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The Formation and Some Properties of Hydrous Manganese(IV) Oxide

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The properties of two kinds of hydrous manganese(IV) oxides (abbreviated as hydrous MnO_2) prepared by the reduction of $KMnO_4$ and by the disproportionation of K_2MnO_4 in alkaline solutions were investigated by means of chemical analysis, X-ray analysis, IR spectroscopy, wide-line NMR spectroscopy, thermal analysis, magnetic susceptibility measurement, *etc.* The chemical reactivity of the hydrous MnO_2 was also evaluated from the extent of oxidation to K_2MnO_4 by the reaction with an alkaline $KMnO_4$ solution at 80 °C. The properties and reactivity of the hydrous MnO_2 predominantly depended on the pH of the suspensions. At a pH 8 or higher, amorphous ternary compounds of manganese(IV) oxide with an approximate composition of $K_2O\cdot 4MnO_x\cdot 4H_2O$ ($x=1.97$—2.00) were formed. The IR spectra and wide-line NMR spectra showed that the chemically bound water was in two different forms. The hydrous MnO_2 had the greater chemical reactivity, being easily soluble as manganate(VI) ions by the reaction described above. The contents of the chemically bound water and alkali in the hydrous MnO_2 decreased with a decrease in the pH of the suspensions and upon the acid-treatment of the precipitates. This variation in the chemical composition caused a decrease in the reactivity and a marked variation in the thermal behavior. The structure of the hydrous MnO_2 was discussed on the basis of findings regarding the magnetic susceptibility and its temperature dependence.

The synthetic manganese(IV) oxide prepared by the reduction of $KMnO_4$ in alkaline solutions is generally called "Hydrous MnO_2"[1] because of a large content of chemically bound water. It is also a giant molecule which is seldom stoichiometric. In the chemical industries, the hydrous MnO_2 is formed only in the production of saccharin as a by-product. Therefore, studies of its properties and chemical reactivity have been performed in comparison with those of various MnO_2 substances prepared by the pyrolysis of manganese(II) compounds or by the oxidation of manganese(II) ions in acid solutions. According to Regner *et al.*[2] and Sterr and Schmier,[3] the hydrous MnO_2 has the formula of $3MnO_2\cdot MOH\cdot 2H_2O$ (M=K, Na) and the structure of δ-MnO_2, but there remains a lack of understanding the relationship between the various properties and the conditions of preparation. The present authors have now studied the reactivity of various kinds of hydrous MnO_2 in order to develop an alkaline $KMnO_4$ solution for use in air-pollution control, such as the removal of nitrogen oxides from waste gas,[4] and have found that the properties and reactivity are greatly influenced by the conditions of formation. The main purpose of this paper is to report on the factors influencing the chemical composition, the reactivity, and some properties of the hydrous MnO_2 prepared by the reduction of alkaline $KMnO_4$ solutions and by the disproportionation of alkaline K_2MnO_4 solutions.

Experimental

Materials. $KMnO_4$ and K_2MnO_4 were used as the starting materials. The $KMnO_4$ was a commercial extra pure reagent. The K_2MnO_4 was prepared by the decomposition of $KMnO_4$, boiling it in a 6 M (1 M=1 mol dm^{-3}) potassium hydroxide solution and then keeping it dry in a desiccator over phosphorus(V) oxide.

Preparation of Hydrous MnO_2. The hydrous MnO_2 substances were prepared by the following two reactions. (1) A four-necked flask was equipped with a reflux condenser, a dropping funnel, a glass electrode of a pH meter, and a thermometer. A definite quantity of an alkaline solution of 0.1—0.2 M $KMnO_4$ in the range from 300 to 500 cm^3 was introduced into the flask, and then heated to the desired temperatures (30, 56, 86 °C). A solution of the reducing agent, such as H_2O_2, K_2SO_3, and KNO_2, in the dropping funnel was then added, drop by drop (100 cm^3/h), to the $KMnO_4$ solution during violent agitation by means of a magnetic stirrer. Potassium hydroxide was used as an alkali component, while potassium hydrogencarbonate was suitably used as a pH controller. After the completion of the addition, the suspensions were stirred for a further 30 min. The products were then separated from the suspensions by filtration, washed with distilled water, and dried overnight at 110 °C. (2) A definite quantity of an alkaline solution of 0.6 M K_2MnO_4 in the range from 300 to 500 cm^3 was introduced into the flask, and then the mixture was heated to 50 °C. A 0.5—1.0 M H_2SO_4 solution in a dropping funnel was added, drop by drop (100 cm^3/h), to the K_2MnO_4 solution with violent agitation until the pH of the suspensions attained the desired value. The subsequent treatment of the precipitated hydrous MnO_2 was the same as has been described above (1).

