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DIFFERENTIAL THERMAL ANALYSIS - EVOLVED GAS ANALYSIS OF SYNTHETIC GOETHITE

CHR. J.W. KOCH
Chemistry Department, Royal Veterinary and Agricultural University,
DK-1871 Copenhagen V. (Denmark)

ABSTRACT

Samples of synthetic goethite have been studied by combined DTA-EGA. The total CO_2 content of the samples ranged between 1.0 and 2.7 %wt. The origin of the evolved CO_2 is discussed and it is proposed that the samples contain CO_2 as surface complexes and incorporated in the crystal structure.

INTRODUCTION

Synthetic goethite (α-FeOOH) has been intensively studied for many years as a model compound for the interfacial properties of iron oxides (ref.1). The capability of iron oxides to strongly adsorb CO_2 has been known for a long time (refs.1,2,3) and from the work of Evans et al. (ref.4) it appears that CO_2 greatly influences the interfacial properties of goethite. However, due to the absence of quantitative data on the content and binding forms of CO_2 in the studied samples, there is still great uncertainty about the possible influence of CO_2 on the interfacial properties of goethite.

In the present work different samples of goethite have been studied by DTA-EGA in an attempt to obtain more information on its interaction with CO_2. From the literature it appears that no such study has been undertaken previously.

MATERIALS AND METHODS

The studied samples were prepared using the procedure of Atkinson et al. (ref.5) and by aging of iron nitrate solutions at different OH/Fe ratios. Details for the preparation of samples 2 and 3 are given in refs.6,7. Samples 5 and 6 were prepared similar to sample 1 (ref.6), but at an OH/Fe ratio of 2.0 and using aging periods of 215 and 450 days respectively.

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DTA-EGA was carried out using a Stanton-Redcroft 673-4 apparatus with Pt-Rh thermocouples and Pt crucibles using Al_2O_3 as reference. The evolved CO_2 and H_2O were detected by an Analytical Development Co. infrared analyzer having sensitivity ranges 0-1000 ppm CO_2 and 0-10000 ppm H_2O. $NaHCO_3$ was used as standard for the determination of CO_2. Heating of the sample was carried out at a rate of 10 ^oC per min. in an atmosphere of N_2 (analytical quality) flowing at 250 cm^3 per min. A DTA sensitivity of 50µV was used.

The specific surface areas of the samples were determined from H_2O adsorption at $p/p_0 = 0.2$ (Table 1). Further investigations of the samples were carried out by X-ray diffraction, Mössbauer spectroscopy and infrared spectroscopy and revealed no other phase than goethite in the samples (refs.6,7 and unpublished results). However, the presence of a small amount of adsorbed nitrate in samples 5 and 6 was detected by infrared spectroscopy.

RESULTS AND DISCUSSION

In Fig. 1 is shown the DTA-EGA curves of sample 6. The DTA curve shows a weak, broad endotherm at 115 ^oC, a strong endotherm at 265 ^oC followed by an exothermal peak at 305 ^oC. The H_2O-EGA curve shows a weak, broad peak at 125 ^oC and a strong peak at 275 ^oC with a small shoulder at approx. 370 ^oC. It is noted that the H_2O-EGA peaks are very broad and that there is a substantial amount of H_2O released from the sample up to a temperature of approx. 500 ^oC. The weak endothermal peak is mainly caused by desorption of H_2O from the surface of the crystallites and the strong endothermal peak is associated with the dehydroxylation of the sample ($2\alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2O_3 + H_2O$) (ref.8). The broadening of the H_2O-EGA curve is caused by the simultaneous processes of formation of micropores in the crystallites and diffusion of the H_2O to the surface (ref.9). The reaction causing the exothermal peak is at present not understood. It has been suggested that it is associated with a recrystallization process or physical changes of the sample (ref.8). With minor variations of peak positions the DTA and H_2O-EGA curves of sample 6 (Fig. 1) are also typical of the other samples. However, the exothermal peak of sample 2 is very weak (not shown).

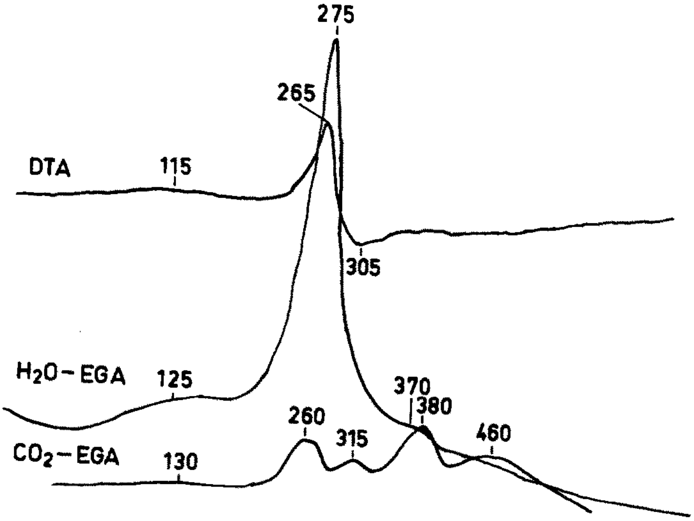

Fig. 1. DTA-EGA curves of sample 6, peak position on curves are given in °C, sample weight: 60.7 mg.

In Fig. 2 is shown the CO_2-EGA curves of samples 2,5 and 6. From these curves the content of CO_2 in the samples was calculated (Table 1). It is seen that the curves exhibit several broad peaks varying both in the relative intensity and position of the peaks. The most notable differences between the samples are the absence of the peak at approx. 315 °C and the development of two peaks at approx. 435 and 475 °C on the curve of sample 2. Sample 4 exhibits a pattern similar to samples 5 and 6.

