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The Electrification of Iron Oxide in Water

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The electrification of iron oxides pretreated at various temperatures from 600 to 1200 °C has been investigated in water by measuring the ζ-potential as a function of the pH. From the surface-chemical point of view, iron oxides pretreated at temperatures lower than 800 °C behave differently from those pretreated at higher temperatures; the isoelectric point of the former samples reaches an equilibrium value in a few hours, while that of the latter samples increases slowly to an equilibrium value with an increase in the surface hydration. On the other hand, the equilibrium isoelectric point of iron oxide decreases sharply upon heat treatment at 800—1000 °C, corresponding to the change in the chemical composition of iron oxide from Fe_2O_3 to Fe_3O_4.

Metal oxide surfaces are usually hydrated in water to produce surface hydroxyl groups, which should have extensive effects on the surface properties of metal oxides.[1-4] The electrification of metal oxide surfaces has also been explained in terms of the dissociation of surface hydroxyl groups and the adsorption of H^+ on them:[5,6]

$$MO^-(s) + 2H^+ \rightleftharpoons MOH_2^+(s) \quad (1)$$

The sign of the charge, positive or negative, carried on the surface may be considered to depend on the nature of the metal oxides and the surface properties. With regard to the former effect, Parks[6] has found the empirical rule that the larger the ionic valency, and the smaller the ionic radius of the metal ion, the smaller the isoelectric point of metal oxide. On the other hand, the effects of the crystal structure and of the surface state (especially the surface hydration) on the surface charge have not been investigated in detail. Here, on iron oxide carefully prepared, the effect of the surface hydration on the surface charge is examined, and the dependence of the electrification on the pretreatment temperature is discussed.

Experimental

Materials. Three kinds of iron oxides were prepared in this work. The addition of an excess amount of 3 mol/l ammonia water to a 1 mol/l $Fe(NO_3)_3$ solution yielded a precipitate of iron hydroxide gel. The precipitate was washed fully with distilled water through a glass filter and then dried at 100 °C for 24 hr. Dried iron hydroxide was decomposed in air at 600 °C into iron oxide and washed with distilled water. Furthermore, iron oxide was heated in air at various temperatures between 600 °C and 1400 °C for 3 hr. Finally, the samples were thoroughly washed with distilled water until the conductivity of the filtrate became nearly that of pure water (FI). Since soluble impurities were detected in the filtrate after the recalicination of the FI samples, calcination and washing were repeated more than ten times in order to purify the samples further. This procedure improved the purity of samples so much that we were not able to detect soluble impurities in the final filtrate (FII). Pure iron (99.99%) was oxidized in air at 1400 °C for 3 hr to produce Fe_3O_4. This sample was then crushed in an agate mortar and heated in air at various temperatures between 200 °C and 1400 °C (FIII).

The nitrogen adsorption was measured at the temperature of liquid nitrogen on the FII samples, and the specific surface areas obtained were 6.57 and 1.50 m^2/g for samples treated at 600 and 800 °C (FII-600 and FII-800) respectively. For the samples treated at temperatures higher than 1000 °C, the specific surface area was found to be less than 0.1 m^2/g.

X-Ray diffraction analysis proved that iron oxides calcined below 1200 °C exhibit the rhombohedral α-Fe_2O_3 structure, while in the sample calcined at 1400 °C two types of structures coexist: a large part of Fe_3O_4 and a very small part of α-Fe_2O_3.

1) M. M. Egorov and V. F. Kiselev, *J. Phys. Chem.* (USSR). **36**, 318 (1962).

2) W. H. Wade and N. Hackerman, *J. Phys. Chem.*, **64**, 1196 (1960).

3) J. P. Peri and R. B. Hannan, *ibid.*, **64**, 1526 (1960).

4) R. Mars, J. J. F. Scholten, and P. Zwietering, "Advances in Catalysis," Vol. 14, ed. by D. D. Eley, H. Pines, and P. B. Weisz, Academic Press, New York (1963), p. 101.

