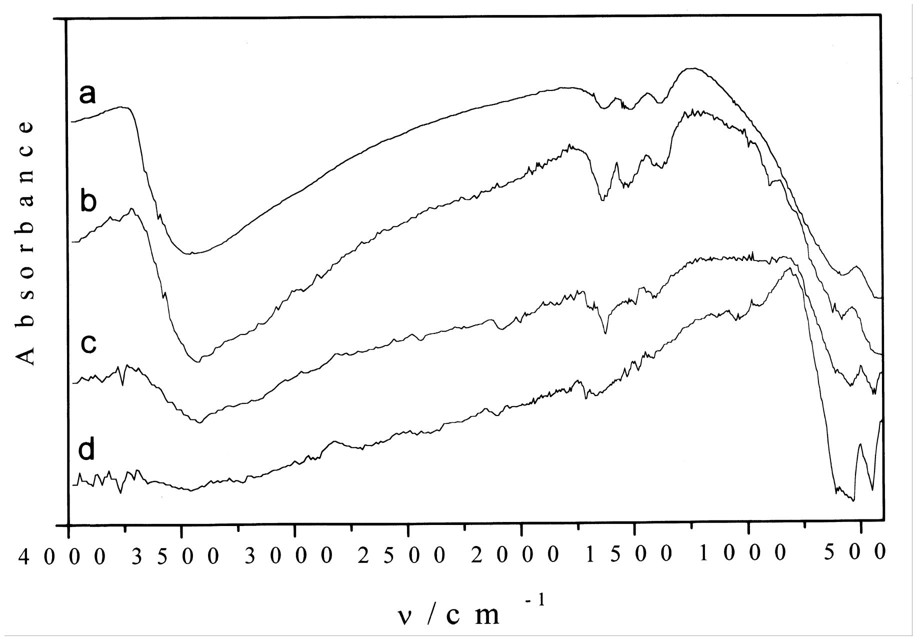

Figure 1. IR spectra of some samples (**a**: ferrihydrite; **b**: F; **c**: F8HA and **d**: F8HB).

Figure 2. IR results of the samples derived from F by steam treatment in alkaline media.

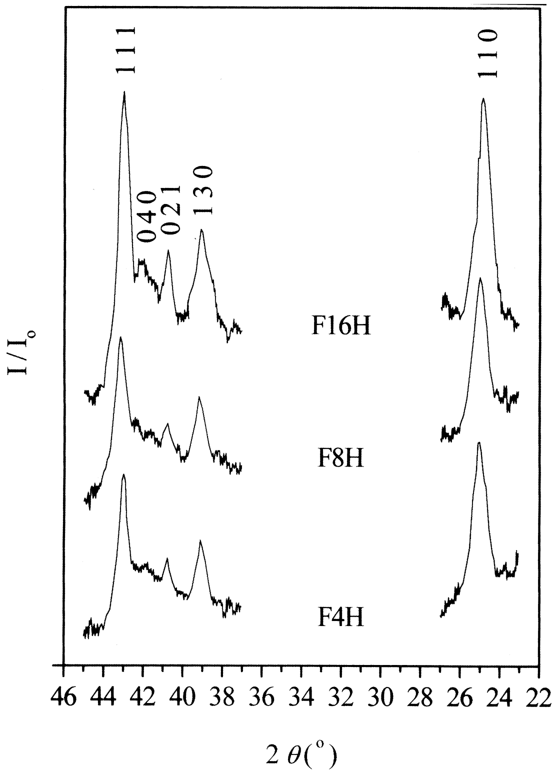

Figure 3. Enhancement of some diffraction lines rising treatment time.

Table 2
XRD results of sample F16H

JCPDS Pattern 2-0281 (Goethite)			Sample F16H		
d(Å)	I/I_0	hkl	d(Å)	I/I_0	hkl
4.18	100	110	4.13	100	110
3.38	10	120	3.38	14	120
2.69	30	130	2.68	30	130
2.58	8	021	2.56	12	021
2.49	16	040	2.49	11	040
2.45	25	111	2.44	45	111
2.25	10	121	2.24	20	121
2.19	20	140	2.18	20	140
1.79	8	211	1.79	10	211
1.72	20	221	1.71	20	221
1.69	10	240	1.69	10	240
1.60	6	231	1.60	8	231
1.56	16	160	1.55	20	160
1.50	10	250	1.50	13	250
1.45	10	061	1.45	10	061

The DTA and TG records of hydroxide F are presented in Figure 4. The DTA curve shows a sharp endothermic peak near 200°C with a shoulder at higher temperatures (between 250-300°C) which is associated to the evolution water from humidity and the loss of the OH^- groups respectively, although the mass decrease extends till very high temperatures. An exothermic effect was observed between 500 to 700°C.