Analysis of Chemical Composition of Hydrous MnO_2. The hydrous MnO_2 substances were dried overnight in an electric oven in air to eliminate the adsorbed water and subsequently analyzed for available oxygen, manganese, and potassium contents. The available oxygen was determined by the standard oxalic acid method.[5] Absorption spectroscopy was used for the determination of the manganese content. In this analysis, the manganese(II) ion obtained by the reduction of the sample with oxalic acid was oxidized to the permanganate ion by potassium periodate in the presence of a mixed acid (HNO_3: H_3PO_4: H_2O=1: 1: 1). The x-value in MnO_x was calculated from the resulting data. The potassium content was determined by atomic absorption spectroscopy. The balance was regarded as the chemically bound water.

Characterization of Hydrous MnO_2. The X-ray diffraction patterns were obtained using a Rigaku Denki Geigerflex D-2F with Mn filtered Fe $K\alpha$ radiation, with 25 kVP and 10 mA. The IR absorption spectra were obtained using a Shimadzu I-430 spectrometer with the KBr pellet technique. The wide-line NMR absorption spectra measurements were made at 40 MHz using a Nippon Denshi JNMW-40 spectrometer equipped with a 9000 variable-frequency oscillator. The samples were pressed to form tablets in order to increase the proton number per unit volume. The surface area was measured by means of the BET nitrogen adsorption at 78 K, after outgassing at 373 K. The samples were prepared by the acetone drying of the hydrous MnO_2 suspensions after filtration in order to keep the original particle shape. The magnetic susceptibility was measured at temperatures from 77 to 298 K using a magnetic balance with a maximum magnetic field strength of 2 T. DTA and TG were performed using a Rigaku Denki Thermoflex over the range from room temperature to 1200 °C. The rate of temperature rise was 10 °C/min.

Evaluation of Chemical Reactivity of Hydrous MnO_2. The chemical reactivity of the hydrous MnO_2 with an alkaline $KMnO_4$ solution was measured as follows. The hydrous MnO_2** (5.00×10^{-3} mol Mn) was stirred in a 200 cm^3 Erlenmeyer flask with a 100 cm^3 portion of a 6.0 M potassium hydroxide solution. Subsequently, a 1.586 g portion of fine-ground $KMnO_4$ (1.000×10^{-2} mol) was added to the hydrous MnO_2 suspension, after which the reaction was continued under violent agitation for a period of 2 h at 80 °C† as

$$MnO_2 + 2KMnO_4 + 4KOH = 3K_2MnO_4 + 2H_2O. \quad (1)$$

After having been filtered, the amount of the residual hydrous MnO_2 was determined by the absorption spectroscopy previously described. The chemical reactivity was defined as the degree of the oxidation (abbreviated as D.O. hereafter), which is given by

$$\text{D.O. } (\%) = \frac{[MnO_2]_0 - [MnO_2]_t}{[MnO_2]_0} \times 100$$

$[\ ]_0$: Initial amount, $[\ ]_t$: amount after 2 h.

Results and Discussion

The chemical composition and reactivity of the hydrous MnO_2 prepared by the reduction of alkaline $KMnO_4$ solutions and by the disproportionation of

Table 1. Reduction conditions of potassium permanganate solutions, chemical composition and reactivity, D.O., of the hydrous MnO_2 substances

No.	Conditions						Composition a)				D.O.
	$KMnO_4$ M	KOH M	$KHCO_3$ M	pH	Temp °C	Reducing agent	MnO_2 wt%	x in MnO_x	K_2O wt%	H_2O wt%	%
1	0.1	0.2	—	13.3—12.5	86	0.6%-H_2O_2	66.3	1.93	17.2	16.5	54.8
2	0.1	0.2	1.0	9.2—9.3	86	0.6%-H_2O_2	66.3	1.93	17.0	16.7	57.1
3	0.1	0.2	—	13.3—12.8	30	3%-H_2O_2	67.7	1.97	18.1	14.2	81.9
4	0.1	0.2	—	13.3—12.8	86	3%-H_2O_2	67.4	1.90	16.1	16.5	66.0
5	0.1	0.2	—	13.3—12.6	50	0.1 M-K_2SO_3	68.2	1.98	18.4	13.4	79.6
6	0.1	—	0.1	8.5—9.6	50	0.1 M-K_2SO_3	67.1	1.99	17.6	15.3	69.3
7	0.1	0.2	—	13.1—11.7	86	0.1 M-K_2SO_3	67.4	1.98	17.1	15.5	56.6
8	0.2	0.1	—	12.8—12.1	50	0.3 M-KNO_2	67.9	2.00	16.4	15.7	80.8
9	0.2	—	0.5	8.1—9.1	50	0.3 M-KNO_2	70.0	1.99	16.8	13.2	74.6
10	0.2	0.1	0.5	9.3—9.5	50	0.3 M-KNO_2	68.3	1.98	16.9	14.8	93.9
11	0.2	0.1	0.5	9.3—9.6	30	0.3 M-KNO_2	67.2	1.98	15.1	17.7	91.1
12	0.2	0.1	0.5	9.3—9.5	86	0.3 M-KNO_2	73.1	1.98	14.9	15.1	61.9

a) The calculated chemical composition of the $K_2O \cdot 4MnO_2 \cdot 4H_2O$ formula is as 18.3 K_2O, 67.7 MnO_2, and 14.0 H_2O (wt%).

