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HIGH TEMPERATURE SYNTHESIS AND CHARACTERISTICS OF Al-SUBSTITUTED IRON ALKOXIDE

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ABSTRACT

A crystalline solid identified as Al-substituted iron alkoxide is obtained from the reaction at 246°C of glycerol with synthetic Al-bearing goethite, when the latter's composition is: $Fe_{0.904}Al_{0.096}OOH$. X-ray powder diffractograms (XRD) of this solid show a significant shift of the d spacings in comparison to a previously reported pure iron glycerate complex derived from synthetic α-FeOOH. The composition of the metallic alkoxide, calculated from chemical analysis data is: $[(C_3H_5O_3Fe_{0.98}Al_{0.02})]_n$. When this powder is calcined at 1000°C, well-crystallized Al-substituted hematite is produced, whose XRD patterns indicate a shift of the characteristic hematite lines to lower values. The partial (isomorphic) substitution of Fe by Al may also be ascertained from the hydrolysis of the $[(C_3H_5O_3Fe_{0.98}Al_{0.02})]_n$ complex by boiling water; then the XRD and chemical analyses of the resulting product show limited formation of a spinel solid solution. In contrast, hydrolysis of pure iron alkoxide yields high amounts of ferrimagnetic spinel (mainly $FeO \cdot Fe_2O_3$). Some characteristics of the Al-substituted iron alkoxide and of its hydrolysis and calcination products are briefly examined.

INTRODUCTION

Room temperature reactions of glycerol with metal ions yield coordination metallic complexes which are soluble in water and have variable composition [1–3]. In 1970, a high temperature reaction between glycerol and oxides or hydroxides of Co, Zn, Mn and Fe was reported [4]. Crystalline metal–glycerate complexes (alkoxides) resulted from such reactions, carried out at variable temperatures, which depend on the nature of the initial metallic compound employed. These complexes are generally insoluble in water as well as in organic and inorganic solvents, suggesting a polymeric configuration.

The iron alkoxide synthesis is favored at the reflux temperature of glycerol, allowing water to escape from the system and using goethite, α-FeOOH, as the metallic source. Other iron oxy-hydroxides of hydroxides are also completely transformed to an iron–glycerol complex when sub-

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mitted to the above reactions [5,6]. In a second reaction step the iron alkoxide complex may be converted to magnetic iron oxide upon hydrolysis by boiling water. During this conversion a change in color is observed in the solid from green to black.

So far, these reactions have been carried out from pure α-FeOOH as the starting (iron source) material. In the present work we have performed the glyceration reaction employing synthetic Al-substituted goethites, containing up to 9.6 mol% Al. The resulting metallic alkoxides have been studied by X-ray diffraction (XRD), infrared spectroscopy (IR), etc. and their properties were briefly examined. The second reaction step, where such metallic complexes can be converted into spinel materials, is further emphasized.

EXPERIMENTAL

Aluminum-bearing goethites, $Fe_{(1-x)}Al_xOOH$, where x = moles Al (x varies between 0 and 9.6), were prepared according to previous procedures [7] from $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ solutions and controlled precipitation. Aging of the precipitates was carried out at 70°C for 14 days.

Each of these powders (3 g) was thoroughly reacted with water-free glycerol (50 cm^3) at ~ 246°C for 16 h in a flask fitted with a large condenser tube. The resulting solids (first reaction step) were separated by centrifugation, washed with distilled water until free of glycerol (we currently employ a ceric ammonium nitrate test), finally washed with acetone and dried in a vacuum desiccator. Hydrolysis of these solids (second step) was made with boiling water (in excess) for about 90 min. Calcination of the metallic alkoxides, by gradually heating to 1000°C was done in a calibrated muffle, in air.

The parent synthetic goethites, their respective complexes (alkoxides) and the solids resulting from the different treatments (hydrolysis, calcination, etc.) of these metallic alkoxides were analyzed and characterized as follows: aluminum and iron were determined by atomic absorption spectrometry (AAS) (Varian Techtron 1200 unit) with previous dissolution of the sample in hot conc. HCl (total iron and Fe^{2+} were also determined by dichromatometry in the synthetic goethites and derivatives). Carbon and hydrogen microanalyses were performed by an outside laboratory. X-ray diffractograms of random powders were taken with a Philips PW 1730 diffractometer, at a 0.5° 2θ goniometer speed, using FeK_α radiation. Infrared absorption spectra were run with a Perkin-Elmer 567 spectrophotometer, using 0.25% CsI disks. All chemical reagents were of analytical grade. The CsI salt for IR spectroscopy was "suprapur" (Merck) and only spectroscopic grade acetone was used. Water-free glycerol was purchased from Fisher Scientific Company.