Analyzing the corresponding temperatures at the maximum of each exoeffect an appreciable increment was detected from samples F to F16H. In the same way, an inverse relationship is noticed plotting the peak area (Figure 5) which reduces as ageing increases. The DTA transition temperatures are shown in Table 3 for all the samples. The TG curve remains practically invariable from one sample to another. The general dehydration mechanism could be formulated as:

Figure 4. DTA and TG records of hydroxide F.

Figure 5. DTA exoeffect intensities and peak temperatures plotted vs. treatment time.

$$\alpha\text{-FeOOH} \cdot 0.72H_2O(s) = \alpha\text{-FeOOH} \cdot 0.05H_2O(s) + 0.67\ H_2O(g) \qquad [1]$$

$$\alpha\text{-FeOOH} \cdot 0.05H_2O(s) = 0.5\ \alpha\text{-}Fe_2O_3 \cdot 0.1H_2O(s) + 0.5\ H_2O(g)\ [2]$$

$$\alpha\text{-}Fe_2O_3 \cdot 0.1H_2O(s) = \alpha\text{-}Fe_2O_3(s) + 0.1\ H_2O(g) \qquad [3]$$

When qualitative phase analysis was carried out by X-ray diffraction for samples F8HA and F8HB, it could be seen that both products correspond to the -Fe_2O_3 phase. The evaluation of the powder X-ray diffraction pattern of sample F8HA is given in Table 4 and the IR spectra of the two samples (F8HA and F8HB) are shown in Figure 1c and 1d.

The iron oxihydroxide obtained in cold starting from a ferric sulfate solution presents a disordered structure which, transforms into goethite phase when treated in alkaline media without sulphate ions.

A defective goethite has some thermoanalytical differences compared with a crystallized one. In the DTA record of disordered

Table 3

Temperature transitions in DTA

Compound	Effect	Character	T*start.* (°C)	T*max.* (°C)	T*end* (°C)
F	1.	Endo	50	170	330
	2.	Endo	330	350	395
	3.	Exo	450	580	685
F2H	1.	Endo	40	135	295
	2.	Endo	295	335	375
	3.	Exo	525	615	685
F4H	1.	Endo	60	165	305
	2.	Endo	305	345	395
	3.	Exo	540	635	725
F8H	1.	Endo	50	165	310
	2.	Endo	310	350	385
	3.	Exo	550	640	735
F16H	1.	Endo	30	140	300
	2.	Endo	300	335	400
	3.	Exo	650	725	805

Table 4
XRD analysis results for the sample F8HA

JCPDS Pattern (Hematite)			Sample F8HA		
d(Å)	I/I_0	hkl	d(Å)	I/I_0	hkl
3.68	18	012	3.67	20	012
2.69	100	104	2.69	100	104
2.51	75	110	2.52	100	110
2.20	18	113	2.20	50	113
1.84	63	024	1.83	40	024
1.69	63	116	1.69	50	116
1.60	13	018	1.60	30	018
1.49	50	214	1.48	40	214
1.45	50	300	1.45	50	300

goethites the endothermic effect corresponding to the superficial dehydration water and those due to the dehydroxilation process appear overlapped (16).

The non-structural water associated with the hydroxide is not totally released in the initial heating stage but still lasts after the OH^- groups leave the structure. However, the evolution of this remnant water does not involve a net heat energy absorption since the exothermic character of the transformation due to the more orderly hematite phase formation prevails.

The iron oxide obtained by the dehydration of the disordered goethites deals with a great quantity of defects, which, upon reaching a temperature between 580 to 725°C, are partially eliminated with heat energy evolution. The heat evolved depends on the crystallinity grade of the original oxihydroxide. From the kinetic point of view (17), a system composed by the same group of atoms (Fe and O), forming a similar structure but with proportionally different net tensions, should present the same energy transition state level before reaching the same final state of energy content (-Fe_2O_3 defects free). As each original oxide presents minor level of energy due to the fact that it possesses lesser concentration of defects, then the phenomenon involves a minor quantity of heat each time (see Figure 5), but requires a greater activation energy and therefore a greater temperature.

Conclusions

1. The fast ageing of ferrihydrite gives rise to the formation of defective goethite which possess different thermoanalytical characteristics from the well crystallized.

2. A better crystallized goethite could be obtained by long treatment times of the disordered oxihydroxide.

3. Alpha iron(III) oxide obtained as a result of the thermal decomposition of the goethite has a quantity of defects proportional to the original oxihydroxide. The hematite after the exothermic DTA effect, appears pure and better crystallized.

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