

The Heat of Immersion in Water and the Nature of the Surface Hydroxyl Group of Maghemite and Hematite

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(Received March 5, 1988)

The heats of immersion in water of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) were measured in comparison to those of hematite ($\alpha\text{-Fe}_2\text{O}_3$) prepared from the same maghemite by crystal transformation with heat treatment, and outgassing up to 200 °C. The heats of immersion and the heat of hydration of maghemite were lower than those of hematite throughout the measurement conditions. These differences were concluded to be due to the differences in bulk crystal structure, especially the density of the crystal. That is, the heat of hydration at the stage of physisorption depends on the surface hydroxyl group density, corresponding to the bulk crystal density. Also the surface hydroxyl groups are strongly affected by the polarization of the bonds in the bulk, this results in the difference of the heat of hydration at the stage of chemisorption (formation of the hydroxyl groups) and the acidity of the hydroxyl groups. This view is confirmed on the polymorphs of other metal oxides.

Maghemite is widely used as a magnetic material for magnetic recording tape, and hence information on the surface properties of maghemite is essential for controlling the manufacturing conditions. However, little work has been reported on the surface properties of maghemite, and no work has been reported on the heat of immersion in water, whereas there have been many reports on hematite.²⁻¹⁰ Our previous work¹⁾ looked at the IEP (Isoelectric point) and the PZC (Point of zero charge) of maghemite, and clarified that the difference in these characteristics for maghemite and hematite arose from differences in the crystal structure. In the present work, the interaction between water and the surface of maghemite and the nature of the surface hydroxyl groups are investigated through the measurement of the heat of immersion and the adsorption isotherm, with hematite as a reference.

Experimental

Materials. The maghemite sample used in the present work was prepared from the acicular synthetic $\alpha\text{-FeOOH}$ (goethite) by sequential dehydration, reduction and oxidation processes. The hematite sample was prepared by heat treatment of the above maghemite sample in air at 550 °C. Impurities of the sample surface influence the value of the heat of immersion.³⁾ So in all cases the samples were purified as follows: First, washing with an alkali solution then distilled water and finally by electro dialysis. The samples and the purification procedure are the same as reported previously.¹⁾

Surface Area Measurements. The specific surface area of the samples was measured by applying the BET theory¹¹⁾ to the nitrogen adsorption data obtained at the temperature of liquid nitrogen, assuming the cross-sectional area of nitrogen molecule to be 16.2 Å².

Heat of Immersion Measurements. A twin type heat conduction calorimeter (Tokyo Rikou MPC-2) was used. The sample was treated in a Pyrex glass ampoule at the desired temperature for 5 h in a vacuum of 2×10^{-4} Pa before sealing. The heat of immersion measurements were carried

out with doubly distilled water at 25.0 ± 0.1 °C. The heat of breaking of the ampoule was found to be 0.26 J.

Water Content Measurements. The water desorbed from the sample by evacuating at a given temperature was condensed in a cold trap of liquid nitrogen, followed by reevaporation and recondensation in a cold trap of dry ice. The water content of the sample was determined by the measurement of the amount of reevaporated water volumetrically, by using an all glass apparatus equipped with Baratron pressure gauge, assuming the water content to be zero at 1000 °C.

Water Adsorption Measurements. The sample was first prepared by evacuating at 25 °C for 5 h in a vacuum of 2×10^{-4} Pa. The adsorption of water on the sample was then measured gravimetrically at 25.0 ± 0.1 °C, using a Cahn 2000 electrobalance housed in an all glass apparatus. Water vapor pressure was measured by Baratron pressure gauge.

Results and Discussion

Adsorption of Water on the Surface. Maghemite is a less stable form of iron oxide¹²⁾ than hematite and becomes reduced under vacuum at temperatures higher than 250 °C, releasing oxygen and turning dark. Therefore, to measure the intrinsic surface properties, the heat treatment was always carried out under 200 °C. The samples treated under this condition were confirmed to contain no detectable divalent iron ions by analysis.