RESULTS AND DISCUSSION

The synthesis and properties of multimetallic glycerate complexes, employing Al-bearing synthetic goethites as metallic sources, depend very much on the degree of substitution of Fe by Al in the starting material.

Figures 1 and 2 show the comparative X-ray powder diffractograms of the starting materials and of products from the first and second reaction steps. The X-ray patterns represented in Fig. 1 are of synthetic goethite containing 4.3 mol% Al (a) and of its derivatives (b and c). These three patterns are identical to those corresponding to pure α-FeOOH and its reaction products after the first and second stages, since this degree of Al substitution does not shift the *d* spacings in any of these materials.

The X-ray data of crystalline iron glycerate complex were first reported

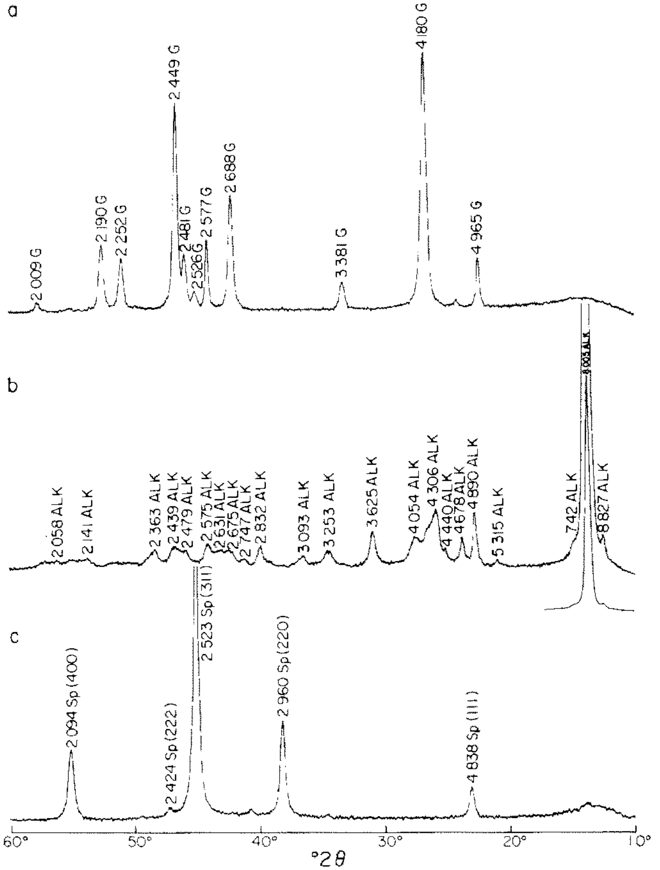

Fig. 1. X-ray diffractograms of: (a) synthetic goethite or goethite containing 4.3 mol% Al; (b) sample (a) reacted with glycerol; (c) samples (b) hydrolysed by boiling water. G = goethite, ALK = alkoxide, Sp = spinel. Spacings are given in Å.

