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OBSERVATION OF SURFACE CHARACTERISTICS BY DSC AND DTA

R. C. MACKENZIE, E. PATERSON and R. SWAFFIELD

The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, Scotland

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The three types of hydroxyl groups on surfaces of goethite crystals have previously been shown to be distinguishable by inflections on the leading edge of the dehydroxylation endotherm on DSC curves. The same inflections can be observed on DTA curves and it is now established that the main prerequisite for their observation is rapid removal of water vapour from particle surfaces, although small particle size (i.e. large surface area) and uncontaminated surfaces are also important.

DSC studies of the dehydroxylation of synthetic goethite [1, 2, 3] have revealed that the dehydroxylation endotherm is complex, having three small and partially reversible peaks superposed on its leading edge. This is in sharp distinction to the normal DTA behaviour of goethite – namely, a sharp single endotherm [2, 4] – and has been attributed to the existence on particle surfaces of hydroxyl groups with three different types of bonding [1, 2]. DSC has also revealed that the dehydration endotherm can be complex, presumably because of the higher binding energy of the first layer (monolayer) of sorbed water molecules [3]. These observations raise the intriguing question of whether these phenomena can be observed only on DSC curves or whether, with suitable choice of experimental conditions, they would also be revealed by DTA. The present investigation was designed to answer this question.

Experimental

The synthetic goethite used and its method of preparation have already been described [2] and need no further consideration.

Three DTA and DSC instruments were used with various types of specimen holder:

(a) The Du Pont 900 Thermoanalyzer with:
  (i) the heat-flux DSC cell;
  (ii) the high-temperature (1200°) cell with platinum cups sitting on the thermocouple junctions.

(b) The Perkin–Elmer DSC-2 power-compensation instrument.

(c) The Stone 202 system with:
  (i) the SH-11BR ring-thermocouple specimen holder with platinum flat pans;

(ii) the SH-11BP specimen holder with nickel cups sitting on the post-type thermocouples;
(iii) the SH-8BE solid-block specimen holder with exposed thermocouples inside and gas flow through the specimens.

Sample sizes and experimental conditions were varied as described below, but a nominal heating rate of 10 degree/min was maintained throughout.

Results and discussion

The heat-flux DSC curve [1, 2, 3] for the goethite is compared with a power-compensation DSC curve in Fig. 1. Both of these show the three peaks at *ca* 185, 225 and 240° on the leading edge of the dehydroxylation endotherm. The heat-flux DSC curve (Fig. 1a) also shows the hygroscopic moisture peak and a very small effect at about 150° that is invariably present and may well correspond with the "monolayer" peak previously observed by power-compensation DSC [3]. This was not observed on the power-compensation DSC curve in Fig. 1b, as, at the high sensitivity used, the base-line drift was very considerable (note the slope of the base line before the peak).

Examination of the two DSC curves previously published [1, 2] suggested that the resolution of the three small peaks superposed on the dehydroxylation endotherm improved with smaller sample sizes. For this reason, very small samples were used for DTA investigation with the Stone flat-pan, ring-thermocouple system, with the results shown in Fig. 2. Clearly, the best resolution is obtained for the 1 mg sample (curve A) and resolution decreases as sample mass increases

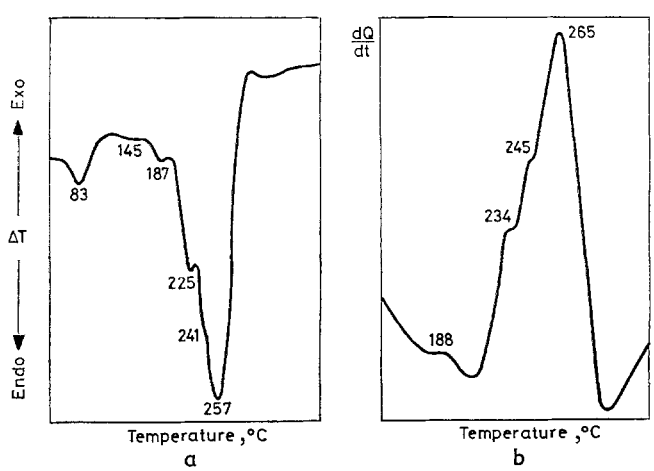

Fig. 1. (a) Heat-flux DSC curve for synthetic goethite on Du Pont 900 Thermoanalyzer (5.2 mg sample; heating rate 10 degree/min). (b) Power-compensation DSC curve for synthetic goethite on Perkin–Elmer DSC-2 differential scanning calorimeter (2.5 mg sample; heating rate 10 degree/min)

(curves B, C, D). For similar sample sizes, although the peaks are just observable, resolution is markedly poorer in deep nickel cups on post-type thermocouples in the Stone system (Fig. 3) and even worse in the deep platinum cups of the Du Pont high-temperature cell (Fig. 4), which does not have a surrounding metal shield. In Fig. 2 the sudden increase in the temperature of the hygroscopic moisture peak from 60 on curve C to 105 on curve D appears to be due to the thicker layer of sample preventing egress of moisture and its removal by the gas stream.

