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Specific Acidities of the Surface Hydroxyl Groups on Maghemite

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Two types of surface hydroxyl groups on maghemite have been identified and their acidities evaluated. One of these surface groups bonds to the surface iron ions of the octahedral sites and shows a stretching vibration mode of infrared absorption at 3690 $\mathrm{cm^{-1}}$. The other bonds to the tetrahedral sites and vibrates at 3630 $\mathrm{cm^{-1}}$. The acidity of the groups positioned at the octahedral sites was evaluated as 12.5 in the pK_a value while that of those on the tetrahedral sites was found to be 7.9. A charge transfer mechanism between these neighboring two types of hydroxyl groups is proposed as an explanation for these acidities.

Maghemite is a ferrimagnetic inverse-spinel type iron oxide which is widely used for magnetic recording tapes. Although of central importance to the characteristics of the tape, little work has been reported on the surface properties of maghemite.

In three previous papers,[1—3] the nature of the surface hydroxyl groups of maghemite were studied with regard to the average acidity as the PZC (Point of Zero Charge) and their surface ionization constants, compared with hematite. It was shown that the average acidity of the surface hydroxyl groups on maghemite is higher than that of those on hematite. The Bronsted basic catalytic activity on the aldolization of ketones on maghemite, however, was found to be higher than that of hematite.[4]

This prior work suggests that two types of surface hydroxyl groups exist on the surface of maghemite, one of these basic and the other acidic. The evaluation of these acidities is essential to complete the characterization of the surface of maghemite.

The present study was undertaken in order to ascertain this information. This was achieved mainly through the comparison of the infrared spectrum of maghemite with that of hematite. For the evaluation of the acidities of the surface hydroxyl groups, the adsorption of the acid-base indicators accompanied by the change in color was used.[5] But this method is hard to apply to colored material such as the maghemite of the present study. From the view point of the IR spectroscopies of surface hydroxyl groups of iron oxides and iron oxyhydroxides, there has been no report on maghemite previous to the present study.[6] There has, however, been many reports concerning hematite[7—11] and iron oxyhydroxides.[12—15]

Experimental

Materials. The maghemite sample used in the present work was prepared from acicular synthetic α-FeOOH (geothite) by sequential dehydration, reduction and oxidation processing. The hematite sample was prepared by a further heat treatment (in air at 550°C for 2 h) of the maghemite phase. In all cases the samples were purified as follows: They were first washed with an alkali solution, then with distilled water, and finally by electrodialysis. The samples and purification procedure are the same as those reported previously.[4] The specific surface areas of the samples were 18.6 $\mathrm{m^2\,g^{-1}}$ for maghemite and 16.0 $\mathrm{m^2\,g^{-1}}$ for hematite as measured by the BET method of nitrogen adsorption at liquid-nitrogen temperature (assuming the cross-sectional area of the nitrogen molecule to be 16.2 Å^2).

Infrared Measurements. Infrared spectra were measured, with a Fourier transform infrared spectrometer, by the diffusion reflection method (the samples were maintained at a specified temperature by a heated sample holder, under a purified nitrogen gas flow). Another common method of carrying out this measurement is to examine the transmission of a thin film sample and use the peak shifts accompanying the adsorption of an organic chemical species to evaluate the acidity of the hydroxyl groups.[16] The reason that the former method was chosen for the present study was to provide consistency with the previous work.[1—4] In this work, much attention was given to the prevention of the reduction of the samples. Such degradation darkens the samples and thereby spoils their surface reflectivity. This is especially true for the case of maghemite which is thermodynamically less stable than hematite.[17] In the present work, this instability prevents the application of the abovementioned method of the adsorption of the organic species.

Water Content Measurements. The Karl Fisher method was employed to measure the amount of residual hydroxyl groups on the surfaces. This procedure is carried out by heating these samples in the same manner as for the infrared measurements and introducing the evaporants into a titration cell. The water content at each temperature step was thus determined by assuming the water content to be zero at 1000°C.[18]

Results and Discussion

Isolated Surface Hydroxyl Groups. The infrared spectrum of maghemite as shown in Fig. 1 has two bands, 3690 and 3630 $\mathrm{cm^{-1}}$, which may be associated with the stretching vibrations of the isolated hydroxyl groups bonded to single $\mathrm{Fe^{3+}}$ ions. There appears to be no perturbation by lateral hydrogen bond interactions with adjacent hydroxyl groups.