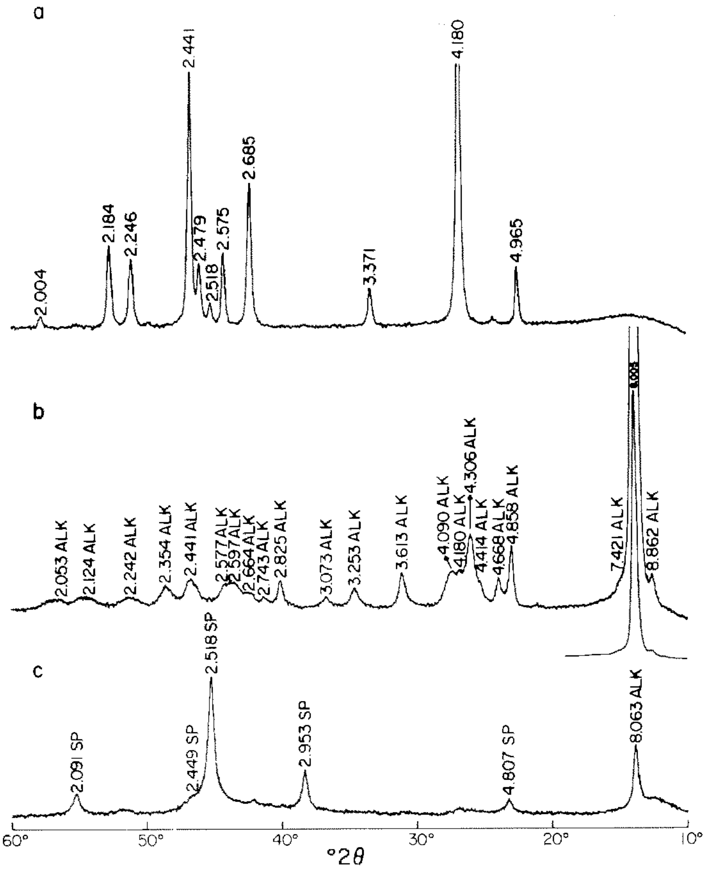

Fig. 2. X-ray patterns of: (a) synthetic $Fe_{0.904}Al_{0.096}OOH$; (b) sample (a) after glyceration reaction; (c) Al-substituted iron alkoxide after hydrolysis. ALK = alkoxide, SP = spinel. Spacings in Å.

by Fuls et al. [5] and by Radoslovich et al. [4]. The diffractogram in Fig. 1b gives the pattern of iron alkoxide showing the strong typical reflection at ~ 8 Å and some atypical lines, appearing eventually at 8.3 and 4.68 Å. No other crystalline phase is detected at this stage; therefore, all the reflections can be attributed to the metallic glycerate complex. As previously observed the iron alkoxide is a soft green solid, containing Fe^{3+} as well as Fe^{2+}. The Fe^{3+}/Fe^{2+} ratio is variable and this is in our opinion one of the factors determining quantitative reproducibility.

Little was known about the mechanism of the hydrolysis of alkoxides [3]. In the second reaction step the hydrolysis of the iron alkoxide yields a black-colored powder which is strongly magnetic and reforms glycerol. Figure 1c shows the X-ray diffractogram of the magnetic powder, displaying a strong reflection at 2.5 Å, accompanied by other lines at 2.96, 2.09 and 4.83 Å. The same maxima have been also reported in the second-stage reaction product of lepidocrocite, γ-FeOOH [6]. These X-ray patterns are characteristic of magnetic spinels which have the structure of magnetite or maghemite. The Fe^{2+} content in the spinels derived from pure goethite is 15.75% according to the dichromatometric determination. Thus, it can be inferred that magnetite, $FeO \cdot Fe_2O_3$ makes up for 75% of the total content in the powder, since Fe^{2+} is not prominent in the spinel structure of maghemite, γ-Fe_2O_3.

In the diffractograms of Fig. 2, the same reaction steps as in Fig. 1 are recorded but using synthetic goethite which contains 9.6 mol% aluminum, $Fe_{0.904}Al_{0.096}OOH$, as starting material. At this degree of Al isomorphic substitution, goethite is again completely transformed into the corresponding metal–glycerate complex, as it can be seen in Fig. 2b where only alkoxide peaks (including the atypical lines at 8.8 and 4.6 Å) are present after the first reaction step. Preliminary results indicate that if the degree of Al substitution in goethite is higher, the latter is not completely transformed.

The Al content found in the alkoxide derived from $Fe_{0.904}Al_{0.096}OOH$ is 1.52% (Table 1). At such Al content, there are significant shifts in the *d* spacings of some alkoxide peaks (Fig. 2b), when compared with those of iron alkoxide derived from pure goethite. The 4.89 and 3.62 Å lines of the latter are shifted to lower positions, namely 4.86 and 3.61 Å, respectively. On the other hand, the shift trend of the 8.83, ~ 8 and 2.83 Å lines is opposite, especially increasing at high Al contents. From these results it can be interpreted that Al substitutes for Fe in the alkoxide structure. This interpretation will be further confirmed by the hydrolysis and calcination results.

The chemical analysis of this Al-bearing iron alkoxide is listed in Table 1. On the basis of these data, the experimental formula derived is: $[(C_3H_{4.85}O_{3.25}Fe_{0.98}Al_{0.09})]_n$, where *n* is most probably 4. Since these sorts of solids are insoluble in common solvents and have a refractory nature (see calcination results) a molecular weight determination was not intended. The most plausible calculated formula corresponds to: $[(C_3H_5O_3Fe_{0.98}Al_{0.02})]_n$.

