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INFLUENCE OF ADSORBED ANIONS ON THE DEHYDROXYLATION OF SYNTHETIC GOETHITE

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The influence of surface structure on the dehydroxylation of synthetic goethite has been studied using heat-flux differential scanning calorimetry. Adsorption of various anions by goethite causes a progressive change in both the amount and environment of surface hydroxyls and this is reflected by changes in the DSC curves. These alterations indicate the importance of surface features in determining the course of dehydroxylation and further suggest that, in studies of this type of reaction, the use of synthetic products known to be free of surface contaminants could prove to be of great value in understanding dehydroxylation mechanisms.

The dehydroxylation reaction that occurs on heating goethite (α-FeOOH) is normally observed on the differential thermal analysis (DTA) curve as a single clearly defined endothermic peak in the temperature range 250°–400°, the actual temperature depending upon the particle size and crystallinity of the sample [1]. Although the majority of the curves reported in the literature show only a single peak, variations have been observed. In some instances a double peak is obtained and a recent investigation using a series of synthetic goethite samples [2] has indicated that the tendency for a double peak system to occur increases as the particle size decreases. Another type of curve with a more complex peak system has been the subject of a preliminary report on the influence of adsorbed phosphate on the dehydroxylation of synthetic goethite [3]. This study has now been extended to include a wider range of anions.

Experimental

Materials

The goethite sample was synthesised using the method described by Atkinson et al. [4]. A partially neutralised, aqueous solution of iron (III) nitrate was aged at room temperature for 50 h, then adjusted to pH 11.5 with aqueous sodium hydroxide solution. The resulting suspension was then maintained at 60° for 5 days in order to promote crystal growth. The goethite obtained using an OH/Fe molar ratio of 2.0 during the initial aging consisted of lath-shaped crystals, the predominant (100) face having approximate dimensions of 150 by 20 nm.

The fluoride-saturated sample was prepared by the addition of an excess of dilute hydrofluoric acid solution (0.005 *M*) to the goethite, followed by evaporation of the suspension to dryness on a water bath. In this way complete exchange of fluoride for singly co-ordinate surface hydroxyl was ensured, excess HF being lost by volatilisation. A similar method was employed for the other anions except that stoichiometric proportions of acid and goethite were used to avoid adsorption of excess acid on other sites.

Methods

Differential thermal analysis was carried out on 25 mg samples using a Du Pont 900 Differential Thermal Analyzer equipped with a 1200° High Temperature cell. The samples were heated at 20 K min^{-1} in an atmosphere of nitrogen flowing at 50 cm^3 min^{-1} and the curves recorded with a ΔT sensitivity of 0.008 mV in^{-1}.

The heat-flux differential scanning calorimetry (DSC) curves were obtained using 10 mg samples in the Du Pont 900 DSC cell, a heating rate of 10 K min^{-1}, a ΔT sensitivity of 0.2 K in^{-1} and a T axis sensitivity of 50 K in^{-1}. The atmosphere was again nitrogen flowing at 50 cm^3 min^{-1}.

Thermogravimetry was carried out using a Stanton Redcroft TG 750 thermobalance. The 10 mg sample was heated at 10 K min^{-1} in a nitrogen atmosphere flowing at 20 cm^3 min^{-1}.

Results and discussion

The heat-flux DSC curve for the dehydroxylation of synthetic goethite shows a complex peak system occuring over the temperature range 150–300° (Fig. 1). Before the principal peak at 260° there is a series of small shoulders at 180, 210 and 235°. Treatment of the goethite with different anions produces only slight changes in the temperature of the principal peak but significantly alters the smaller peaks; indeed, in some instances they are eliminated. On the curves for the fluoride-, chloride- and nitrate-treated samples only one small effect at 235, 230 and 215°, respectively, remains and the dehydroxylation peak retains the asymmetry of that for untreated sample. With the two divalent anions, sulphate and hydrogen phosphate, the asymmetry is much less marked and there is no indication of any of the smaller peaks or inflections noted on the curves for the other samples.