These experiments were all performed in flowing nitrogen and the results suggest that the main prerequisite for resolution of the peaks is the rapid removal from particle surfaces of the water vapour formed by condensation of surface OH groups and that distinctions between DTA and DSC are irrelevant. In order to test this hypothesis, some experiments were performed in the Stone solid-block specimen holder, which might be regarded as being of the "classical" type for DTA but which permits gas flow through the specimen during the determination, thus removing decomposition products rapidly. To enhance the thermal effect from a small sample, sandwich-packing was used, a layer of the sample around the thermocouple junction being sandwiched between two layers of reference material (calcined alumina). In the absence of glas flow no irregularities, apart from a shoulder at 210°, were observed on the dehydroxylation endotherm (Fig. 5, curve D) but with nitrogen flowing through the sample during the determination the usual com-

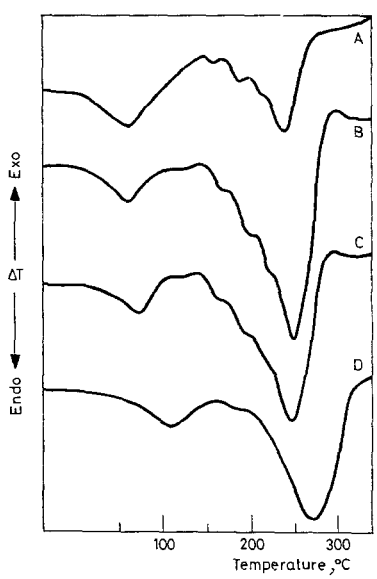

Fig. 2. DTA curves for synthetic goethite on Stone SH-11BR ring-thermocouple specimen holder with platinum pans at a heating rate of 10 degree/min with a nitrogen-flow of 25 cm^3/min: A) 1 mg sample; B) 5 mg sample; C) 10 mg sample (1/5 sensitivity); D) 25 mg sample (1/5 sensitivity)

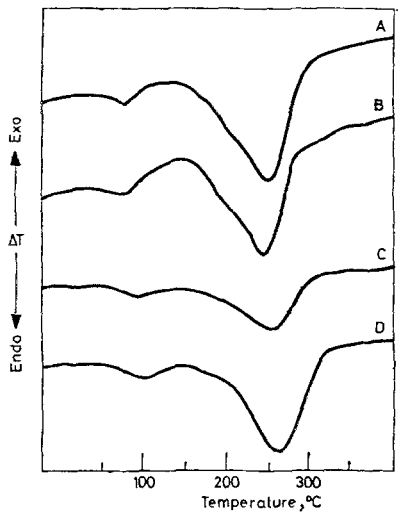

Fig. 3. DTA curves for synthetic goethite on Stone SH-11BP post-type specimen holder with nickel cups at a heating rate of 10 degree/min with a nitrogen-flow of 25 cm^3/min: A) 10 mg sample; B) 10 mg sample diluted with 10 mg reference material (alumina); C) 25 mg sample (1/5 sensitivity); D) 50 mg sample (1/5 sensitivity)

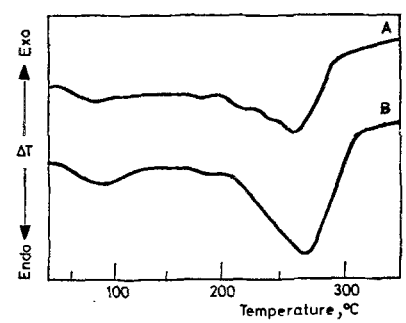

Fig. 4. DTA curves for synthetic goethite on Du Pont 900 Thermoanalyzer with high-temperature (1200 °C) head and platinum cups at a heating rate of 10 degree/min with a nitrogen-flow of 200 cm^3/min: A) 5 mg sample; B) 25 mg sample (1/5 sensitivity)

plement of small peaks appeared (curve C). With the same size of sample diluted with reference material and the same rate of gas flow, the peak size was, as usual, drastically reduced (curve *B*), but the same set of peaks was observed, resolution being slightly poorer because of the small peak size. However, increasing the gas-flow ten-fold, giving, probably, fluidized bed conditions for both the sample and reference, gave a very wide dehydroxylation peak with all the minor peaks well resolved. In this instance, not only are particles well separated from each other, but the water formed by condensation of surface OH groups would be removed

