BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (11), 3387—3388 (1978)

Surface Nonstoichiometry and Isoelectric Point of Manganese Oxide

Tetsuo MORIMOTO, Hidetoshi NAKAHATA, and Shigeharu KITTAKA*,†
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700
† *Department of Chemistry, Faculty of Science, Okayama College of Science, 1-1 Ridaicho, Okayama 700*

(Received May 18, 1978)

The isoelectric point and the nonstoichiometric composition of the surface layer were measured for manganese oxide samples treated *in vacuo* or in air at elevated temperatures. It was found that the surface composition of most samples tested was oxygen-deficient with reference to the bulk composition, and that the IEP was determined by the bulk structure rather than the surface composition. This was ascribed to the fact that the surface is heterogeneous and the dissolution of the solid will take place preferentially at surfaces which involve defect structures or Mn(II) ions.

Transition metals form a variety of nonstoichiometric compounds not only in the interior but also on the surface of the solids. Accordingly, the oxygen content on the surface of such metal compounds as oxides is liable to be excessive or deficient with reference to the bulk composition, as revealed from ESR study[1,2] or the test of the oxidizing power of the solid surface.[3–5] This situation should affect significantly the physical and chemical properties of solid surfaces, but few quantitative relationships between the nonstoichiometry and the properties of solid surfaces have been disclosed. Several authors studied surface excess oxygen in NiO,[3,6] Cr_2O_3,[4,7,8] and MnO_2[5] in connection with their catalytic activity.

In the preceding paper[9] the isoelectric point (IEP) of manganese oxide was studied as a function of pretreatment temperature. The results showed that the IEP of manganese oxide had a value characteristic of the bulk composition of the solid, which changed in three stages with increasing temperature of treatment; the results obtained were interpreted in terms of the idea that the IEP is governed by the valency and the coordination number of surface manganese ions. The IEP of samples treated at temperatures lower than 300 °C had such small values that the existence of Mn(IV) ions with the coordination number 4 on the surface was suggested.

We can naturally expect a drastic change in surface composition when a sample is treated *in vacuo* at elevated temperatures. This paper is concerned with the effect of evacuation treatment on the IEP value of manganese oxide and on the surface composition.

Experimental

Materials. The original sample of manganese oxide used in this study was prepared by the pyrolysis of guaranteed grade $Mn(NO_3)_2 \cdot 6H_2O$ at 160 °C for 400 h in an electric oven.[9] Powdered oxide was washed sufficiently with distilled water and finally electrodialyzed until the electrical conductivity of the supernatant solution was approximately equal to the value of deionized water ($1.43 \times 10^{-6}\ \mho\,cm^{-1}$). Then it was dried at 110 °C for 24 h in an electric oven, followed by the evacuation for 5 h at 300, 800, or 1000 °C in a vacuum of 1.33×10^{-3} Pa (M-300, M-800, and M-1000).

Another series of samples were also prepared by heating the samples M-300, M-800, and M-1000 for 5 h in air at 300, 800, and 1000 °C, respectively (M-300A, M-800A, and M-1000A).

Reaction of Surface Layer with KI. The reactivity of the solid surface with KI was examined in a vessel with the capacity of 300 cm^3, equipped with a breaking system of an ampoule containing the powdered sample. The sample was introduced into an ampoule by 2 m^2, evacuated at room temperature, and sealed. The ampoule was mounted on the ampoule holder and immersed in 100 cm^3 of a buffer solution containing 1.0 g KI. The space above the solution in the vessel was filled with N_2 to avoid the influence of air, and the vessel was thermostatted at 45 °C. After the equilibration of the system, the ampoule was broken and a vigorous shaking of the solution was started. For the preparation of buffer solutions the combination of $Na_2B_4O_7 \cdot 10H_2O$ and KH_2PO_4, which covers the wide range of pH values 5.4—9.0, was selected, because a preliminary test showed that a different combination of constituents of buffer solutions somewhat alters the reactivity of manganese oxide. After the attainment of reaction equilibrium, the amount of iodine was determined by titrating the solution with a standard $Na_2S_2O_3$ solution (1×10^{-3} mol/dm^3) by use of starch as an indicator. At the same time, the amount of Mn(II) ions dissolved was determined spectroscopically after treating the solution with 2% oxine.[10]