Table 2. Disproportionation conditions of potassium manganate(VI) solutions, chemical composition and reactivity, D.O., of the hydrous MnO_2 substances.

No.	Conditions					Composition a)				D.O.
	K_2MnO_4 M	KOH M	pH	Temp °C	Acid	MnO_2 wt%	x in MnO_x	K_2O wt%	H_2O wt%	%
13	0.6	0.1	13.5—12.7	50	0.5 M-H_2SO_4	69.0	1.99	18.2	12.8	72.7
14	0.6	0.1	13.5—4.1	50	0.5 M-H_2SO_4	80.5	1.94	8.8	10.7	37.4
15	0.6	0.1	13.5—3.2	50	0.5 M-H_2SO_4	83.2	1.92	7.7	9.1	14.7
16	0.6	1.0	13.9—13.0	50	1 M-H_2SO_4	66.0	1.99	17.7	16.3	92.4
17	0.6	1.0	13.8—8.1	50	1 M-H_2SO_4	68.4	2.00	16.4	15.2	82.1
18	0.6	1.0	13.6—6.0	50	1 M-H_2SO_4	73.0	1.98	12.5	14.5	75.2
19	0.6	1.0	13.9—4.0	50	1 M-H_2SO_4	80.7	1.94	6.4	12.9	72.4
20	0.6	1.0	13.8—3.3	80	1 M-H_2SO_4	78.9	1.94	7.7	13.4	53.0
21	0.6	1.0	13.9—2.1	50	1 M-H_2SO_4	84.8	1.91	2.2	13.0	22.6
22	1 M H_2SO_4 treatment of Sample No. 16					93.4	1.88	1.1	5.5	15.1
23	10 M KOH treatment of Sample No. 14					81.7	1.94	8.5	9.8	36.9

a) The calculated chemical composition of the $K_2O \cdot 4MnO_2 \cdot 4H_2O$ formula is as 18.3 K_2O, 67.7 MnO_2, and 14.0 H_2O (wt%).

** Because these was no difference in the reactivity between dried and undried samples, the later was used for this reaction.

† It has been found that the reaction is complete under these conditions.

alkaline K_2MnO_4 solutions are given in Tables 1 and 2 respectively.

Effects of pH. In the case of the reduction of a $KMnO_4$ solution, a low pH of the solution causes the reduction of $KMnO_4$ to the manganese(II) ion. The pH was, therefore, kept at about 8 or higher in the following reactions:

$$2KMnO_4 + H_2O_2 = 2MnO_2 + 2KOH + 2O_2 \tag{2}$$

$$2KMnO_4 + 3K_2SO_3 + H_2O = 2MnO_2 + 3K_2SO_4 + 2KOH \tag{3}$$

$$2KMnO_4 + 3KNO_2 + H_2O = 2MnO_2 + 3KMNO_3 + 2KOH \tag{4}$$

The hydrous MnO_2 obtained from the solution of pH$\gg$8 had an approximately constant composition, with the formula of $K_2O{\cdot}4MnO_x{\cdot}4H_2O$ (x=1.97—2.00), as is shown in Table 1. According to the X-ray diffraction patterns, they were all amorphous. The stoichiometry indicates that the hydrous MnO_2 substances shown in Table 1 are similar to the synthetic product studied by Sterr *et al.* and called δ-MnO_2, the formula of which is $KOH{\cdot}3MnO_2{\cdot}2H_2O$, and to the active MnO_2 studied by Regner *et al.*, the K_2O content of which is 11.3—14.9 wt%. However, the hydrous MnO_2 obtained in this experiment had the chemically bound water and a little more K_2O than the synthetic MnO_2 in their earlier studies. These differences in the chemical composition appeared to be dependent on the conditions of the washing treatment of the hydrous MnO_2 after filtration. Especially, the K_2O are involved with the MnO_2 particles with quite small bond forces at the time of the formation of the hydrous MnO_2. Its content was, therefore, decreased by repeated washings with distilled water. The hydrous MnO_2 substances shown in Tables 1 and 2 have been washed with the minimum amount of distilled water possible to remove only physically adsorbed ions, that is, until the absorbed permanganate ion was not observed in the wash water. All of the hydrous MnO_2 substances obtained from the solutions of pH$\gg$8 at low temperatures (30, 50 °C) were chemically active in the reaction (Eq. 1), the D.O. values being high, as is shown in Table 1. The results show that the pH of the original suspensions is an important factor in getting the highly active hydrous MnO_2. In the process of removing NO_x from waste gas with an alkaline $KMnO_4$ solution,[4] the hydrous MnO_2 obtained as a by-product is regenerated to a soluble manganate(VI) by a reaction according to Eq. 1. It is easy to oxidize the manganate(VI) to permanganate by the electrolytic oxidation.