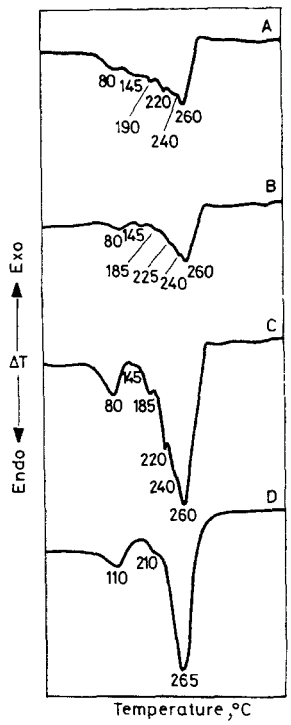

Fig. 5. DTA curves for synthetic goethite on Stone SH-8BE solid-block specimen holder at a heating rate of 10 degree/min: A) 15 mg diluted with 160 mg reference material (alumina) with nitrogen flowing through the sample at 250 cm^3/min; B) the same as A) but with a nitrogen flow of 25 cm^3/min; C) 15 mg sandwich-packed around the thermocouple junction with nitrogen flowing through the sample at 25 cm^3/min; D) 15 mg sandwich-packed around the thermocouple junction in static air

continuously. The very broad dehydroxylation effect observed could be contributed to by the fact that the water vapour pressure around each particle is extremely low coupled possibly with a range in particle size, the effect of which would be occluded when the particles are in close contact.

An attempt to obtain a DTG curve for the sample on the Stanton STA-780 DTA-TG-DTG system was only partially successful, as the high sensitivity necessary with the very small sample used made it very difficult to distinguish true deflections from random variations: however, small variations in the initial slope of the DTG peak could readily be associated with the dimples on the DTA curve, indicating that water loss was involved.

In addition to rapid removal of decomposition products (in this instance water vapour) from the surface, two other conditions are probably necessary for observation of surface characteristics such as those noted above. One is that, as has already been clearly established [1, 2], the surface must be chemically clean. The

other can only be inferred at present, but it would appear that the particles must be small so that the ratio of surfae to lattice OH groups is fairly large. The present sample of goethite was certainly fine grained, the electron microscope showing lath-shaped particles of about 150×20 nm in size and specific surface area measurements giving a value of about 78 m^2/g.

Conclusions

Peaks due to removal of surface hydroxyl groups from particles of synthetic goethite can be observed on both DTA and DSC curves provided that (a) the decomposition product (water) is rapidly removed from particle surfaces by using small samples well exposed to the enveloping gas stream or by adequate gas flow through a relatively small sample, (b) the surface is free from contaminating ions that can replace surface OH groups and (c) the ratio of surface area to particle volume is high. Similar surface phenomena may well yet be observed for other materials provided the same experimental conditions prevail.

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References

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ZUSAMMENFASSUNG — Bei den drei Typen von Hydroxylgruppen an den Oberfläche von Goethitkristallen wurde zuvor festgestellt, daß sie durch den Wendepunkt an der Leitkante der Dehydroxylierungs-Endothermen an den DSC-Kurven zu unterscheiden sind. Dieselben Wendepunkte können auch an DTA-Kurven beobachtet werden und es steht nun fest, daß die Hauptvoraussetzung ihrer Beobachtung in der schnellen Entfernung des Wasserdampfes von der Teilchenoberfläche besteht, obwohl die kleine Teilchengrösse (d. h. eine grosse spezifische Oberfläche) und unkontaminierte Oberflächen auch von Bedeutung sind.

Резюме — Ранее было показано, что на поверхности кристаллов гоэтита могут быть различимы три типа гидроксильных групп исходя из инфлексий на главном конце эндотермы ДСК-кривых. Те же самые инфлексии наблюдались ва ДТА-кривых и теперь установлено, что главной предпосылкой их обнаружения является быстрое удаление паров воды из поверхности честиц. Размеры маленьких частиц (т.е. большая площадь поверхности) и незагрязненность поверхностей также важны.