The infrared spectrum of hematite, however, as shown in Fig. 2, has a single relatively broad band at 3660 $\mathrm{cm^{-1}}$. This band is assigned to the stretching vibration band of an isolated hydroxyl group bonded to a single $\mathrm{Fe^{3+}}$ ion unperturbed by the adjacent hydroxyl groups. Both types of spectra become clearer with increasing sample temperature. Blyholder and

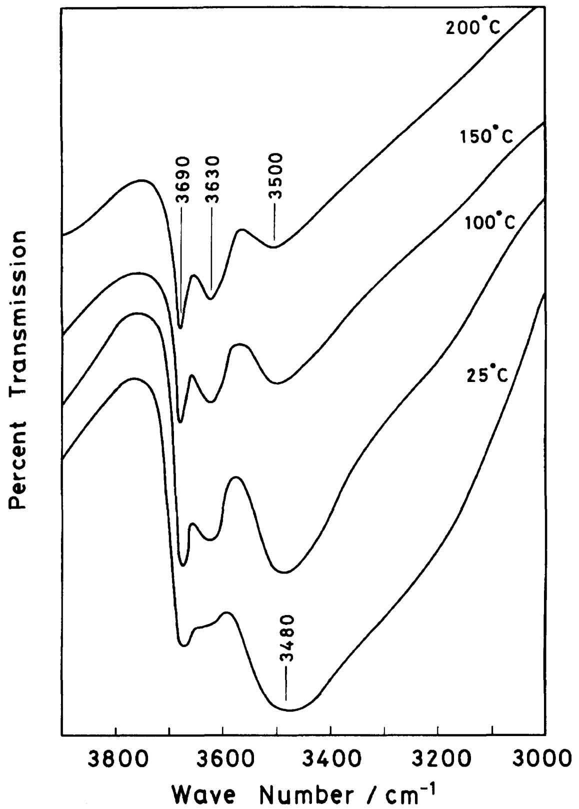

Fig. 1. Infrared spectra of hydroxyl groups on the sample of maghemite (γ-Fe_2O_3).

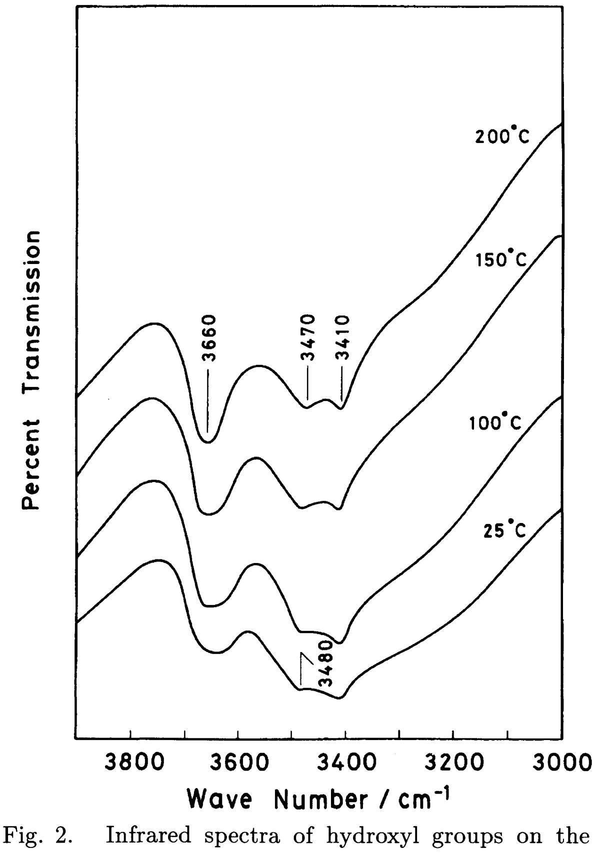

Fig. 2. Infrared spectra of hydroxyl groups on the sample of hematite (α-Fe_2O_3).

Richardson[7] reported the stretching vibration band of the isolated surface hydroxyl groups on hematite to be 3660 cm^{-1}. Rochester and Topham[9] reported 3670 to 3635 cm^{-1} for isolated hydroxyl groups, bonding to hematite heat treated in a manner similar to that employed here. These bands are in accord with the present measurement.