The disproportionation of K_2MnO_4 solutions was performed by the drop-by-drop addition of a H_2SO_4 solution until the pH of the suspensions attained the desired value. Although the pH successively varied during the drop-by-drop addition of the acid in the following reaction:

$$3K_2MnO_4 + 2H_2SO_4 = MnO_2 + 2KMnO_4 + 2K_2SO_4 + 2H_2O \tag{5}$$

the effect was kept negligible by keeping the hydrous MnO_2 in a mother liquor at the each last pH shown in Table 2. Figure 1 clearly indicates the chemical reactivity, D.O., and the MnO_2 content as functions of the pH of the suspensions obtained by the disproportionation. The chemical composition and reactivity of the hydrous MnO_2 were influenced by the pH, especially in the range from pH 6 down. As is shown in Table 2, the hydrous MnO_2 substances precipitated at high pHs had chemical compositions and reactivities similar to those prepared by the reduction of $KMnO_4$ solutions described above. The MnO_2 content increased with a decrease in the pH; the chemical reactivity and the x-value in MnO_x also decreased simultaneously. The same tendency was observed by the acid-treatment of the hydrous MnO_2. A typical hydrous MnO_2, Sample No. 16, was mixed with a 1 M H_2SO_4 solution for 2 h at 50 °C. The chemical composition, reactivity, and D.O. of the resulting acid-treated MnO_2, Sample No. 22, are shown in Table 2. The hydrous MnO_2 lost not only a considerable amount of the chemically bound water and alkali, but also its high chemical reactivity upon the acid treatment. The X-ray diffraction pattern suggests that Sample No. 22 was slightly crystallized as α-MnO_2. On the other hand, when a hydrous MnO_2 with a low reactivity, Sample No. 14, was mixed with a 10 M KOH solution for 3 h at 80 °C, there was no change in the chemical composition and reactivity, as is shown in Table 2. The surface state of the hydrous MnO_2 obtained from the high pH of the suspensions is thermodynamically unstable and active. However, it easily becomes stable upon the acid treatment, though it recovers its original surface state by the alkali treatments only with great difficulty.

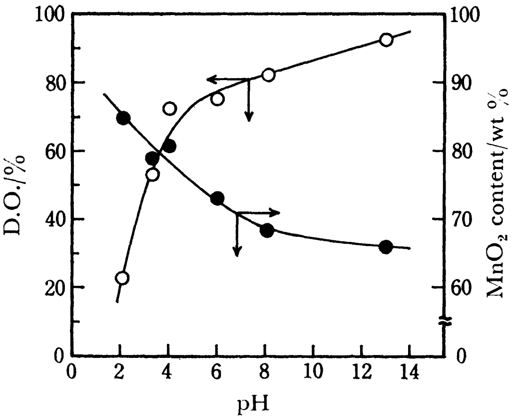


Fig. 1. The chemical reactivity, D.O. and MnO_2 content of the hydrous MnO_2 as a function of pH of suspensions obtained by disproportionation.

In the reaction of the hydrous MnO_2 with an alkaline $KMnO_4$ solution for a period of 2 h at 80 °C, only the manganate(VI) was always obtained as a final soluble manganate species in spite of the differences in the chemical reactivities of the hydrous MnO_2. In addition to the dissolved manganese, the solution contained some unreacted hydrous MnO_2. The results show that the decomposition of the alkaline $KMnO_4$ solution simultaneously occurred as follows: an available oxygen of $KMnO_4$ is wastefully consumed by

$$4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2 \tag{6}$$

the decomposition, which is accelerated by the presence of manganese(IV) oxides.[6,7] The hydrous MnO_2 substances with high D.O. values were, therefore, regarded as the active MnO_2 in reacting with permanganate ions. The reactivity of the hydrous MnO_2 substances with the alkaline $KMnO_4$ solution increased with increases in the chemically bound water and alkali contents. The results show that the chemically bound water and alkali play an important role in the oxidation of the hydrous MnO_2, (Eq. 1).

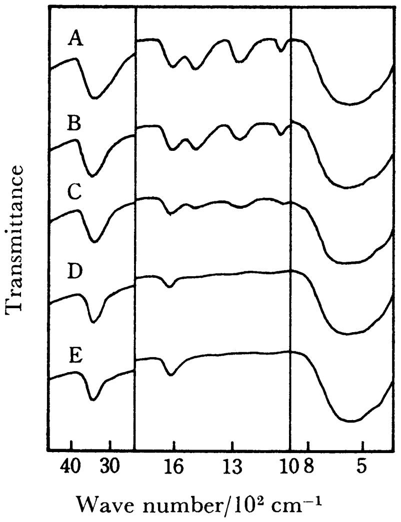


Fig. 2. IR spectra of the hydrous MnO_2 prepared at various pH of suspensions.
A: Sample No. 1—13, 16, 17 (pH>8.1), B: Sample No. 18 (pH 6.0), C: Sample No. 20 (pH 3.3), D: Sample No. 21 (pH 2.1), E: Sample No. 22 (pH<1).