Measurement of IEP. The IEP value was measured by means of the streaming potential method, as described previously.[11]

Results and Discussion

Figures 1, 2, and 3 give the amounts of iodine and Mn(II) ions which were formed by the reaction of KI with manganese oxide surfaces, as a function of pH. The results obtained show that the amount of reaction products decreases exponentially with increasing pH and vanishes at pH 8. Under the present conditions, the dissolution of manganese oxide takes place according to the following reactions:

$$MnO + 2H^+ \longrightarrow Mn^{2+} + H_2O \qquad (1)$$

$$MnO_2 + 4H^+ + 2I^- \longrightarrow Mn^{2+} + I_2 + 2H_2O \qquad (2)$$

$$O(s) + 2H^+ + 2I^- \longrightarrow I_2 + H_2O \qquad (3)$$

Reaction 1 implies the dissolution of Mn(II) oxide, which is an oxygen-deficient compound possibly formed on the surface of manganese oxide, and Reaction 3 the dissolution of excess oxygens on MnO_2 surfaces. If the surface composition of a sample is somewhat smaller in oxygen content than MnO_2, Reactions 1 and 2 will take place simultaneously, whereas if it is somewhat larger than MnO_2, Reactions 2 and 3 will occur simultaneously. The fact that the dissolved amounts of both iodine and Mn(II) ions

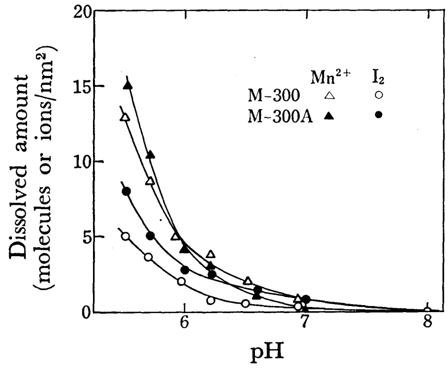

Fig. 1. pH dependence of the amounts of I_2 and Mn(II) ions formed from sample M-300 and M-300A.

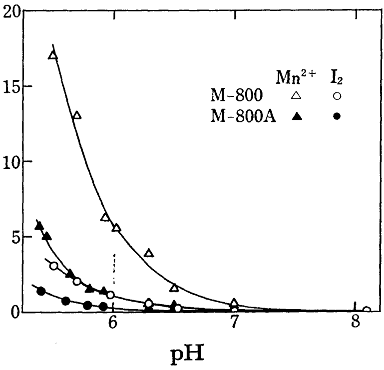

Fig. 2. pH dependence of the amounts of I_2 and Mn(II) ions formed from the sample M-800 and M-800A.

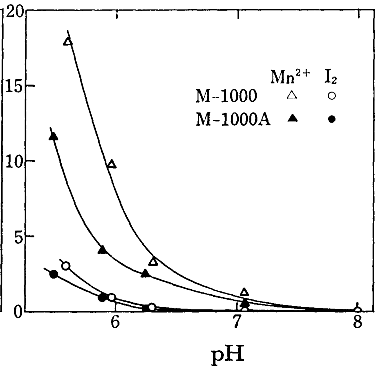

Fig. 3. pH dependence of the amounts of I_2 and Mn(II) ions formed from sample M-1000 and M-1000A.