5) T. Morimoto and M. Sakamoto, This Bulletin, **37**, 719 (1964).

6) G. A. Parks, *Chem. Rev.*, **65**, 177 (1965).

Determination of the Isoelectric Point. The isoelectric points of iron oxide were determined by the measurement of the ζ-potential in solutions with various pH values at 25 °C by means of the streaming potential method.[7] The potential values were calculated by using the Helmholtz-Smoluchowski equation. The pH value of the solutions was controlled with HCl and NaOH, and NaCl was used to adjust the ionic strength of the solutions (10^{-3} mol/l). The solid reagents used were recrystallized once from guaranteed-grade reagents. The water which was used for preparing the iron hydroxide and electrolyte solutions and for washing the samples was redistilled one. The second distillation was performed from an alkaline permanganate solution. Before preparing the electrolyte solution, purified water was bubbled with N_2 in order to exclude any dissolved CO_2.

Measurements of Hydration.[8] FII samples calcined at 600 and 1200 °C were immersed into water for various time intervals in order to obtain differently-hydrated samples. After degassing the hydrated samples in a vacuum of 10^{-5} Torr at 25 °C for 10 hr, by which almost all the physisorbed water molecules were removed. The samples were calcined at 1000 °C and the water vapor released was condensed into a dry-ice trap. The condensed water was vaporized and determined volumetrically at 25.0 °C.

Results and Discussion

Immediately after the calcination of the FII samples at various temperatures, they were mounted in the cell of the streaming potential apparatus; then the potential was measured at intervals. During the time between successive measurements, the solution was forced to stream through the diaphragm by applying pressure with N_2 (100 mmHg); the streaming velocity was 4.1 and 110 ml/hr in the cases of FII-600 and FII-1200 respectively. In Fig. 1, the ζ-potential values of FII samples in solutions of different pH values are plotted against the time elapsed after the contact of the solid surface with a solution. Figure 1 shows that the ζ-potential value increases steeply in the

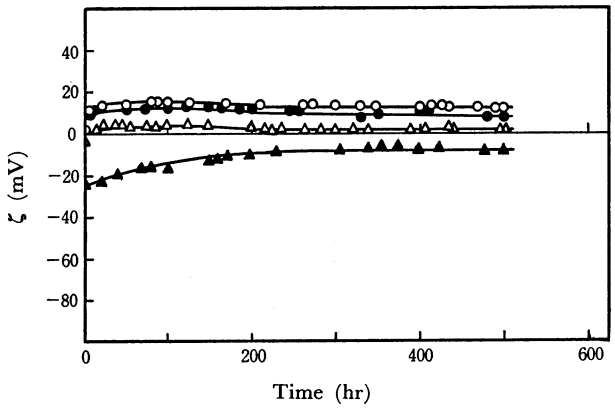


Fig. 1a. ζ-potential of FII pretreated at 600 °C against hydration time. ○: pH 7, ●: pH 8, △: pH 9, ▲: pH 10.

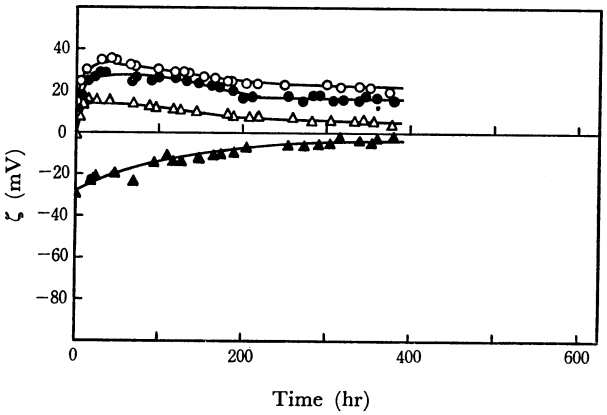


Fig. 1b. ζ-potential of FII pretreated at 800 °C against hydration time. ○: pH 7, ●: pH 8, △: pH 9, ▲: pH 10.

