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The Heat of Immersion of Ferric Oxide in Water

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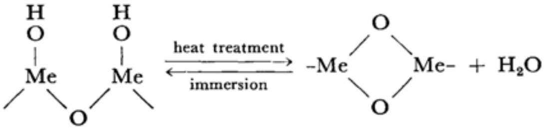
Four kinds of ferric oxide (α-Fe_2O_3) which differ in origin and history have been used for measurements of the surface area, the water content, and the heat of immersion in water. Two cases have been discovered; in one there appears a maximum in the plot of the heat of immersion against the pretreatment temperature according to the origin of the sample, but in the other a maximum does not appear. The heavy hydration treatment carried out prior to the immersion measurements raises the value of the heat of immersion in water, but it has no serious effect on the heat of surface hydration calculated therefrom, as in the case of TiO_2. The average value of the latter was 11.3 kcal/mol H_2O.

Measurements of the heat of immersion have been made on various kinds of insoluble metal oxides in water as well as in organic liquid, and it has been brought to light that the surface hydroxyl groups on metal oxides more or less affect the wetting phenomena.[1,2] Most plots of the heat of immersion in water against the pretreatment temperature show a maximum. This heat-of-immersion anomaly has been explained in terms of the overlapped effect of the chemisorption (the formation of surface hydroxyl groups) and the physical adsorption of water. The surface hydroxyl groups can be removed gradually by heating *in vacuo*, and can be reproduced immediately after immersing the surfaces into water, when the temperature of pretreatment is relatively low. However, when the pretreatment temperature is higher than a limited degree, the rate of the reproduction of the surface hydroxyl groups is remarkably delayed. Thus, the heat treatment at elevated temperatures results in a stabilization of the surface oxide structure made by the reaction:



Usually the maximum in the plot of the heat of immersion *vs.* the pretreatment temperature has been reported to appear in the temperature range from 300°C to 600°C with various kinds of oxides, such as SiO_2,[3,4] Al_2O_3,[5] TiO_2,[6,7] and ZnO.[8] It has been a question for the present authors whether or not the maximum of the heat-of-immersion curve appears with every kind of metal oxide.

This paper will report that two cases have been discovered with α-Fe_2O_3; in one a maximum appears in the plot of the heat of immersion *vs.* the pretreatment temperature, but in the other a maximum does not appear. We have also investigated the effects of hydration treatment on the heat of immersion of α-Fe_2O_3 in water, and on the heat of surface hydration calculated therefrom.

Experimental

Materials. The samples used in the present work are four kinds of α-Fe_2O_3. One of them is the α-Fe_2O_3 presented by the Nippon Bengara Co.; it was prepared by calcining $FeSO_4 \cdot 7H_2O$ at 800°C for 7 hr. This original sample was treated several times with 0.1 N nitric acid in order to remove the basic impurities, and then with 0.1 N ammonia water in order to remove the acidic impurities; then it was washed with distilled water, and finally, by means of electrodialysis, cleaned of electrolytes. The conductivity of supernatant liquid was thus brought to a limiting value. The resultant sample was dried at 110°C for 8 hr in an oven (sample C). Another kind of sample was prepared by the calcination of α-FeOOH (goethite) for 5 hr at 800°C in air; this sample had been made by the oxidation of ferrous sulfate with hydrogen peroxide. This was thoroughly washed with distilled water, and then dried at 110°C for 8 hr in an oven (sample G).

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1) M. M. Egorov, V. F. Kiselev, K. G. Krasil'nikov and V. V. Murina, *Zh. Fiz. Khim.*, **33**, 65 (1959).

2) C. M. Hollabaugh and J. J. Chessick, *J. Phys. Chem.*, **65**, 109 (1961).

3) G. J. Young and T. P. Bursh, *J. Colloid Sci.*, **15**, 361 (1960).

4) J. W. Whalen, *Advan. Chem. Ser.*, **33**, 281 (1961).

5) T. Morimoto, K. Shiomi and H. Tanaka, This Bulletin, **37**, 392 (1964).

6) W. H. Wade and N. Hackerman, *J. Phys. Chem.*, **65**, 1681 (1961).

7) T. Morimoto, M. Nagao and T. Omori, This Bulletin, **42**, 943 (1969).

8) T. Morimoto, M. Nagao and M. Hirata, *Kolloid-Z. u. Z. Polymere*, **225**, 29 (1968).

A part of each sample (C and G) was immersed in hot water at 80°C for 3 days to prepare a highly-hydrated sample, which was then dried as before (samples CH and GH).

Surface-area Measurements. The specific surface areas of the samples were measured by applying the BET theory to the nitrogen adsorption data obtained at the temperature of liquid nitrogen, assuming the cross-sectional area of a nitrogen molecule to be 16.2 Å^2.

Heat-of-immersion Measurements. The calorimeter and the technique for the heat-of-immersion measurement were the same as have been described previously.[5,8] The measurement was carried out at 25°C. The sample was treated in an ampoule at a desired temperature for 4 hr in a vacuum of 10^{-5} Torr before the heat-of-immersion measurements. As the heat of breaking of the ampoule was found to be 0.28 J, this was calibrated for the heat-of-immersion data.