For the following reasons, the two bands for maghemite are assigned to be the bands of the isolated hydroxyl groups bonding to the Fe^{3+} ions at the octahedral and tetrahedral sites of the spinel lattice, respectively. First, the IR spectrum of γ-Al_2O_3 (whose crystal structure is of the same spinel type as that of maghemite) has isolated surface hydroxyl bands at 3740 and 3680 cm^{-1}. Second, the acidity of the 3740 cm^{-1} hydroxyl group is reported to be lower than that of the 3680 cm^{-1} group.[19] This difference of 60 wave numbers coincides well with the present results. It has also been reported that the band of the isolated surface hydroxyl groups bonded to the aluminum ions at the octahedral sites of γ-Al_2O_3, is higher in wave numbers than that from the tetrahedral sites.[20] Further, it is a well established view that the hydroxyl groups bonded to the surface metal ions at the octahedral sites are more basic than those of the tetrahedral sites.[21—23] (The clearer reason through the present study is that the magnitude of the absorption bands are in the ratio of 5 : 3 for the octahedral to tetrahedral sites.)

Perturbed Surface Hydroxyl Groups. The broad bands less than 3600 cm^{-1} are associated with the stretching vibration mode of the hydroxyl groups perturbed by hydrogen bonds. These broad and large bands appear in the spectra only from the samples prepared at temperatures of more than 100°C. The water content data shown in Table 1 argues against the attribution of those perturbing to the hydrogen bonds of the physisorbed water.

Both the bands of maghemite with maxima at 3500 to 3480 cm^{-1} and of hematite at 3480 to 3410 cm^{-1} decrease with increasing sample temperature. These are assigned to the stretching vibration modes under the influence of the hydrogen bonds with the neighboring hydroxyl groups.

Table 1. Water Contents of Samples as the Function of Temperatures

Temp	Maghemite (γ-Fe_2O_3)	Hematite (α-Fe_2O_3)
°C	(H_2O molecules nm^{-2})	(H_2O molecules nm^{-2})
25	6.31	6.83
100	5.08	5.59
150	3.90	4.47
200	2.75	3.39
Vc[a]	5.90	6.41

[a] The saturated surface density of the surface hydroxyl groups in the number of the molecules of chemisorbed water calculated per unit surface area of nm^{-2}.[2]

Blyholder and Richardson[7] have reported 3490 and 3430 cm^{-1} for the surface hydroxyl groups under hydrogen bond perturbation. The band of the perturbed stretching vibration of 3410 cm^{-1} in the present sample is considered to be due to the surface hydroxyl groups on the well developed (0001) plane. These make up the rigid hydrogen bond hexagonal ring structures of the three hydroxyl groups.[9] The band at 3480 to 3470 cm^{-1} is from the hydroxyl groups with less rigid configurations on undeveloped faces. The development of the (0001) face of the hematite sample may be due to the heat-treatment of the sample.

Relative to the bands of isolated hydroxyl groups, the bands with hydrogen perturbation decrease when the sample temperature is raised. A model of the surface chemistry which may take place as the sample temperature is raised is shown in Fig. 3. As the chemisorbed water is released, isolated hydroxyl groups are formed thereby decreasing the number of hydroxyl groups with hydrogen bond perturbations. It was found that the decrease of band intensity associated with the hydrogen bond perturbation of maghemite is greater than that seen from hematite. This is to be expected because the energy of formation of surface hydroxyl groups on maghemite is lower than that of surface hydroxyl groups on hematite.[2]

These bands are larger than the bands of the isolated hydroxyl groups even at 100°C where the physisorbed water is removed and the partial desorption of the surface hydroxyl groups begins. The surface configuration of the lateral hydrogen bonding between the neighboring surface hydroxyl groups, as shown in Fig. 3, is developed to a large scale at the surface of maghemite or hematite.

