Isoelectric Point of Manganese Oxide

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The isoelectric point (IEP) of manganese oxide is measured on samples prepared by heating β-MnO_2 and amorphous manganese oxide, $MnO_{1.75}$, at temperatures from 200 to 1400 °C. The IEP values thus obtained are characteristic of each stage of the oxidation of manganese oxide; that is, <5.1 for MnO_2, 7.6—9.0 for α-Mn_2O_3, and 3.3—5.2 for Mn_3O_4. These values can be explained by the electrostatic interaction theory introduced by Parks, in which the CFSE correction is eliminated. It is also found that manganese ions with specific valencies are responsible for the electrification of the surfaces of manganese oxide.

In order to clarify the origin of the electrification of metal oxides in aqueous media, the present authors have measured the electrokinetic potential (ζ-potential) or isoelectric point (IEP) of TiO_2,[1,2] Al_2O_3, Cr_2O_3, and Fe_2O_3[3-5] in electrolyte solutions. The results obtained indicate that the electrification of these metal oxides is generally determined by the electrostatic interaction between a metal ion on the solid surface and the H^+ ion in the surface hydroxyl group bonded to the metal ion,[4] to which the crystal structure of the oxide and the valency of the metal ion concerned are decisively responsible. A number of papers[6-8] have been published concerning the study of the IEP of metal oxides, but a very few works have related IEP to the crystal structure of a metal oxide and the valency of the component metal ion, which changes step-by-step upon heat treatment.[4,9]

The heat treatment of manganese oxide gives three types, which differ in the valency of the manganese ion, *i.e.*, MnO_2, Mn_2O_3, and Mn_3O_4. Fuerstenau *et al.*[10] have studied the electrification of manganese oxide, but only that of MnO_2. The purpose of this study is to measure the IEP of three kinds of manganese oxides which differ in composition, and to investigate the origin of the electrification of the oxides.

Experimental

Materials. Two samples of manganese oxide were used in this study. One was β-MnO_2 (MI), which was prepared by the pyrolysis of $Mn(NO_3)_2$ by heating it at 160 °C for 500 hr in air. The other was amorphous manganese oxide (MII), which was precipitated by mixing a 1 mol/l $Mn(NO_3)_2$ solution with 3 mol/l ammonia water in the presence of H_2O_2. The two samples were treated at various temperatures from 200 to 1400 °C for 3 hr in air, and then washed with distilled water until the ionic impurities in the filtrate disappeared; this resulted in the complete hydration of the surfaces.

The crystal structure of the samples was analyzed by the X-ray diffraction method, and the thermal analysis was carried out by means of the TGA method, in which the temperature was raised at the rate of 20 °C/min.

Measurement of IEP. The IEP of the samples was obtained by measuring the ζ-potential in aqueous solutions of various pH values. The ζ-potential was measured at 25.0 °C by using the streaming potential method, the Helmholtz-Smoluchowski equation being used as has been described previously.[3] The pH value was varied with HCl and NaOH. In order to keep the thickness of the electrical double layer constant and in order to eliminate the effect of surface conductance on the ζ-potential measurement,[11,12] the ionic strength was adjusted at 10^{-3} mol/l by using a NaCl solution. The deionized water used for the experiments was further purified by double distillation from an alkaline permanganate solution; prior to the measurement N_2 was bubbled in to remove any dissolved carbon dioxide.

Results and Discussion

Figure 1 shows the TGA data of the samples. It may be seen from Fig. 1 that the decomposition of MI starts at 540 °C and finishes at 650 °C to form Mn_2O_3, and that the latter decomposes at 920 °C to produce Mn_3O_4. On the other hand, the first sharp decomposition of MII occurs between 420 and 560 °C, while the second one occurs in the same temperature range as that of MI. X-Ray analysis showed that the MI sample has the structure of β-MnO_2, whereas the MII sample is amorphous; it has a nonstoichiometric composition, $MnO_{1.75}$, at room temperature, as is found by calculating from the data in Fig. 1. Furthermore, it was found that both samples represent α-Mn_2O_3 from 600 to 900 °C and Mn_3O_4 over 1000 °C, while the crystallinity of the α-Mn_2O_3 and Mn_3O_4 prepared from MII is more excellent than that prepared from MI.

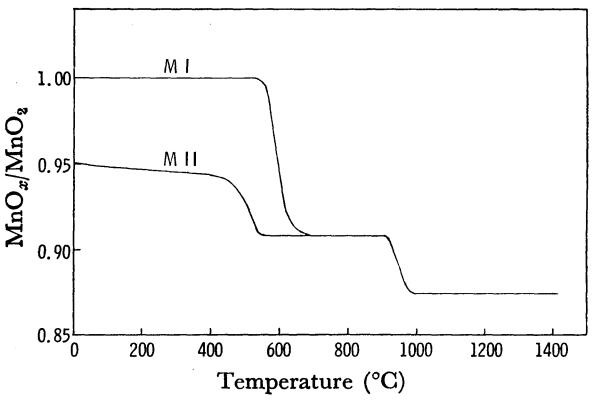

Fig. 1. TGA curve of manganese oxides.

The ζ-potential of MI is plotted against the pH value in Fig. 2. It may be seen clearly from Fig. 2 that the pH value of the zero point of charge, *i.e.*, IEP, changes remarkably with the pretreatment temperature of the samples. The IEP of MI and MII is plotted in Fig. 3 as a function of the temperature of pretreatment.