TABLE 1. COMPOSITION OF SURFACE LAYER OF MANGANESE OXIDE

Sample	Surface area[a)] ($m^2 g^{-1}$)	Crystal structure[b)]	x value in MnO_x pH 5.4–5.5	5.6–5.7	5.9–6.0	6.2–6.3	6.5–6.6	*IEP*
M-300	2.24	β-MnO_2	1.40	1.37	1.36	1.30	1.19	<3
M-300A	1.86	β-MnO_2	1.53	1.55	1.66	1.94	2·44	<3
M-800	0.960	Mn_3O_4	1.19	1.16	1.16	1.15	1.14	4.54
M-800A	1.31	α-Mn_2O_3	1.27	1.27	1.25	1.21	1.22	8.17
M-1000	0.536	Mn_3O_4	—	1.16	1.07	1.03	—	3.30
M-1000A	0.605	Mn_3O_4	1.15	—	1.12	1.11	—	3.22

a) Measured by N_2-adsorption, assuming the molecular area to be 0.162 nm^2.
b) Determined by X-ray analysis.

increase rapidly with decreasing pH is due to the increase in solubility and oxidation potential of manganese oxide with pH, as shown in Eqs. 1, 2, and 3.

The data in Figs. 1—3 permit the calculation of the composition of dissolved substances, as given in Table 1, where the x value in MnO_x is listed. In addition, the thickness of the dissolved layer can be estimated. It was found to be about 2.4 layers at maximum at pH 5.5 (Fig. 1) by assuming that the real surfaces are mainly composed of the (110) plane,[12)] which has a Mn(IV) ion density of 5.55 nm^{-2}. Table 1 indicates that the surface composition of samples evacuated at elevated temperatures is deficient in oxygen with reference to the bulk composition, and that the succeeding treatment in air at the same temperature as before does not give such a large increment in surface oxygen. Thus the surface is still kept deficient in oxygen with respect to the bulk composition, except for the case of M-300A.

In Table 1, the *IEP* values of samples are also listed. Here, one can see that the sample treated *in vacuo* at 800 °C exhibits a small *IEP* value 4.54, but this increases to 8.17 when treated in air, and is accompanied by the conversion from Mn_3O_4 to α-Mn_2O_3 of the bulk composition. The present results, including this finding, have the same tendency as those obtained in the previous work:[9)] manganese oxide gives *IEP* values characteristic of the bulk structure, which changes with heat treatment at different temperatures. Admittedly, no intimate correlation was found between surface composition and *IEP*. It seems at first sight strange that the *IEP* does not depend on the surface composition, but is determined by the bulk structure. This may be due to the fact that the solid surface is heterogeneous, and consequently the reaction with KI or the dissolution of the solid takes place preferentially at the surface, which involves defect structures or Mn(II) ions. On the same surface, a more stable structure which is dissolved only with difficulty should also be present: manganese ions on this part of the surface will determine the *IEP* of samples.

Finally, the extremely small *IEP* values of the 300-treated samples, *i.e.* less than 3, still have not been elucidated in this study; but there remains the possibility of the existence of Mn(IV) ions with the coordination number 4, which comes from the oxygen-deficient states of the surface.

References

1) R. D. Iyenger and M. Codell, *Adv. Colloid Interface Sci.*, **3**, 365 (1972).
2) Y. Mizokawa and S. Nakamura, *Jpn. J. Appl. Phys.*, **14**, 779 (1975).
3) T. Uchijima, M. Takahashi, and Y. Yoneda, *Bull. Chem. Soc. Jpn.*, **40**, 2767 (1967).
4) S. Weller and S. E. Voltz, *J. Am. Chem. Soc.*, **76**, 4695 (1954).
5) Y. Inoue, S. Hasegawa, and T. Kawaguchi, *Nippon Kagaku Zasshi*, **91**, 1034 (1970).
6) T. Uchijima, M. Takahashi, and Y. Yoneda, *J. Catal.*, **9**, 403 (1967).
7) J. Deren, J. Haber, A. Podgorecka, and J. Burzyk, *J. Catal.*, **2**, 161 (1963).
8) J. Deren and J. Haber, *J. Catal.*, **4**, 22 (1965).
9) T. Morimoto and S. Kittaka, *Bull. Chem. Soc. Jpn.*, **49**, 1586 (1974).
10) K. Motojima, H. Hashitani, and T. Imahashi, *Anal. Chem.*, **34**, 571 (1962).
11) S. Kittaka, *J. Colloid Interface Sci.*, **48**, 327 (1974).
12) L. G. Berry and B. Mason, "Mineralogy," W. H. Freeman and Co., San Francisco (1959), p. 373.