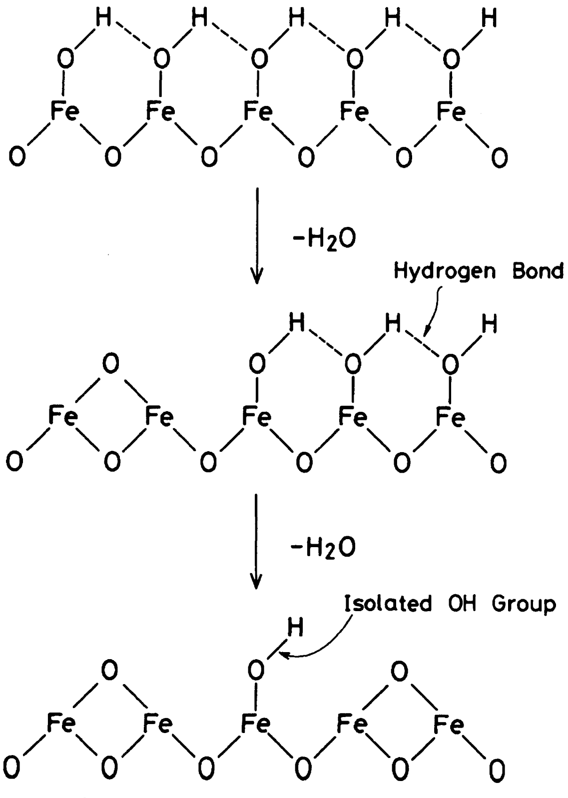

Fig. 3. Schematic models of the formation of the isolated surface hydroxyl group by the dehydration of the lateral hydrogen bonded surface hydroxyl groups.

The average wave number of the bands of maghemite is higher than that of those of hematite. The reason for this difference is that a weaker on average hydrogen bond perturbation arises from the longer average distance between surface hydroxyl groups pinned to the crystal structures.[2]

Differences of Surface OH Groups between Maghemite and Hematite. In the previous work,[4] the basic catalytic activities of the surface hydroxyl groups on maghemite and hematite were examined through aldolization or retro-aldolization. The results were analyzed in terms of the pH values of the PZC by the semiempirical method of Yoon et al.[23] The basicity of the surface hydroxyl groups bonded to the Fe^{3+} ions at the octahedral sites of maghemite as calculated by the above-mentioned method is slightly higher than that of hematite, of which surface hydroxyl groups are all of those at the octahedral sites, due to its crystal structure of the corundum type.[24] Nevertheless, the wavenumber difference of the isolated surface hydroxyl groups at the octahedral sites between maghemite and hematite, of 30 cm^{-1}, is half of the value of 60 cm^{-1} found for the octahedral and the tetrahedral sites of maghemite. The basic catalytic activities, the surface densities of the surface hydroxyl groups of the octahedral sites, and the basic catalytic activities per one surface hydroxyl group of the octahedral sites are listed in Table 2. It appears that the basicity of the surface hydroxyl groups of the octahedral sites of maghemite is far higher than that estimated in the previous study.[4]

Evaluation of the Acidities of the Surface OH Groups on Maghemite. In our previous work, the intrinsic ionization constants of K_a (Fe–OH=Fe–O^-+

Table 2. Surface Hydroxyl Groups of the Octahedral Sites of Maghemite and Hematite

	Maghemite (γ-Fe_2O_3)	Hematite (α-Fe_2O_3)
Surface density[a] (OH's nm^{-2})	7.4	12.8
Basic catalytic activity[b] (mol m^{-2})	7.1×10^{-4}	4.6×10^{-4}
Partial value of PZC_i[c] (in pH scale)	9.47	9.34
Catalytic activity per OH's[d] (molecules s^{-1} OH's^{-1})	0.160	0.057

a) Calculated from the data.[2] b) Determined from the data.[4] on the retro-aldolization reaction of diacetone alcohol to acetone at 30°C for 10 h. c) Calculated from the data[4] following the semiempirical method.[23] d) Calculated from the values of a) and b).

H^+) were determined from potentiometric titrations by the double-extrapolation method.[3,25] The results for maghemite and hematite are consistent with the present data. The values of pK_a were 8.3±0.3 for maghemite and 10.2±0.3 for hematite, respectively. The two types of surface hydroxyl groups of maghemite have different acidities of $K_a{}^0\gamma$ and $K_a{}^t\gamma$ for the octahedral and the tetrahedral sites, respectively. The K_a of maghemite ($=K_a\gamma$) is written as follows:

$$K_a\gamma = \left(5K_a{}^0\gamma + 3K_a{}^t\gamma\right)/(5+3).$$

Because of the large difference between $K_a{}^0\gamma$ and $K_a{}^t\gamma$ ($K_a{}^0\gamma \ll K_a{}^t\gamma$), this relation may be written as