These changes in the thermal behaviour of goethite must be associated with the mechanism by which the anions are adsorbed. In the dehydrated system, all the anions are adsorbed by a ligand exchange mechanism but, whereas a monodentate species, such as fluoride, chloride or nitrate, replaces one singly co-ordinated surface hydroxyl, the divalent anions, sulphate and hydrogen ortho-phosphate, function as bidentate ligands and replace two adjacent hydroxyl groups [5]. Since these reactions are limited to the surface, it must be concluded that the nature of the surface plays an important role in determining the course of the dehydroxylation reaction.

Before the exact nature of this dependency can be elucidated a number of other observations have to be considered. It is already known that the surface of the predominant (100) face of synthetic geothite (Fig. 2) contains singly, doubly and triply co-ordinated hydroxyl groups [6] and from an examination of the structure it is clear that all the surface hydroxyls will belong to one of these three types. Thus, the three small peaks observed on the DSC curve for the untreated sample (Fig. 1a) are probably due to dehydroxylation of these surface hydroxyls. Although previous studies using a number of thermoanalytical techniques have indicated that the dehydroxylation of brucite, $Mg(OH)_2$, is initiated at the surface [7], this is the first instance in which the dehydroxylation of surface hydroxyls has been observed on the DSC curve.

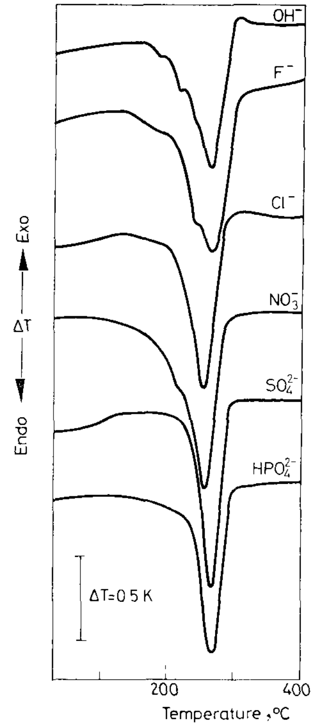

Fig. 1. Heat-flux DSC curves for synthetic goethite samples saturated with anion indicated on curve

It is also interesting to note that the surface dehydroxylation reactions are, to some extent, reversible. Thus, if heating is stopped immediately after the first shoulder at 190°, the sample cooled in the DSC cell and then reheated, the peak occurs at the same temperature with approximately the same area after correction for background effects. Each of the other two shoulders is reversible in the same manner, although heating beyond the second shoulder causes an irreversible loss of the first, and the second becomes irreversible after heating to the third. These observations suggest that if removal of a particular type of hydroxyl is complete then irreversibility results, since it is likely that overlap of the loss of the various hydroxyl types occurs.

Finally, the influence of the various anions on the DSC curves parallels the extent to which the surface is stabilised by their adsorption. Clearly, the bidentate species such as sulphate and hydrogen orthophosphate will be most effective and with the additional hydrogen bonding to other surface hydroxyls and oxide ions, respectively, the stability of the surface hydroxyls will be further enhanced.

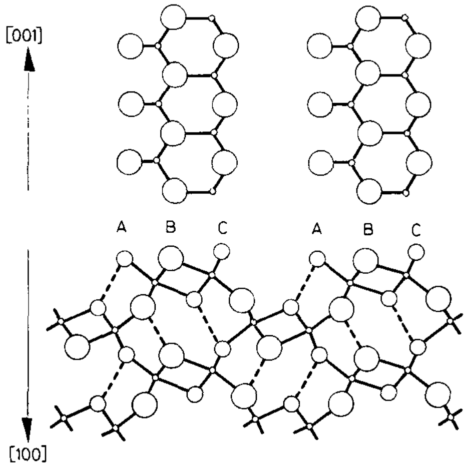

Fig. 2. Plan (a) and section (b) of the predominant (100) face in synthetic goethite, *A* representing singly co-ordinated, *B* doubly co-ordinated and *C* triply co-ordinated hydroxyl

In contrast to DSC, TG revealed no significant differences in the initial stages of the dehydroxylation reaction for any of the anions but differences were observable in the later stages (Fig. 3). Thus, in addition to the weight losses representing dehydration and dehydroxylation a third weight loss occurred at 400–500° and 600–700° for the nitrate- and sulphate-treated samples, respectively.