IR and NMR Absorption Spectra. The IR spectra for the hydrous MnO_2 prepared at various pH values of the suspensions are given in Fig. 2. Sample No. 16, prepared at a high pH, has the typical composition of the hydrous MnO_2, and its spectrum displays five distinct bands at the frequencies of 440—620, 1050, 1280, 1510, 1630, and 3400 cm^{-1}. The bands at 1630 and 3400 cm^{-1} are the OH stretching band and the OH bending vibration band respectively. The broad band at 440—620 cm^{-1} is based on the Mn-O bond. The spectrum of the typical hydrous MnO_2 is characterized by additional three bands at 1050, 1280, and 1510 cm^{-1}. It seems likely that these three bands are based on the OH bending vibration combined with the Mn atom. However, it is possible that the bands are based on the bending vibration of the hydroxyl group containing alkali because of the correlation between the intensity of the absorbance and the K_2O content. No clear reversion could be made. Despite many studies[8] of the IR spectra of the natural MnO_2 ores and the synthetic MnO_2 obtained from the acid solutions by the use of various methods, these three bands shown in Fig. 2 have not yet been reported. The intensity of the absorbance of these three bands gradually becomes weaker with a decrease in the pH, until those for such hydrous MnO_2 substances as Sample No. 21, prepared at the lowest pH in this experiment, are ultimately not observed. A similar tendency was observed in the case of the acid-treated hydrous MnO_2, Sample No. 22. According to the chemical analysis, these hydrous MnO_2 substances still have a considerable amount of the chemically bound water, most of it in the form of the H_2O molecule. The evaluation of the chemical reactivity was possible by the measurement of the IR spectra because of the close correlation between the intensity of absorbance of the three bands and the chemical reactivity of the hydrous MnO_2.

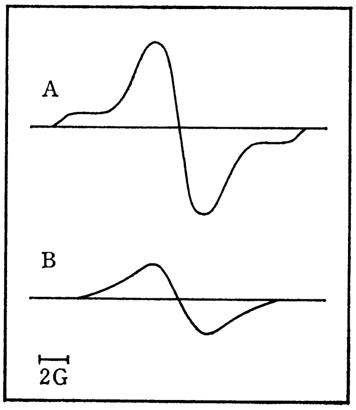
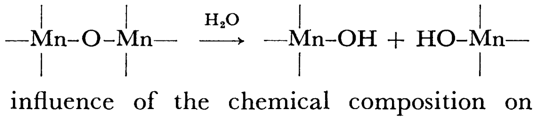


Fig. 3. Typical NMR spectra of the hydrous MnO_2. A: Sample No. 3, B: Sample No. 22 (Acid-treated MnO_2).

A typical NMR spectrum of the hydrous MnO_2, Sample No. 3, is shown in Fig. 3(A). This spectrum consists of a narrow absorption line, ΔH 3.8 G, superimposed on a broad one, ΔH 15.5 G. The broad line and the narrow one appear to be dependent on the hydroxyl group combined with the MnO_2 polymeric structure and on the H_2O molecule with a comparatively weak interaction to the lattice atom respectively. Glemser[9] distinguished between adsorbed water and chemically bound water by NMR spectroscopy for δ-MnO_2 and γ-MnO_2. These MnO_2 substances showed a broad line, with a superimposed narrow line with a width of 2.1—2.2 G which is due to the physically adsorbed water. The proton causing the narrow line in Fig. 3(A) is not so free in the hydrous MnO_2 structure. Therefore, it appears to belong to the H_2O molecule combined with the lattice. The hydrous MnO_2 obtained from the alkaline solution is a kind of hydro-gel, for it is amorphous and contains a large amount of water and alkali. The water in such gels never has a definite form in the bond state such as the physically adsorbed water and the water of crystallization have. In the case of the hydrous MnO_2, the water may be contained in a porous structure of the MnO_2 polymer in various bond states, and the polymer chain is cleaved to form the hydroxyl group as follows:



$$\text{—Mn–O–Mn—} \xrightarrow{H_2O} \text{—Mn–OH} + \text{HO–Mn—}$$

The influence of the chemical composition on the reactivity of the hydrous MnO_2 indicates that the H_2O molecule in the hydrous MnO_2, which forms most of the chemically bound water, is not merely the physically adsorbed water. The NMR spectrum of the acid-treated hydrous MnO_2 containing 5.5 wt% of chemically bound water, Sample No. 22, is shown in Fig. 3(B). While a broad absorption line vanished, a narrow one still remained with a weak intensity. These spectra indicate the same results as those of the IR spectra shown in Fig. 2.