$$K_a\gamma = 3/8K_a{}^t\gamma = 10^{-8.3\pm0.3}.$$

The value of p$K_a{}^t\gamma$ is thus calculated to be 7.9±0.3. On the relationship between the wavenumbers of the stretching vibration of hydroxyl groups and the values of pK_a, Goulden[26] confirmed a linear correlation for the series of carbanols. Hair[16] has also made clear that the isolated surface hydroxyl groups on metal oxides can be discussed from the point of view of the hydroxyl groups of organic compounds. It is suggested that the linear correlation would be expected to be consistent for the hydroxyl groups of a series of a limited analogous chemical species.[27] In the present study, three types of surface hydroxyl groups, bonded to iron ions at the octahedral and at the tetrahedral sites of maghemite and at the octahedral sites of hematite, can be looked at as the limited analogous hydroxyl groups and are thus expected to show linear correlation. The acidity of the $K_a{}^0\alpha$ surface hydroxyl groups is 10.2±0.3. When the above-mentioned assumption is valid, the p$K_a{}^0\gamma$ of the surface hydroxyl groups bonded to the iron ions of the octahedral sites should be extrapolated as 12.5±0.3, as shown in the Goulden plot of Fig. 4. The electron transfer along the surface of maghemite from the hydroxyl groups bonded to iron ions of the tetrahedral sites to those of the octahedral sites is depicted in Fig. 5. This process is similar to that reported by Chapman and Hair[28] for the fluorination of the silica surface accompanied by the increase of acidity of the neighboring silanol. This inclination of the surface charge explains the origin of the higher basicity of the hydroxyl groups bonded to the iron ions at the octahedral sites of maghemite. It is the reason for the unexpected difference between maghemite and hematite in the acidity of the surface hydroxyl groups bonded to the iron ions at the octahedral sites.[4]

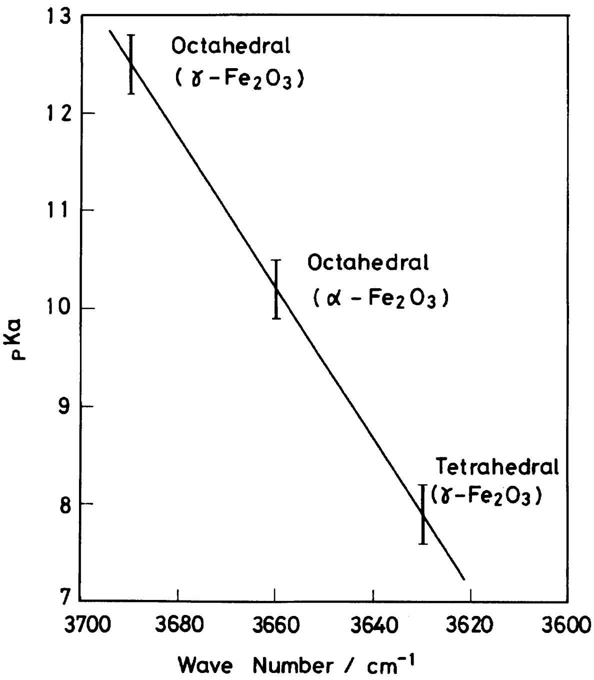

Fig. 4. Goulden plot for the surface hydroxyl groups on maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3).

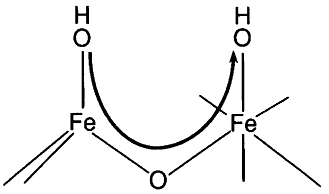

Fig. 5. Schematic model of the electron transfer from the surface hydroxyl group bonded to the iron ion of the tetrahedral site to that of octahedral site on maghemite (γ-Fe_2O_3).

Conclusion

(1) Two types of the isolated surface hydroxyl groups on maghemite have been identified. One is bonded to the surface iron ions of the octahedral sites with an IR band at 3690 cm^{-1}, and the other to the tetrahedral sites with a 3630 cm^{-1} absorption.

(2) The perturbation of the stretching vibration mode of the hydrogen bonds between neighboring surface hydroxyl groups of maghemite is less than those of hematite, due to the longer in average site distance.

(3) The acidity (pK_a values) of the surface hydroxyl groups of the octahedral sites of maghemite was determined to be 12.5 and that of the tetrahedral sites was 7.9, respectively.

(4) The acidity of the surface hydroxyl groups of the octahedral sites of maghemite is lower than that of hematite. The reason for this was concluded to be the electron transfer from the surface hydroxyl groups of the tetrahedral sites to those of the octahedral sites.

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