In general, the glyceration reaction and alkoxide synthesis can be written as follows:

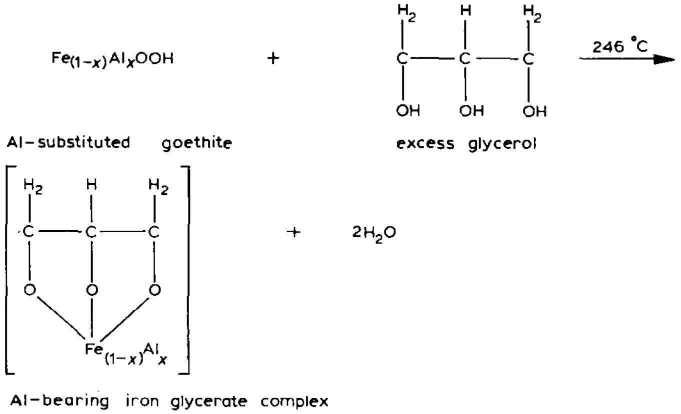

TABLE 1

Chemical analysis [a] of $[(C_3H_5O_3Fe_{0.98}Al_{0.02})]_n$ alkoxide [b]

Component	Al	$Fe_{(total)}$	Fe^{2+}	C	H
Composition (%)	1.52	36.56	7.81	24.16	3.23

[a] Corrected for H_2O^- content on separate samples.

[b] Oxygen content calculated by difference.

The basic mechanism of alkoxide formation involves condensation and redox reactions. As in the pure iron alkoxide structures, Fe is present in both oxidation states, and the initial glycerolic structure is preserved during rearrangement [5]. During this rearrangement, the metallic octahedral layer of goethite can accommodate carbon, through oxygen linkages, forming metallic alkoxide linkages, M–O–C. In our compounds, the metallic component M represents the isomorphic substitution of Fe by Al.

Figure 3 presents the IR absorption spectra of synthetic $Fe_{0.904}Al_{0.096}OOH$ and its metallic glycerate derivative. The Al-goethite spectrum shows absorptions at 895 and 798 cm^{-1} (Fig. 3a) compared to Fe–O–H diagnostic bands of pure α-FeOOH which appear, respectively, at 885 and 795 cm^{-1}. There is no shift, however, in the absorption maxima of the metallic alkoxides derived from Al-substituted goethites. This can be seen, for example, from the spectrum of the metallic alkoxide (Fig. 3b) displaying frequencies at the same positions as those exhibited by the iron alkoxide of pure goethite [5]. Particle size and morphology are important factors to consider in the interpretation of IR spectra of iron oxides. The IR results of iron glycerate complexes may be also influenced by the Fe^{2+}/Fe^{3+} ratio, since the several oxidation states introduce variations in the crystal lattice, provoking changes in the rigidity and configuration of the structural units [4].

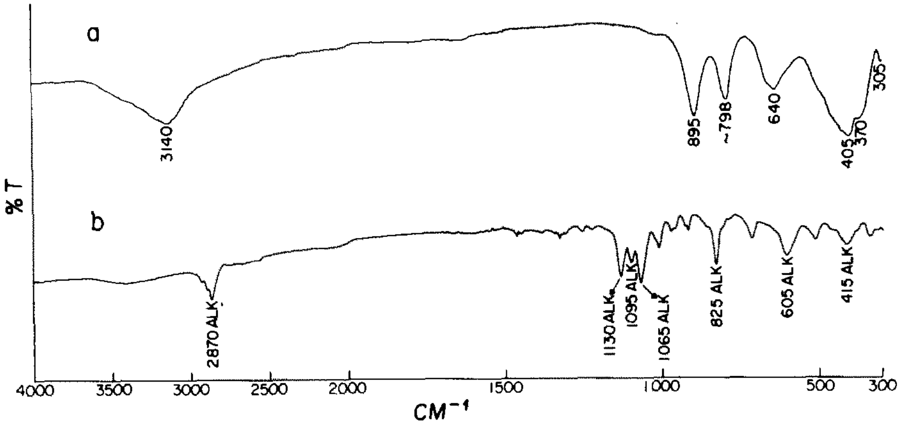

Fig. 3. IR spectra of: (a) Al-bearing goethite, $Fe_{0.904}Al_{0.096}OOH$; (b) sample (a) reacted with glycerol. ALK = alkoxide.

The IR spectrum of the liquid fraction separated after glyceration (first reaction step) of the Al-substituted goethites (on Irtran-2 windows), reveals only absorption bands of pure glycerol. Analytical tests were negative for Al and gave Fe traces in this fraction. Thus, the presence of soluble metallic alkoxide is not significant here.