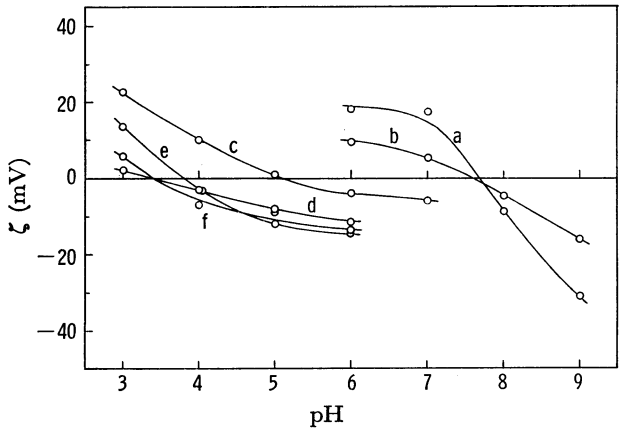

Fig. 2. ζ-potential of manganese oxide MI against pH, pretreated at a 500, b 800, c 900, d 1000, e 1200 and f 1400 °C.

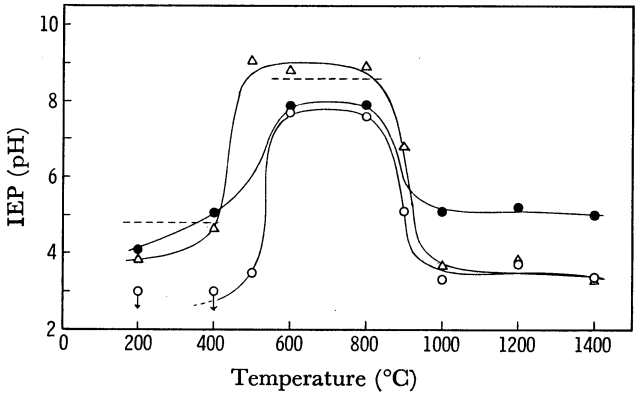

Fig. 3. IEP of manganese oxides against pretreatment temperature, ○ MI, ● crushed MI, and △ MII.

In this figure, the IEP of the samples which were obtained by crushing MI in an agate mortar is also added. Since the measurement of the ζ-potential of the samples pretreated below 400 °C (below 500 °C in the case of MI), however, was very difficult because of the high electric conductivity of the solids, the IEP in this temperature range was determined from the point where the sign of the streaming potential changed.

The comparison of the change in composition (Fig. 1) with the change in IEP (Fig. 3) makes it possible to infer that each oxidation state of manganese oxide has a characteristic value of IEP: that is, <5.1 for MnO_2, 7.6—9.0 for α-Mn_2O_3, and 3.3—5.2 for Mn_3O_4. Parks[6] has introduced a simi-empirical relation which describes the IEP of metal oxides can be expressed by this equation:

$$\text{IEP} = A - 11.5\left[\frac{Z}{R} + 0.0029a\right]. \quad (1)$$

Here, A is a constant which depends on the extent of surface hydration and the coordination number of surface metal ions, being 18.6 for fully-hydroxylated surfaces of metal oxides containing octahedrally-coordinated metal ions; Z is the valency of the metal ion. R is the distance between a surface metal ion and the H^+ ion in the surface hydroxyl group attached to the metal ion, that is, the sum of the radius of the metal ion and the diameter of the adjacent O^{2-} ion. a is the crystal-field stabilization energy for the hydration of metal ions, the second term in the bracket being the correction term for the coulombic interaction between a H^+ ion and the surface of a metal oxide. A preliminary calculation indicates that this correction is generally small in the present samples.

By introducing the crystallographic data into Eq. (1), IEP can be calculated to be 4.8 and 8.6 for β-MnO_2 and α-Mn_2O_3 respectively; they are represented as dotted lines in Fig. 3. Figure 3 shows that the observed and calculated values of IEP agree well with each other except for the data on uncrushed MI below 500 °C. It is interesting to note that IEP approaches more closely to the calculated value when the sample is crushed. This may be due to the fact that, on pyrolyzing and oxidizing the original samples at 160 °C in air, an excess of oxygens is bonded to surface metal ions, thus giving rise to a higher oxidation state of the metal ions.

As is well known, the structure of Mn_3O_4 is a spinel exhibiting the tetragonal form. The oxidation state of manganese ions and their coordination number to oxygen in Mn_3O_4, however, are subject to dispute; the formulas of $Mn^{2+}[Mn_2^{3+}]O_4$,[13] $Mn^{3+}[Mn^{2+}Mn^{3+}]O_4$,[14] and $Mn^{2+}[Mn^{2+}Mn^{4+}]O_4$[15] have been proposed, where the manganese ions in and outside the bracket are those of the coordination numbers of 6 and 4 respectively. The calculation of IEP for every type of these manganese ions according to Eq. (1) gives the values of 12.2, 9.6, and 5.8 for the octahedrally-coordinated Mn^{2+}, Mn^{3+} and Mn^{4+}, and 9.2 and 5.6 for the tetrahedrally-coordinated Mn^{2+} and Mn^{3+}, respectively. The observed value, 5.1, of IEP on the crushed MI approximates the calculated values, 5.6 and 5.8. This suggests that the octahedrally-coordinated Mn^{4+} and/or tetrahedrally-coordinated Mn^{3+} ions will determine the IEP of the samples. On the other hand, the IEP of uncrushed MI and MII are considerably smaller than these calculated values. This fact may be considered to depend on the characteristic features of the surfaces of Mn_3O_4 treated at elevated temperatures. If the Mn^{4+} ions tetrahedrally coordinated by oxygens are formed on the surfaces, then the calculated IEP will result in the value of 2.1. Thus, it may be possible to infer that the tetrahedrally-coordinated Mn^{4+} ions coexist along with tetrahedrally-coordinated Mn^{3+} and/or octahedrally-coordinated Mn^{4+} ions on the actual surface of Mn_3O_4.

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