The specific surface areas (S_{N_2}) of the samples by BET method of nitrogen adsorption are shown in Table 1. The smaller value for the comparative hematite sample can be explained by the shrinkage due to the increase in crystal density caused by the crystal transformation. The change of the shape can not be detected by electron microscopic observation,¹⁾ and no substantial change in the values of the samples was detected following the heat treatment.

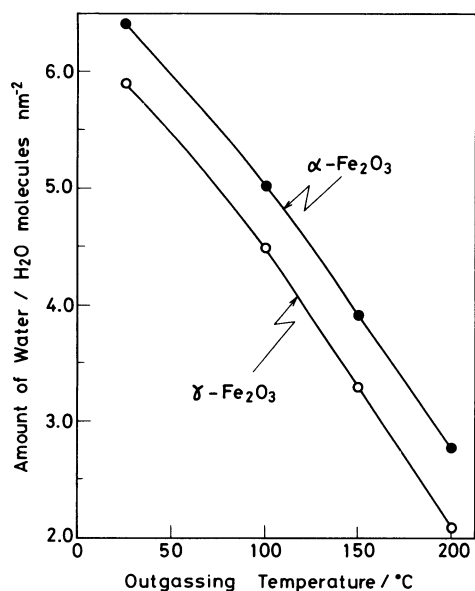
The water content of the samples is shown in Fig. 1, where the amount of water is expressed by the number of water molecules per unit of surface area. Almost perfect desorption of the physisorbed water is

Table 1. Specific Surface Area (S_{N_2}) and Surface Density of Adsorbed Water (V_p and V_c)

	S_{N_2}	V_p	V_c	V_p/V_c
	$m^2 g^{-1}$	H_2O molecules nm^{-2}	OH groups nm^{-2}	
Maghemite	18.6	5.52	11.80	0.47
Hematite	16.0	5.85	12.82	0.46

Table 2. X-Ray Density (D_x), Unit Volume of Fe^{3+} ($V_{Fe^{3+}}$) and Surface Density of Fe^{3+} ($S_{Fe^{3+}}$)

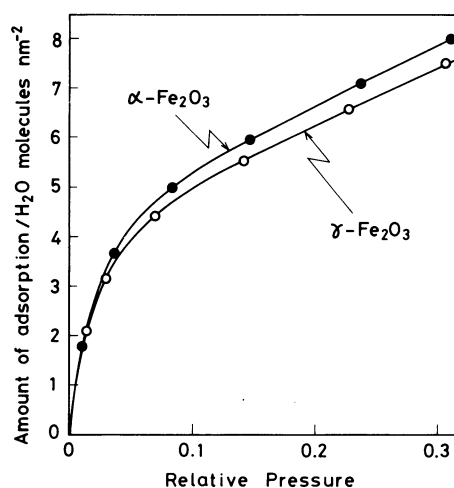
	D_x	$V_{Fe^{3+}}$	$S_{Fe^{3+}}$	
	$g cm^{-3}$	\AA^{-3}	Fe^{3+} ions nm^{-2}	
Maghemite	4.907	27.03	11.10 (Dx)	8.73 (111)
Hematite	5.277	25.13	11.66 (Dx)	9.15 (0001)

Fig. 1. Water content of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) at various temperatures.

attained by the evacuation at 25 °C in a vacuum of 2×10^{-4} Pa. The number of chemisorbed water molecules is shown as the hydroxyl groups per unit area (V_c) in Table 1.

The water adsorption isotherms of the samples are shown in Fig. 2. The ordinate in the figure represents the amount of water adsorbed per unit area. These isotherms indicate that the water is physically adsorbed on the hydroxyl groups formed on the surface. By applying the BET method¹¹⁾ to the isotherm, the amount of water per unit area in the physisorbed monolayer (V_p) was calculated and are shown in Table 1.