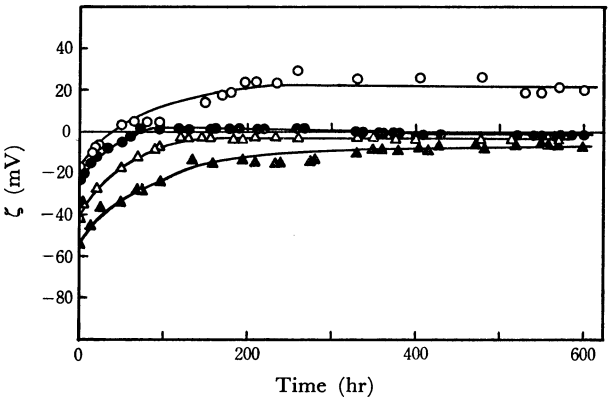


Fig. 1c. ζ-potential of FII pretreated at 1000 °C against hydration time. ○: pH 3, ●: pH 4, △: pH 5, ▲: pH 6.

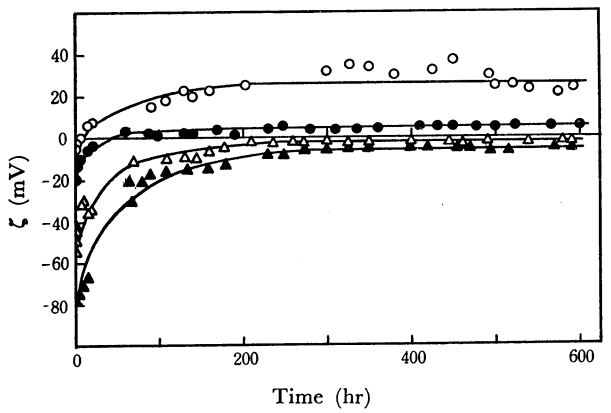


Fig. 1d. ζ-potential of FII pretreated at 1200 °C against hydration time. ○: pH 3, ●: pH 4, △: pH 5, ▲: pH 6.

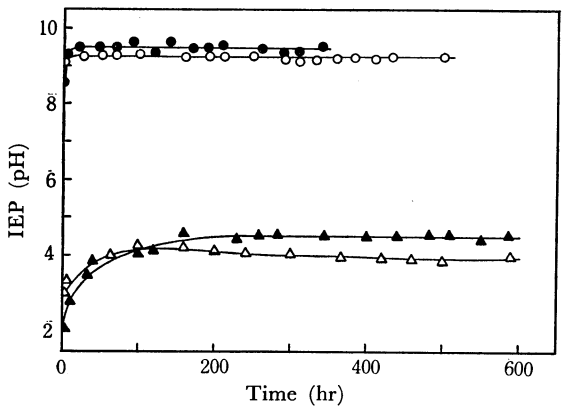


Fig. 2. Isoelectric point (IEP) of FII against hydration time. Pretreatment temperature, ○: 600 °C, ●: 800 °C, △: 1000 °C, ▲: 1200 °C.

7) T. Morimoto, This Bulletin, **37**, 386 (1964).
8) T. Morimoto, M. Nagao, and F. Tokuda, *J. Phys. Chem.*, **73**, 243 (1969).

first stage and then slowly; in some cases, the sign of the surface charge changes from negative to positive. The ζ-potential value of FII–600 and FII–800 could attain an equilibrium in a few hours, but it took a long time in the cases of FII–1000 and FII–1200 (about 200 hr). From the data given in Fig. 1 the isoelectric point can be determined to be changed with the immersion time (Fig. 2). It may be understood from Fig. 2 that the isoelectric point of iron oxides calcined at lower temperatures rapidly approaches higher equilibrium values, while those calcined at higher temperatures attain lower equilibrium values very slowly.