Effects of Temperature. The chemical composition of the hydrous MnO_2 varied depending upon the temperature of the suspensions shown in Table 1, but this variation was not so remarkable as the effect of the pH. The contents of the chemically bound water and alkali in the hydrous MnO_2 slightly decreased with an increase in the temperature of the suspensions, and the chemical reactivity decreased because of the reduction of the active sites in the reaction (Eq. 1). The x-value in MnO_x of the hydrous MnO_2 prepared by reduction at a high temperature decreased to 1.90—1.93 when the H_2O_2 solution was used as a reducing agent. However, this tendency was not observed in the case of the hydrous MnO_2 prepared by the use of other kinds of reducing agents. The difference in the amount of available oxygen of the hydrous MnO_2 appeared to originate from the reducing force of the reducing agent used. The redox of the manganese ion and the replacement of O^{2-} by any other ions occur without any changes in the crystal lattice in manganese(IV) oxides, well known as typical homogeneous, solid redox systems.[10)]

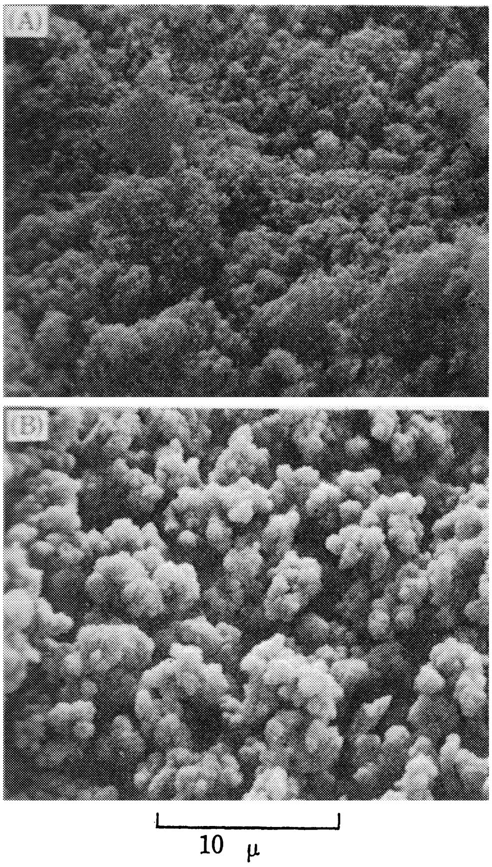


Fig. 4. Scanning electron micrographs of the hydrous MnO_2 prepared by reduction.
(A): Reduction by H_2O_2 (Sample No. 3), (B): Reduction by KNO_2 (Sample No. 8).

A H_2O_2 solution, therefore, reacts with the precipitated hydrous MnO_2 to produce the scarece oxygen hydrous MnO_2 at high temperatures because of the strong reducing force.

Effects of Reducing Agents. The particle shape of the hydrous MnO_2 varied with the kind of reducing agent in spite of the constant chemical composition and reactivity. Some typical SEM photographs of the hydrous MnO_2 are shown in Fig. 4. While the hydrous MnO_2 prepared by reduction with the H_2O_2 solution (**A**) was irregularly piled with fine amorphous particles, the one prepared with the KNO_2 solution (**B**) coagulated to quite a large spherical shape. The hydrous MnO_2 prepared with the K_2SO_3 solution also coagulated to a spherical shape, but the size of the second-order particle was smaller than that prepared with the KNO_2 solutions. A spherical-shape hydrous MnO_2 such as Sample No. 8 has been also produced as a by-product of the absorption of NO_x gas with a high alkaline solution of $KMnO_4$. The surface area of a representative hydrous MnO_2 is tabulated in Table 3. As would be from the particle shape shown in Fig. 4, the surface area varied with the conditions of preparation. The hydrous MnO_2 substances prepared both by the reduction of $KMnO_4$ with the H_2O_2 solution and by the disproportionation of the K_2MnO_4 solution have large surface areas. Figure 5 indicates the chemical reactivity, the D.O., and the MnO_2 content as functions of the surface area of the hydrous MnO_2 in Table 3. Although Samples Nos. 3, 5,

Table 3. Surface area of the hydrous MnO_2 measured by the BET method

No.	Surface area / m^2/g
3[a)]	136.6
5[a)]	16.1
8[a)]	9.1
16[b)]	92.6
21[b)]	147.5

a) Prepared by reduction. b) Prepared by disproportionation.

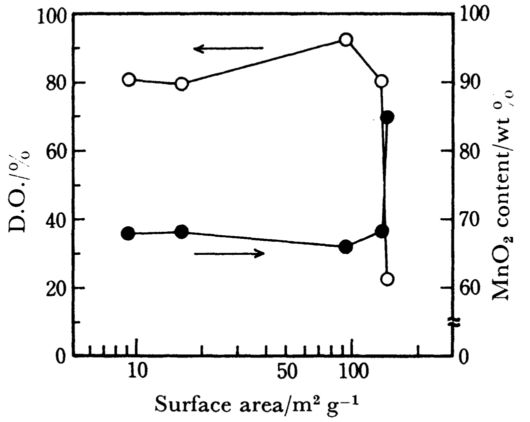


Fig. 5. The chemical reactivity, D.O. and MnO_2 content of the hydrous MnO_2 as a function of the surface area measured by the BET method.