The samples in the present work have an acicular shape inherited from the starting goethite, this series of solid phase reactions follow the topotaxial rule.¹⁴⁾ The cylindrical face of the particle forms the main part of the total surface area, and is mainly the (111) plane in the case of maghemite, and the (0001) plane in the case of hematite. The number of the surface

Fig. 2. Adsorption isotherms of water vapor on maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) at 25 °C.

iron ions per unit area ($S_{Fe^{3+}}$) for the (111) plane of maghemite and the (0001) plane of hematite calculated crystallographically¹⁵⁾ are shown in Table 2. The values for the real surfaces of the samples may be larger than these values, because of the incorporation of the higher indexed planes due to the curvature of the surface. A convenient method to approximate the values is to calculate the average number of surface iron ions per unit area ($S_{Fe^{3+}}$) from the volume of unit cell per iron ion ($V_{Fe^{3+}}$) which is derived from the X-ray density data.¹³⁾ Values for the average number of surface iron ions per unit area ($S_{Fe^{3+}}$) are shown in Table 2. They are almost equal in number to the number of surface hydroxyl groups (V_c) in Table 1. This numerical correspondence was reported by Morimoto et al.,¹⁶⁾ and that the ratio $V_p:V_c$ is nearly 1:2, which led them to suggest the model where one physisorbed water connects two neighboring surface hydroxyl groups through hydrogen bonds. The $V_p:V_c$ ratio for maghemite and hematite from our result supports the above model.

Heat of Immersion and Heat of Hydration. The relation between the heats of immersion and the

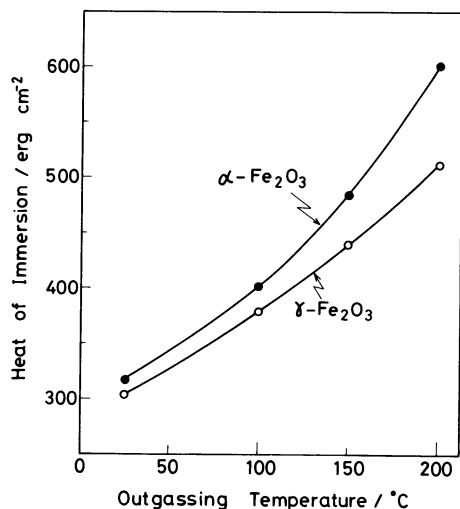


Fig. 3. Heat of immersion in water of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) as a function of outgassing temperature.

outgassing temperature for both samples is shown in Fig. 3. The amount of heat generated increased according to the outgassing temperature for both samples. Outgassing temperatures below 200 °C are low enough to allow complete rehydroxylation of the dehydrated sites.⁶ The hematite sample shows a larger heat of immersion than the maghemite sample all through the temperature range of the measurement. The difference of the heat of immersion between the samples increased with increasing outgassing temperature.

The points for the highest water content of the samples corresponding to outgassing at 25 °C, indicate the heat of immersion for the completely hydroxylated state, that is, the surface is perfectly covered with chemisorbed water, as shown by the values of the $S_{\text{Fe}^{3+}}$, V_c and V_p . The value of the heat of immersion at this stage is 304 erg cm⁻² for the maghemite, and 317 erg cm⁻² for the hematite. The values of the heat of the immersion for hematite at this stage, are reported as 280 erg cm⁻² by Jurinak and Burau,³ 322 erg cm⁻² by Furuichi et al.,¹⁰ and 367 erg cm⁻² by McCafferty and Zettlemoyer.⁵ The present value for hematite compares favorably with other reported values, considering the differences of the samples and the conditions of measurement.

The heats of immersion for the lowest water content corresponding to outgassing at 200 °C, are 513 erg cm⁻² for the maghemite and 602 erg cm⁻² for the hematite. Healy and Fuerstenau²¹ reported that the various metal oxides show a linear relation between the values of the heat of immersion (after outgassing at 200 °C) and the values of PZC. A metal oxide with a high value of PZC shows a large heat of immersion. The previous study¹ made it clear that the value of PZC of maghemite (pH 5.5) is lower than that of