Since the weight loss for the sulphated sample occurs at a temperature in excess of the upper limit of the heat-flux DSC cell the samples were also examined by DTA (Fig. 4). The small shoulders on the main peak are not so well-resolved with DTA as with heat-flux DSC, the only curve to show an inflection being that for the untreated sample which gave a shoulder at 200°. Apart from this shoulder the dehydroxylation peaks for all six samples are virtually identical. Similarly, all the curves show the small thermal effect at 670–680° associated with a change in the magnetic properties of the dehydroxylation product, α-Fe_2O_3 [1]. However, small differences are observable, the curves for the fluoride- and chloride-saturated samples exhibiting a small exothermic effect at 410 and 380 °C, respectively, and those for the nitrate- and sulphate-treated samples an endothermic peak at 410 and 660°, respectively. No peak, apart from that at 675°, appears on the curve for the phosphated goethite in the temperature range 400 to 1000°. Since infrared absorption spectroscopy shows that sulphate and nitrate disappear from the system in the temperature range of the respective DTA peaks, it can be deduced that the additional peaks represent loss or decomposition of the saturating anion. The absorbed phosphate, however, exhibits remarkable thermal stability, in agreement with the observations of Parfitt et al. [8], who noted that the HPO_4^{2-} ion forms a particularly stable complex with the surface of goethite.

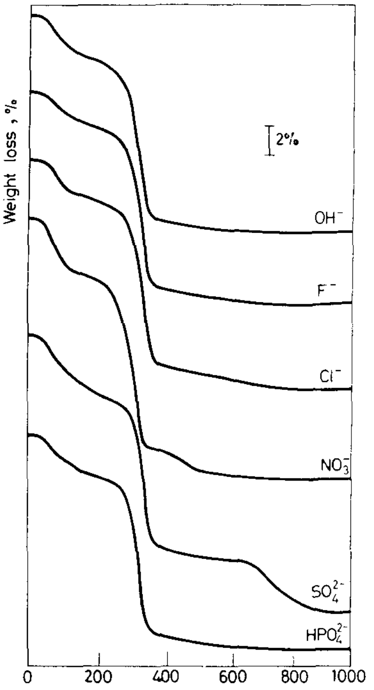

Fig. 3. TG curves for synthetic goethite samples saturated with anion indicated on curve

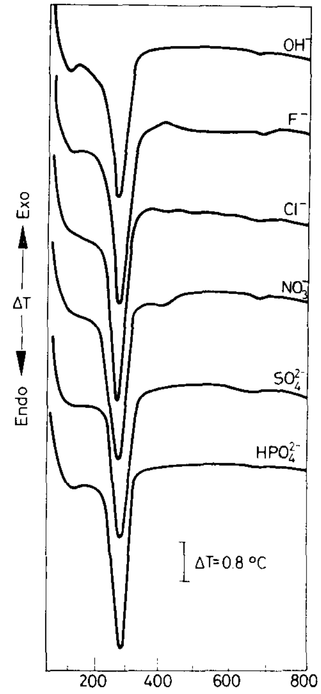

Fig. 4. DTA curves for synthetic goethite samples saturated with anion indicated on curve

For the untreated sample a dehydroxylation weight loss of 11.8% was obtained, compared with a theoretical value of 10.1%. The difference between these two values probably reflects (a) an excess hydroxyl content due to protonation of surface oxide ions and (b) the contribution of water co-ordinated to exposed iron (III) ions at crystal edges. However, for the treated samples the saturating anion is lost immediately after dehydroxylation and the respective weight losses cannot be resolved (Fig. 3). In view of this, the total percentage weight loss for both dehydroxylation and anion loss has been calculated for all the reactions involving monodentate ligands and plotted against the formula weight of the anion (Fig. 5). A linear relationship was obtained and the intercept of this line on the ordinate gives the percentage weight loss due to dehydroxylation of non-exchangeable hydroxyl (both surface and bulk). Subtraction of this value from the weight loss of the untreated goethite gives a value of 550 μmol of exchangeable hydroxyl per gram of sample, in good agreement with the anion exchange capacity of 500 μmol g^{-1} calculated by Russell et al. [5].