Water-content Measurements. The water content of α-Fe_2O_3 was measured by the successive-ignition-loss method[5,8] by using an all-glass apparatus equipped with an oil manometer. As the gases other than water vapor were found to be present in the gas phase evolved at higher temperatures, they were determined by the technique described previously.[7] For instance, the gases other than water vapor which were evolved at 300, 600, and 800°C amounted to 0.10, 0.23, and 0.27 molecules/100 Å^2 for the sample GH. The water-content values given in Fig. 2 are those free from these quantities.

Results and Discussion

The specific surface area of α-Fe_2O_3 is given in Fig. 1 as a function of the temperature of pretreatment. The data show that the surface area of these samples remains unchanged up to about 500—600°C; with a further rise in the temperature, it decreases sharply, indicating a remarkable sintering.

In Fig. 2 the water content of α-Fe_2O_3, represented in OH's/100 Å^2, is plotted against the temperature of pretreatment. Much as in the cases of the other oxides,[5,7,8] the water content of α-Fe_2O_3 decreases steeply until about 400°C, and then it does so very slowly. The hydration treatment has a considerable effect upon the water content, which becomes larger in the sample subjected to a heavy hydration procedure, as was seen in the case of TiO_2.[7]

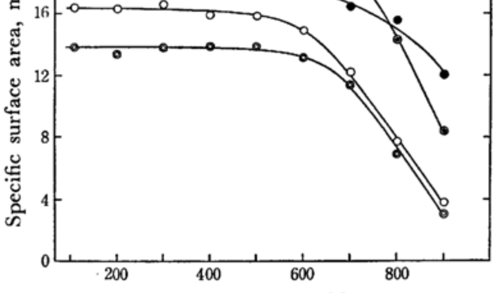

Fig. 1. Dependence of the specific surface area of α-Fe_2O_3 on pretreatment temperature.
○, Sample C; ◎, Sample CH; ●, Sample G; ⊙, Sample GH

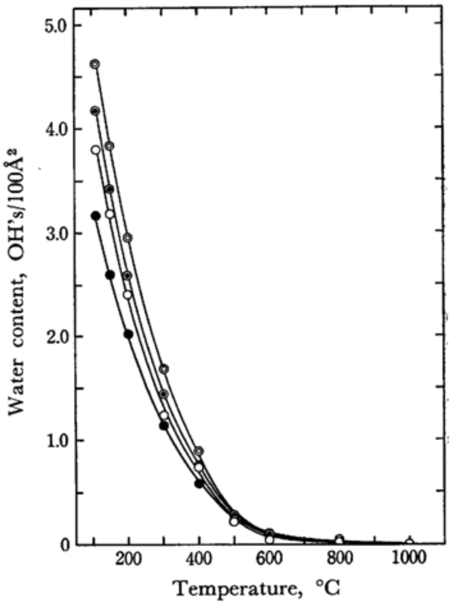

Fig. 2. Water content of α-Fe_2O_3 at various temperatures.
○, C; ◎, CH; ●, G; ⊙, GH

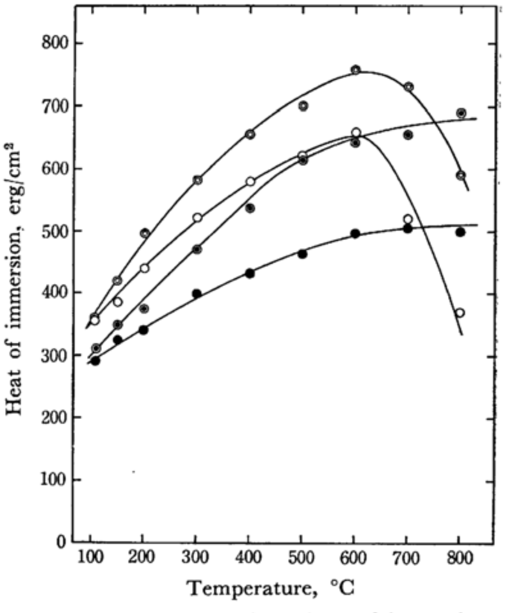

Fig. 3. Dependence of the heat of immersion of α-Fe_2O_3 in water on pretreatment temperature.
○, C; ◎, CH; ●, G; ⊙, GH

Figure 3 shows the relation between the heat of immersion of α-Fe_2O_3 in water and the temperature of pretreatment. It may be seen from Fig. 3 that the heat-of-immersion value is greater in the sample with a large water content resulting from a heavy hydration procedure.

The heat of immersion of the samples C and CH increases initially with a rise in the temperature of pretreatment; it reaches a maximum at 600°C, and then decreases slowly. Such maxima in the heat-of-immersion curve have been reported with such oxides as SiO_2,[3,4] Al_2O_3,[5] TiO_2,[6,7] and ZnO.[8]

On the other hand, the features of the heat-of-immersion curve of the samples G and GH are quite different from those of the former two samples; at first it increases to 600°C, as in the cases of the samples C and CH, but after that the heat-of-immersion value remains almost unchanged, unlike as in the latter cases, and thus no maximum appears. We have never encountered such a situation in which one sample of a substance reveals, and another one does not reveal, a maximum in the heat-of-immersion curve.