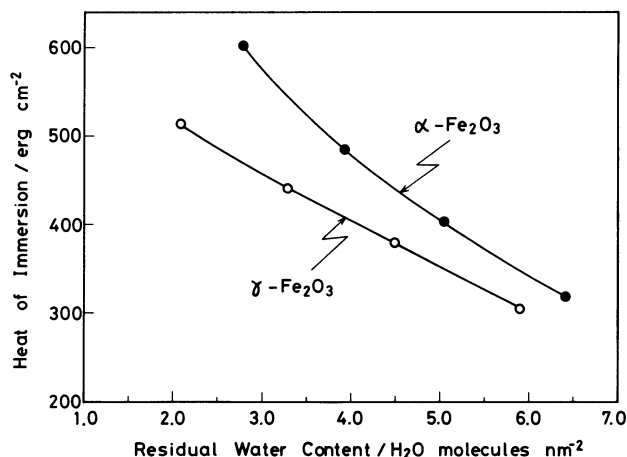
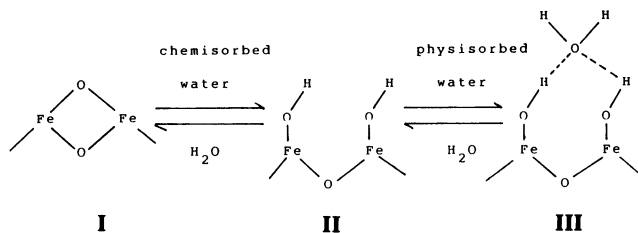


Fig. 4. Heat of immersion in water of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) as a function of water content.

hematite (pH 6.7). The present results on the heats of immersion for samples outgassed at 200 °C fit the above relation.

Figure 4 shows the plots of the heat of immersion against the residual water content for both samples. The heat of surface hydration is calculated by the slope of these plots. At the stage of complete hydroxylation, shown in the below scheme [II-III], the heats of hydration are 32.2 kJ mol⁻¹ for the maghemite and 37.6 kJ mol⁻¹ for the hematite.



The heat of hydration at this stage corresponds to the physisorption of water, that is the construction of the hydrogen bonds, as in the above model III, between the oxygen atom of the physisorbed water and the two protons of the neighboring surface hydroxyl groups. The validity of this model in the present work is supported by the numerical correspondence of V_c and V_p in Table 1.

The average distance between the neighboring hydroxyl groups on the surface, relates to the density of hydroxyl groups on the surface (V_c), which is related to the average surface density of Fe³⁺ ($S_{\text{Fe}^{3+}}$) and the average bulk density of Fe³⁺ ($V_{\text{Fe}^{3+}}$) in Table 2. When the distance between the neighboring groups is long, the hydrogen bonds of the above model III are weak, and the heat of hydration is low. The average distance between the neighboring hydroxyl groups of maghemite is longer than that of hematite, as shown by the values of V_p and V_c . Thus, the heat of hydration

at the stage of physisorption of maghemite should be lower than that of hematite. This speculation is strongly supported by the experimental heats of hydration. The heat of the formation of the hydrogen bonds is given by halving the value of the heat of hydration (one water molecule forms two hydrogen bonds). This gives values less than 20 kJ mol⁻¹, which is reasonable for hydrogen bond formation.

The heat of surface hydration for the stage when half of the surface is dehydrated, that is the heat of surface rehydration, is shown in the above scheme [I-II], and is 35.1 kJ mol⁻¹ for the maghemite and 60.6 kJ mol⁻¹ for the hematite. The maghemite shows the lower heat of hydration throughout the present study.

On the heat of hydration of the hematite, several different values have been reported, 101 kJ mol⁻¹ by Healey et al.,²⁰ 66 kJ mol⁻¹ by Furuichi et al.,¹⁰ 47.2 kJ mol⁻¹ by Morimoto et al.,⁶ and 34.3 kJ mol⁻¹ by Rossi et al.⁹ These scattered values are caused by differing levels of ionic impurities, the difference of particle shape, differences in the preparation and outgassing conditions.

For comparing the intrinsic values of the heat of immersion and the heat of hydration for the maghemite and hematite, the above mentioned conditions were virtually identical. Consequently, the differences of the heat of immersion and the heat of hydration are due to the difference of the crystal structure.

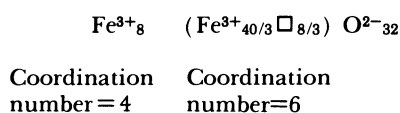
The maghemite (γ -Fe₂O₃) has the spinel type crystal structure, and the hematite (α -Fe₂O₃) has the corundum type crystal structure.¹⁷ These crystal structures correspond to γ -Al₂O₃ and α -Al₂O₃, respectively. In the comparative studies on the heat of immersion of γ - and α -Al₂O₃, γ -Al₂O₃ always shows a lower value for the heat of immersion than α -Al₂O₃.¹⁸⁻²⁰ These results are in good agreement with our results on maghemite and hematite.