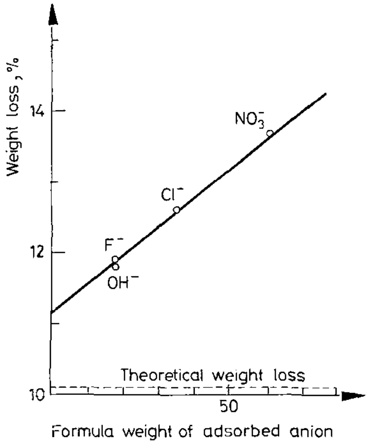

Fig. 5. Plot of percentage weight loss due to dehydroxylation and anion decomposition against formula weight of adsorbed anion

Conclusions

The increasing sophistication of thermal analysis, in particular differential scanning calorimetry, enables significant differences in the dehydroxylation peak of synthetic goethite to be observed when the surface is modified by adsorption of different anions. These differences include changes in the shape of the main dehydroxylation peak as well as modifications to three smaller peaks observed on the curve for the untreated sample. It seems likely that these small peaks are due to dehydroxylation of the surface hydroxyl groups. The results provide further evidence on the importance of surface structure in determining the mechanism of dehydroxylation reactions and suggest that the use of well-characterised synthetic products known to be free of surface contaminants could prove to be of great value in understanding dehydroxylation mechanisms.

References

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Résumé — On a étudié par analyse calorimétrique différentielle (DSC) l'influence de la structure de surface sur la déshydroxylation de goethites synthétiques. L'adsorption d'anions divers par la goethite entraîne une variation progressive à la fois de la quantité et de l'environnement des hydroxyles de surface, ce qui se reflète dans les variation des courbes DSC. Ces altérations indiquent l'importance des propriétés de surface quand il s'agit de déterminer le cours de la déshydroxylation et suggèrent en outre que l'emploi de produits synthétiques connus comme étant exempts de contaminants de surface, pourrait être de grande valeur dans des études de ce type de réactions, pour comprendre les mécanismes de déshydroxylation.

Zusammenfassung — Der Einfluß von Oberflächenstrukturen auf die Dehydroxylierung synthetischer Goethite wurde unter Anwendung der Wärmestrom-Differential-Abtastkalorimetrie untersucht. Die Adsorption verschiedener Anione durch Goethit verursacht eine progressive Änderung sowohl der Menge als auch der Umgebung der Oberflächenhydroxyle und dies wird durch die Änderungen der DSC-Kurven wiedergespiegelt. Diese Änderungen zeigen die Bedeutung der Oberflächenbeschaffenheiten bei der Bestimmung des Verlaufs der Dehydroxylierung und weisen ferner darauf hin, daß bei Studien dieses Reaktionstyps der Einsatz synthetischer Produkte, die bekanntlich frei von Oberflächenverunreinigungen sind, sich hinsichtlich der Klärung der Dehydroxylierungsmechanismen als sehr wertvoll erweisen könnte.

Резюме — С помощью теплово-поточной дифференциальной сканируйющей калориметрии было изучено влияние структуры поврежности на дегидроксилирование синтетического гоэтита. Адсорбция гоэтитом различных анионов приводит к изменению как количества, так и окружения поверхностных гидроксилов и это отражается изменениями кривых ДСК. Эти изменения означают важность особенностей поверхности в определении хода дегидроксилирования и кроме того предполагает, что при изучении этого типа реакции, использование синтетических веществ, свободных от поверхностных загрязнений, может оказать большое значение для понимания механизмов дегидроксилирования.