The appearance of the maximum in the plot of the heat of immersion of metal oxide in water against the temperature of pretreatment has been explained in terms of the overlapped effect of the chemisoprtion and physical adsorption of water.[3-8] As the temperature of pretreatment rises, the surface hydroxyl groups on metal oxides can be increasingly removed by condensation dehydration.[9,10] When the surfaces thus treated are immersed in water, rehydroxylation will occur on the dehydrated sites. At the same time, the additional heat of reaction will be released together with the heat evolution due to physical interaction between the solid surfaces and the water molecules. At temperatures higher than that of a maximum point, the rehydroxylation on the oxide surface is delayed by the stabilization of the surface oxide structure;[3,5] the higher the temperature, the greater the stabilization. Thus, the contribution of rehydroxylation heat decreases at extremely high temperatures, resulting in a depression of the observed heat of immersion. The fact that the heat-of-immersion curve of the samples G and GH does not reveal a maximum, but only a slow break at almost the same temperature as that of the maximum in the cases of the samples C and CH, indicates that the stabilization of the oxide structure of these samples is not remarkable. The weak stabilization of oxide structure permits a partial rehydroxylation.

Previously the water vapor adsorption isotherms have been investigated on the samples CH and GH.[11] This investigation showed that the amounts of water chemisorbed on the sample CH were 7.59 and 6.73 OH's/100 Å^2 when treated at 600°C and 800°C respectively, whereas on the sample GH it was 7.91 OH's/100 Å^2 in either case. This implies that when the sample is treated at 800°C, the rehydroxylation is incomplete with the sample CH, whereas with the sample GH it is complete; at the same time, this finding substantiates the stabilization theory accounting for the heat-of-immersion anomaly. However, the reason why it is difficult for the stabilization of surface oxide structure to occur on the sample GH has not yet been solved; it may depend on the crystal properties of the sample, which are decided by the origin and the history of the sample.

We can obtain the heat of surface hydration by assuming the complete rehydroxylation of dehydrated sites in the range of lower temperatures of pretreatment than the maximum point. Figure 4 represents the plots of the heat of immersion against the water content of α-Fe_2O_3. The same plotting can be made also for the samples G and GH, as is shown in Fig. 4. The slopes of these plots indicate the heat of formation of surface hydroxyl groups, that is, the heat of surface hydration; the results are tabulated in Table 1.

It can be seen from Table 1 that the heat of surface hydration is almost the same for every sample, being 11.3 kcal/mol H_2O on the average,

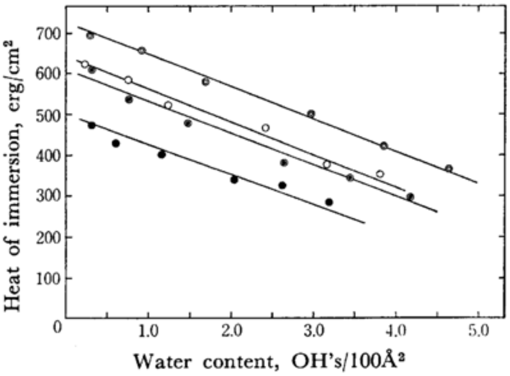

Fig. 4. Relation between the heat of immersion and the water content on α-Fe_2O_3.
○, C; ◎, CH; ●, G; ⊙, GH

TABLE 1. HEAT OF SURFACE HYDRATION OF α-Fe_2O_3 (kcal/mol H_2O)

Sample	C	CH	G	GH
Heat of surface hydration	11.8	11.4	10.3	11.6

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[9] T. Morimoto, M. Nagao and F. Tokuda, This Bulletin, **40**, 2723 (1967).

[10] T. Morimoto, M. Nagao and F. Tokuda, *ibid.*, **41**, 1533 (1968).

[11] T. Morimoto, M. Nagao and F. Tokuda, *J. Phys. Chem.*, **73**, 243 (1969).

irrespective of the origin and the history of the sample. This value of heat of surface hydration is quite small compared with the value, 24.2 kcal/mol H_2O, which was obtained for α-Fe_2O_3 by Healey *et al.*12) by combining the heat-of-immersion data and the water adsorption data. At any rate, neither the preparation nor the hydration treatment of the sample has any serious effect on the heat-of-surface-hydration value, as was in the case with TiO_2.7) The hydration treatment rather affects the value of the heat of immersion itself, as may be seen in Fig. 3. Thus, it is reasonable to consider that the hydration treatment causes the increased physical interaction between the surfaces of α-Fe_2O_3 and the water molecules, much as with the previous consideration in the case of TiO_2.7)

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12) F. H. Healey, J. J. Chessick and A. V. Fraioli, *ibid.*, **60**, 1001 (1956).