The values for the heat of immersion of γ - and α -Al₂O₃ also follow the tendency described by Healy and Fuerstenau,²¹ as the value of PZC for γ -Al₂O₃ is lower than that of α -Al₂O₃.²²

Difference of the Nature of Surface Hydroxyl Groups Based on Difference of Crystal Structure.

The average difference in the acidity of the surface hydroxyl groups between maghemite and hematite was reported as the difference of the IEP or the PZC of 1.1 to 1.2 pH units.¹⁾

The unit lattice of maghemite is expressed by the following formula:²³



In the above formula a vacant lattice point of coordination number 6 is expressed by \square , i.e. 6 oxygen

ions adjacent to the Fe³⁺ ion site. Fe³⁺ ions are arranged at positions of coordination number 4 and 6 in a ratio of 3:5. On the other hand, hematite is a corundum-type oxide in which all of the Fe³⁺ ions have a coordination number of 6.

Parks²⁴) proposed a semiempirical equation for the PZC of metal oxides and metal hydroxides as follows:

$$\text{PZC} = A - 11.5(Z/R + 0.0029a)$$

where A is a constant depending on the coordination number of the metal ion and the hydration state of the surface. Z is the valency of the metal ion, R is the distance from the surface metal ion to the hydrogen ion in the surface hydroxyl group attached to the metal ion, and a is the crystal field stabilization energy of the metal ions by the hydroxide ions. The last term is zero when the metal ion is Fe³⁺ with a coordination number of 6 or 4.²⁵) The PZC value is more acidic by 2.4 pH units for four-coordinated than for six-coordinated metal ions, corresponding to the difference of the above constant A at the same hydration state. Thus the difference in the PZCs between maghemite and hematite is calculated to be $2.4 \times 3 / (3+5) = 0.9$, assuming that the additivity rule holds.²⁶)

Yoon et al.²⁷) has proposed improvements to Parks' equation: for complex oxides in which the correction of the crystal field stabilization energy is not required,

$$\text{PZC} = 18.43 - 53.12 \sum f_i (v/L_s)_i - 0.5 \sum f_i \log((2-v)/v)_i$$

where v is the bond valence, i.e., the valency of the metal ion per coordination number, and $L_s (=L+r)$ is the sum of the mean M-O bond length (L) and the O-H distance (r), taken to be 1.01 Å. The f_i 's are the ratio of the bonds to the total number of bonds. The value of PZC for maghemite is lower than that for hematite by 1.40 pH units as calculated by the above formula with the data for maghemite (γ -Fe₂O₃)²⁸) and hematite (α -Fe₂O₃).¹⁷)

The above mentioned calculations support the proposition that the bonding energy between H⁺ and O²⁻ of the surface hydroxyl groups of maghemite is lower than that of hematite, which is further supported by our experimental values.¹⁾ As a matter of course, the difference in the heats of hydration at the [I-II] stage, shown in the previous scheme, further includes the difference in the bond formation energy of the Fe-O(-H) bonds for maghemite and hematite.

To discuss the Fe-O bond of the surface hydroxyl groups, it is necessary to examine the nature of this bond in the bulk. As aforementioned, the crystal density (D_x) of maghemite is lower than that of hematite, which means that the average bond length Fe-O of maghemite is longer than that of hematite. The ions are less ionic and the bonds are less polar²⁹) in maghemite than in hematite, which is supported by the lower electron density of the oxygen atoms of maghemite than of hematite as measured by XPS.³⁰)

(The same characteristics are also reported for γ - and α - Al_2O_3 .³¹⁾ The difference in the ionic characteristics of the bulk bonds should also be reflected in the surface hydroxyl groups.