In Fig. 3, the water content of the FII–600 and FII–1200 surfaces is plotted as a function of the immersion time. This is expressed as the number of OH groups per 1 g of the sample left on the surface after long outgassing at 25 °C. It has been made clear that the water content thus obtained is mostly composed of chemisorbed water.[9] It can be seen from Fig. 3 that the surface of FII–600 can hydrate very rapidly in water to attain a saturated water content, while the hydration of FII–1200 proceeds very slowly. Taking into account the specific surface area, the water content of FII–600 can be expressed as about 13 OH's per 100 Å^2, irrespective of the hydration time. On the other hand, the specific surface area of FII–1200 is so small that it could not be determined exactly and that it was impossible to estimate the density of the surface water content, but it is evident that the density increases with the hydration time. The difference in hydration properties between the FII–600 and FII–1200 surfaces may be considered to correspond to the difference in the surface structure. Figure 4 shows the isoelectric point and the water content of FII–600 and FII–1200 as a function of the hydration time, where a good parallelism can be seen between the two quantities in each iron oxide.

It has been proposed that surface hydration may

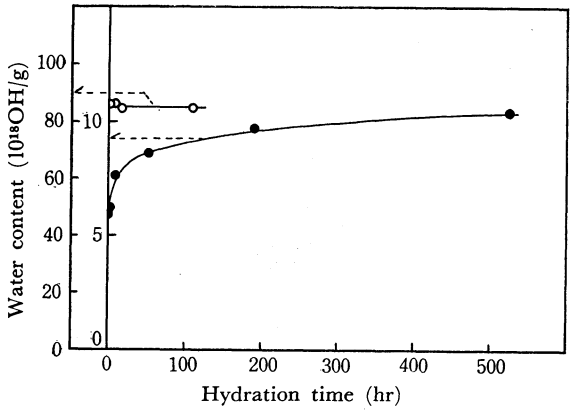


Fig. 3. Water content of FII against hydration time. Pretreatment temperature, ○: 600 °C, ●: 1200 °C.

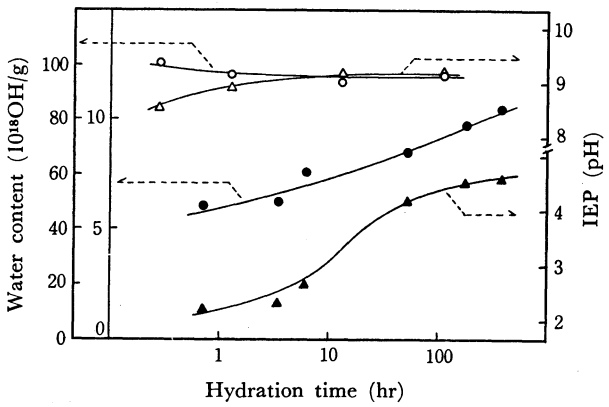
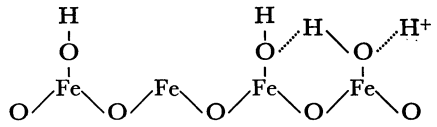


Fig. 4. Water content and IEP of FII against hydration time. ○: Water content, △: IEP. Open symbol, 600 °C; filled symbol, 1200 °C.

affect the surface charge of metal oxide.[6,10–12] However, no experimental evidence for this proposition has been reported. Therefore, the present results of direct measurements of the isoelectric point and of the surface hydration give the first verification of the proposition (Fig. 4). An increase in the water content of the FII surface must be due to the increase in chemisorbed water, as has been described above.

As is shown in Fig. 4, the progress of hydration gives rise to an enhanced density of the surface water content of iron oxide, which may itself possibly result in the mutual interaction of neighboring hydroxyl groups through hydrogen bonding:



The hydrogen-bond formation will make the oxygen atom less free and, at the same time, slightly richer in electron density compared with that in an isolated hydroxyl group, facilitating the attraction of another proton to it from the solution. Thus, it is reasonable that the isoelectric point of iron oxide is raised by the progress of hydration.