TABLE 4. PHASE VARIATIONS OF THE HYDROUS MnO_2 WITH HEATING

K/Mn molar ratio	Temperature rising			
0.5	amor.[a] →	amor. $K_2Mn_4O_8$[b]	→ $K_2Mn_4O_8$	
0.125	amor. →	KMn_8O_{16}[c]	→ $K_2Mn_4O_8$ Mn_2O_3[d]	→ $K_2Mn_4O_8$ Mn_3O_4[e]
0.05	amor. →	Mn_2O_3 amor.	→ Mn_2O_3 $K_2Mn_4O_8$	→ Mn_3O_4 K_2Mn_4O

a) Amorphous. b) Potassium permanganite. c) Cryptomelane. d) Bixbyte. e) Hausmannite.

and 8 were prepared under the same conditions except for the kind of reducing agent, there was no correlation between the chemical reactivity and the surface area. Sample No. 16, obtained from the suspension with a pH of 13.0, had the same chemical composition and reactivity as Samples Nos. 3, 5, and 8. On the other hand, the chemical reactivity of Sample No. 21, obtained from a suspension with a pH of 2.1, decreased very much in spite of its large surface area. The results show that the diffusion of the permanganate ion into the particles of the hydrous MnO_2 is fast, without any correlation to the apparent surface area, and that the chemical reactivity is only influenced by the chemical composition, that is, the number of active sites as has previously been described. The hydrous MnO_2 prepared by the disproportionation of K_3MnO_4, which if formed by the oxidation of pyrolusite with KOH–KNO_3 molten salts,[11] was similar to those obtained in this experiment.

Thermal Behavior. TG and DTA curves of the hydrous MnO_2 substances obtained from suspensions with various pHs were classified into the three types shown in Fig. 6. The DTA curves varied according to the pH of the suspensions. As has been described previously, the chemical composition, especially the K_2O content of the hydrous MnO_2, also varied according to the pH of the suspensions. Therefore, the K_2O content appeared to cause the varying thermal behavior of the hydrous MnO_2. The results of the X-ray analysis and chemical analysis of the heated samples obtained at different temperatures are shown in Table 4. Sample No. 16, the K/Mn molar ratio of the chemical composition of which was about 0.5, gradually crystallized to form potassium permanganite,[12] $K_2Mn_4O_8$, during the heating process and was completely transformed to $K_2Mn_4O_8$ above 900 °C. The continuous weight loss in the heating process to about 900 °C indicated on the TG curve, which was due to the release of a large amount of the chemically bound water, corresponded with the broad endothermic peak of the DTA curve. The chemically bound water still remained in the hydrous MnO_2 at a considerable high temperature, and the IR spectrum of the sample heated at about 700 °C had the absorption bands based on the chemically bound water. On the other hand, Sample No. 19, with a K/Mn molar ratio of 0.15, rapidly crystallized to form cryptomelane,[13] KMn_8O_{16}, with a sharp exothermic peak at 450 °C. This exothermic peak was generally shown on the DTA curves of the hydrous MnO_2 with a K/Mn molar ratio of about 0.1—0.3. The nearer the K/Mn molar ratio came to the theoretical value, 0.125, the larger and sharper the exothermic peak became. On further heating, this material was decomposed into $K_2Mn_4O_8$ and bixbyte,[14] Mn_2O_3, which was then further decomposed into hausmannite,[15] Mn_3O_4, with an increase in the temperature. In the case of Sample No. 21, the K/Mn molar ratio of which was still small, the exothermic peak due to the formation of KMn_8O_{16} was not seen on the DTA curve. The thermal behavior of the hydrous MnO_2 prepared by the reduction of the $KMnO_4$ solution was quite similar to that of such a hydrous MnO_2 as Sample No. 16. Table 4 shows that the DTA curves of the hydrous MnO_2 substances continuously varied according to the change in the K_2O content. The other kinds of manganese(IV) oxide with no K_2O content, such as synthetic β-MnO_2 and γ-MnO_2, indicated similar thermal behavior, as is shown in Fig. 6, upon the addition of potassium hydroxide to the samples. Therefore, the presence and amount of potassium must be checked in advance in the study of the thermal behavior of manganese(IV) oxides.