From previous investigations (ref.3) it is expected that the samples contain adsorbed CO_2 at the surface. However, as seen from Table 1, there is no correlation between the total CO_2 content and the specific surface area of the samples. This suggest that not all the CO_2 of the samples originates from an adsorbed complex. Although the thermal stability of the surface complex of CO_2 on goethite is not known, it could be expected to be relatively unstable as Russell et al. (ref.3) reported that it could be destroyed by evacuating the sample at temperatures close to room

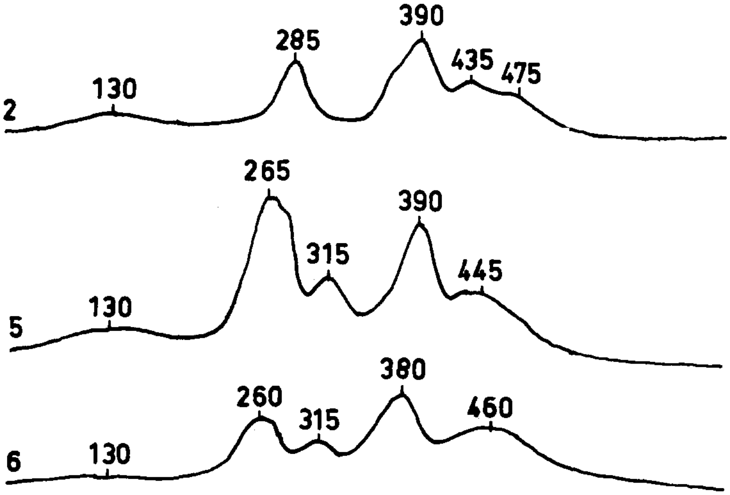

Fig. 2. CO_2-EGA curves of samples 2,5 and 6, peak position on curves are given in ^oC, note different sample weights: 106.2, 125.3 and 60.7 mg respectively.

TABLE 1

CO_2 content and specific surface area,S, of the samples, 130-CO_2 designates the CO_2 with peak temperature at approx. 130 ^oC.

Sample	Total CO_2,%wt	130-CO_2,%wt	S,m^2/g
2	1.1	0.1	49
3	1.0	-	-
5	1.9	0,3	117
6	2.7	0.2	102

temperature. From Fig. 2 it is seen that the CO_2-EGA curves of all the samples exhibit broad peaks at approx. 130 ^oC. The amount of CO_2 evolved at this temperature - designated 130-CO_2 in Table 1 - is reasonably correlated to the specific surface area of the samples. Based on this correlation it is proposed that the surface complexes of CO_2 are given off from the sample over a broad temperature range with a maximum at approx. 130 ^{o}C.

The major fraction of the CO_2 in the samples (between 90 and 80%) is thus not due to surface complexes. It is worth to consider the possibility that the CO_2 could originate from a contamination of the samples. However, investigation of the samples using other techniques (see above) did not reveal the presence of contaminating phases. Based on this finding it is proposed that the major fraction of the CO_2 is due to the presence of a complex form of CO_2 within the crystals of goethite.

No information is at present available on the binding form of CO_2 within the crystals. It is possible that the CO_2 is bonded in several different forms. The different maxima observed on the CO_2-EGA curve could be explained from this. However, it should be noted that the major part of the CO_2 is evolved from the samples at temperatures at and above the starting of the decomposition of goethite into hematite. It is therefore likely that the shape of the CO_2-EGA curve would be influenced more by the physical characteristics of the transformation of goethite than by the bonding of CO_2 within the crystals. Support for this explanation is found from the fact that the two major peaks of the CO_2-EGA curves at approx. 270 and 390 ^{o}C both are simultaneous with the major peak and shoulder on the H_2O-EGA curve (Fig. 1).

No explanation for the absence of the peak at approx. 315 ^{o}C on the CO_2-EGA curve of sample 2 can be given presently. However, the simultaneous weakening of the exothermal peak of the DTA curve might indicate a correlation to a reaction occuring at this temperature.

CONCLUSIONS

It is found that samples of synthetic goethite contain CO_2 both as adsorbed complexes at the surface and within the crystals. The results indicate that the evolution of CO_2 from the bulk is influenced by the same processes as the evolution of H_2O, i.e. formation of micropores and diffusion to the surface.

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REFERENCES

1 R.L. Parfitt, Adv. in Agronomy, 30 (1978) 1-50.
2 L.A.G. Aylmore, Clays and Clay Miner., 22 (1974) 175-183.
3 J.D. Russell, E. Paterson, A.R. Fraser and V.C. Farmer, J. Chem. Soc. Faraday Trans. I, 71 (1975) 1623-1630.
4 T.D. Evans, J.R. Leal and P.W. Arnold, J. Electroanal. Chem., 105 (1979) 161-167.
5 R.J. Atkinson, A.M. Posner and J.P. Quirk, J. inorg. nucl. Chem., 105 (1968) 2371-2381.
6 S. Mørup, M.B. Madsen, J. Franck, J. Villadsen and C.J.W. Koch, J. Magnetism Magnetic Mater., 40 (1983) 163-174.
7 C.J.W. Koch, M.B. Madsen and S. Mørup, Surface Science, (in press).
8 R.C. Mackenzie and G. Berggren, in R.C. Mackenzie (Ed.), Differetial Thermal Analysis, Vol. 1, Academic Press, London and New York, 1970, pp. 271-302.
9 R. Derie, M. Ghodsi and C. Calvo-Roche, J. Thermal Anal., 9 (1976) 435-440.