From this point of the view, Healy et al.³²⁾ introduced this ionic characteristics concept as "volume field strength", and successfully showed the linear relationship between the PZCs and the "volume field strength" for the polymorphs of manganese oxides. This electrostatic field is proportional to $(V_m)^{-2/3}$, where V_m is the volume of the unit cell per metal ion. And the value of PZC is given by the following formula:

$$\text{PZC} = A_1(V_m)^{-2/3} + B_1$$

This formula indicates that the value of PZC increases as V_m decreases, A_1 and B_1 are constants for the oxide series. The plots of this relation for maghemite and hematite are shown in Fig. 5. The plots of the polymorphs of manganese oxides from Healy et al.,³²⁾ and of γ - and α - Al_2O_3 (PZC values²²⁾ and V_m values from the crystal densities³³⁾ are also shown in Fig. 5. Almost the same slope can be found for the plot of each polymorph. This fact supports the view of Healy et al.³²⁾ that the surface hydroxyl groups are strongly influenced by the electrostatic field within the lattice of the crystal. In other words, the surface hydroxyl groups are strongly affected by the polarization of the bonds in the bulk. The degree of the polarization becomes higher, as the bond length becomes shorter corresponding to an increasing the bulk crystal density. This increase in the polarization of the bonds in the bulk affects the surface hydroxyl groups, that is the acidity of the hydroxyl groups, which can be characterized by the parameter PZC, decreases.

In addition to this, it is suggested that the line of each metal ion has a different intercept, and this difference may be caused by the degree of the polarization of the bonds between the metal ion and

the oxygen ion or the ionic characteristics of the metal ion, which is characterized by the electronegativity of the metal ion. The order of the intercept $\text{Mn}^{4+} > \text{Fe}^{3+} > \text{Al}^{3+}$ corresponds well to the electronegativity of the metal ion.³⁴⁾

Conclusion

(1) The surface density of hydroxyl groups for maghemite is lower than for hematite, corresponding to the difference in the density of the bulk crystal.

(2) The amount of the water physisorbed in a monolayer on maghemite is less than that for hematite, corresponding to the lower surface density of hydroxyl groups.

(3) The heat of the surface hydration at the stage of physisorption for maghemite is lower than for hematite, because the average distance between neighboring hydroxyl groups for maghemite is longer than for hematite.

(4) The heat of the surface hydration at the stage of chemisorption (the formation of the surface hydroxyl groups) for maghemite is lower than for hematite. This difference is caused by the different degree of the polarization of the bonds in the bulk which extends to the surface hydroxyl groups.

(5) The surface hydroxyl groups are strongly affected by the bulk, especially the polarization of the bonds in bulk. The degree of the polarization becomes higher, both as the bond length becomes shorter, corresponding to a higher bulk crystal density, and as the electronegativity of the metal ion becomes higher. This polarization of the bond in the bulk affects the surface hydroxyl groups, resulting in the dissociation of the hydroxyl groups, that is the acidity of the hydroxyl groups decreases.

The authors wish to thank Dr. Michael L. Hair of Xerox Research Centre of Canada for useful discussions, and Dr. Stephen Baker of Sony Corporation Research Center for reading the manuscript.

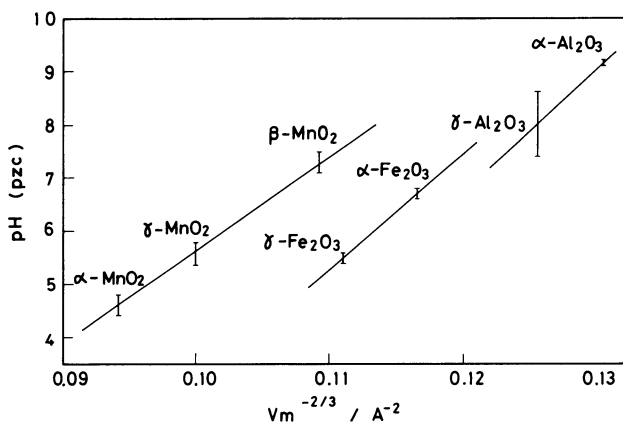


Fig. 5. Inter-relationship of the values of the PZCs (pH_{pzc}) and the average volume of the unit cell per metal ion (V_m) for various metal oxides series.

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