In contrast to the solid obtained from the hydrolysis of pure iron alkoxide, the hydrolysis (second reaction step) of $[(C_3H_5O_3Fe_{0.98}Al_{0.02})]_n$ produced a dark-brownish powder, weakly attracted by a magnet. The X-ray pattern of this powder (Fig. 2c) indicates that a mixed spinel is the major crystalline phase formed, since the *d* spacings shift to lower values compared to those characteristic of pure iron spinel (Fig. 1c). These shifts suggest that solid solution of Al_2O_3 takes place in the spinel Fe_3O_4 structure, which can explain the decrease in magnetic attraction of such Al-bearing Fe spinel materials. The presence of Al also weakens the magnetic attraction of magnetite obtained from thermal treatment of natural goethites in alkali-iodide disks [8].

The figures also show proportional decrease in all X-ray line intensities with Al substitution (Fig. 2c), indicating a diminution in the amount of spinel (SS) formation. This can also be inferred from the Fe^{2+} content found

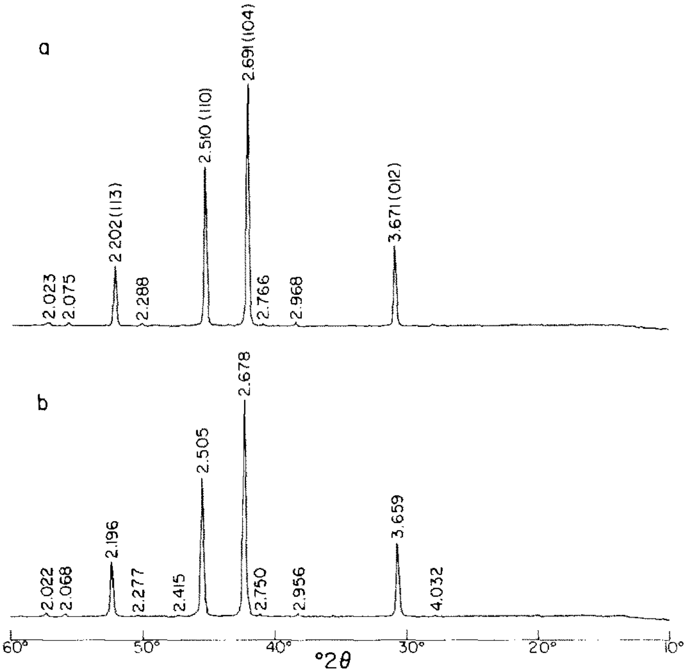

Fig. 4. X-ray diffratograms of hematites obtained after calcination at 1000°C of: (a) synthetic pure iron glycerate; (b) $[(C_3H_5O_3Fe_{0.98}Al_{0.02})]_n$ alkoxide. Spacings are given in Å.

in this product (5.03% compared to 15.75% Fe^{2+} determined in the spinel derived from pure Fe alkoxide). Small amounts of alkoxide finally remaining after the hydrolysis (see peak at 8.06 Å) do not change the overall picture. The Al content (found by AAS) in these Al-bearing spinels is 2.72% and it is related to the Al content of the corresponding metallic alkoxides as well as to that found in the original Al-substituted goethite (3.05% Al).

Additional evidence for the substitution of Fe by Al in our metallic glycerate complexes is furnished by the calcination results of these complexes. Calcination of both complexes $[(C_3H_5O_3Fe_{0.98}Al_{0.02})]_n$ and the pure iron alkoxide (for comparison), was carried out in air, to 1000°C, at this preliminary stage. As a consequence of this treatment, the green soft alkoxide solids were turned to hard, stable powders of variable pink coloration. These properties and the changes in particle size of the reaction products are further investigated.

The *d* spacings, peak widths and intensity ratios in the X-ray traces of the calcination products (Fig. 4) correspond to well-crystallized hematites. These patterns show, moreover, a shift to lower values of the *d* spacings of hematite obtained from the $[(C_3H_5O_3Fe_{0.98}Al_{0.02})]_n$ complex, particularly the (012), (104) and (110) strong reflections.

These shifts are due to the isomorphous substitution of Fe by Al in the hematite crystal and are in agreement with other data on this sort of substitution in iron oxides. The isomorphous substitution of Fe for Al in the hematite crystal must be inherited from the corresponding substitution in the metallic alkoxide. A similar relation is kept between Al-bearing Fe spinel (solid solution) resulting from the second reaction step and the Al-substituted Fe alkoxide from which it is derived.

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