In Fig. 5, the equilibrium value of the isoelectric points of iron oxides is plotted against the calcination temperature. Generally, it can be seen from Fig. 5

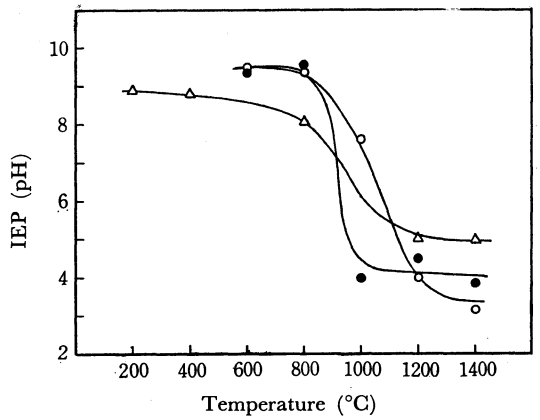


Fig. 5. Equilibrium IEP value of FI, FII and FIII against pretreatment temperature. ○: FI, ●: FII, △: FIII.

9) T. Morimoto and H. Naono, This Bulletin, **46**, 2000 (1973).
10) M. D. Robinson, J. A. Pask and D. W. Fuerstenau, *J. Amer. Ceram. Soc.*, **47**, 516 (1964).
11) Y. G. Berube and P. L. de Bruyn, *J. Colloid Interface Sci.*, **27**, 305 (1968).
12) D. J. O'Connor, P. G. Johansen and N. S. Buchanan, *Trans. Faraday Soc.*, **52**, 229 (1956).

that the isoelectric point of iron oxides (FI, FII) calcined below 800 °C shows an almost constant value (9.3—9.5), irrespective of the pretreatment temperature, while it falls sharply when pretreated at temperatures higher than 800 °C. The isoelectric point of FI falls sharply upon treatment at a temperature higher than in the case of FII, but an additional test showed that prolonged heating for more than 6 hr made the isoelectric point of FI similar to that of FII. The FIII samples which were prepared by the crushing and subsequent calcination of iron oxide in air at various temperatures represent the isoelectric points approximate to those of FI and FII; the variation in the isoelectric point between 800 and 1000 °C is similar to that of FI and FII.

Isoelectric points of the samples treated at lower temperatures (FI, FII, and FIII) are 8.1—9.5, approximate to the values of 8.2—9.1[13,14] reported for Fe_2O_3 samples, while the values (4.0—5.7) obtained with the samples treated at higher temperatures are close to that for Fe_3O_4 (6.5).[15] X-Ray diffraction analysis demonstrated that the crystal structure of FI and FII changes from Fe_2O_3 to Fe_3O_4 upon treatment at 1400 °C. Furthermore, the crystal structure of FIII calcined below 1200 °C was found to be α-Fe_2O_3, like those of the other two samples, though the FIII sample exhibits the Fe_3O_4 structure just after preparation by oxidizing pure iron. These facts suggest that iron oxides calcined below 800 °C have the higher isoelectric points characteristic of the Fe_2O_3 crystal structure, whereas those calcined above 1000 °C have the lower isoelectric points characteristic of the Fe_3O_4 structure, which might be produced on the surface even at temperatures (1000—1200 °C) lower than the decomposition temperature (1390 °C)[16] of Fe_2O_3 to Fe_3O_4.

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14) G. K. Korpi, "Measurement of Streaming Potentials," M. S. Thesis, Department of Metallurgy, MIT, 1960.
15) P. H. Tewari and A. W. Mc Lean, *J. Colloid Interface Sci.*, **40**, 267 (1972).
16) A. Muan, "Phase Diagrams," Vol. 2, ed. by A. Alper, Academic Press, New York (1963), p. 5.