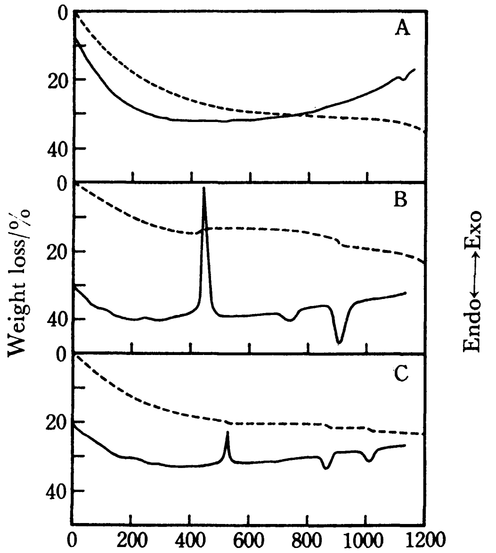


Fig. 6. TG and DTA curves of the hydrous MnO_2 prepared by disproportionation at various pH of suspensions.
A: Sample No. 16 (pH 13.0), B: Sample No. 19 (pH 4.0), C: Sample No. 21 (pH 2.1), amount of sample (mg)——A: 22.3, B: 21.9, C: 17.5, ----: TG, ——: DTA.

Table 5. Magnetic susceptibilities of the hydrous MnO_2 substances and the other kinds of MnO_2

No.	$\chi/10^{-6}$, (Temp/°C)
3[a]	65.1(26.5), 74.7(−25.0), 87.5(−75.3), 105.0(−112.7), 130.8(−159.7), 167.1(−195.8)
5[a]	62.2(26.5)
8[a]	66.2(26.5)
16[b]	46.9(23.0), 68.8(−64.8), 89.3(−126.0), 108.5(−155.2), 137.5(−195.8)
19[b]	53.1(23.5)
21[b]	55.4(18.8), 57.1(−7.8), 64.6(−62.0), 77.5(−107.0), 90.7(−144.6), 118.6(−195.8)
26 (α-MnO_2)	36.6(23.5)
27 (β-MnO_2)	27.2(21.9), 27.3(−17.2), 29.6(−75.0), 30.9 (−114.4), 33.4(−150.5), 34.3(−195.8)
28 (γ-MnO_2)	33.5(22.8)
29 (δ-MnO_2)	52.9(23.4)

a) Prepared by reduction. b) Prepared by disproportionation.

Two different DTA curves have been reported for the hydrous MnO_2 substances by Sterr *et al.* and by Regner *et al.* According to Sterr *et al.*, the DTA curve of the hydrous MnO_2 has an exothermic peak at 520 °C, but the DTA reported by Regner *et al.* has no exothermic peak. In view of our results, these different phenomena of the DTA curves appear to be dependent on the K_2O content of the hydrous MnO_2.

Magnetic Susceptibility. The structures and states of manganese(IV) oxides can be investigated by the measurement of their magnetic susceptibilities because of the paramagnetic property due to the unpaired electrons in the 3 d orbit. The magnetic susceptibilities of some typical hydrous MnO_2 substances are shown in Table 5 in contrast with those of the well-known α-, β-, γ-, and δ-MnO_2. The values in Table 5 are the magnetic susceptibilities per gram of MnO_2. The magnetic susceptibilities of the hydrous MnO_2 substances were all high, especially the values of those prepared by the reduction of the $KMnO_4$ solution by the H_2O_2 solution. Selwood *et al.*[16] have measured the magnetic susceptibilities of various kinds of manganese(IV) oxides, all confined within the range of 25—45×10^{-6} (25 °C). The high magnetic susceptibility of the hydrous MnO_2 substances can be attributed to the free spin of the unpaired electrons of the paramagnetic ion (Mn^{4+}). In other words, the distribution of ions is disordered, and the mutual interference of ions is extremely weak in the MnO_2 lattice. According to the magnetic classification of oxides by Selwood *et al.*, the hydrous MnO_2 substances could all be classified as typical "Disperse Oxides." The magnitude of the magnetic susceptibilities of the other MnO_2 substances was of the order of: $\delta\text{-}>\alpha\text{-}\gtrsim\gamma\text{-}>\beta\text{-}MnO_2$. There is a good agreement between our results and those of earlier workers. β-MnO_2 is the most stable crystal phase of all the MnO_2, and it has the highest degree of crystallization, according to the results of X-ray analysis. Therefore, β-MnO_2 had the lowest magnetic susceptibility, and its temperature dependence was not observed because of the interruption due to the free distribution of the spin of the unpaired electron. β-MnO_2 can be magnetically classified as a typical "Massive Oxide." The relationship between the magnetic susceptibilities of the hydrous MnO_2 substances and the pH's of the suspensions obtained by the disproportionation of K_2MnO_4 solution is shown in Fig. 7. The magnetic susceptibility increased with a decrease in the pH, which was itself due to the increase in the number of unpaired electrons in the hydrous MnO_2, namely, the decrease in the x-value of MnO_x. The temperature dependence of the magnetic susceptibility in the range from 77.4 K to room temperature is shown in Fig. 8. It was possible to calculate the

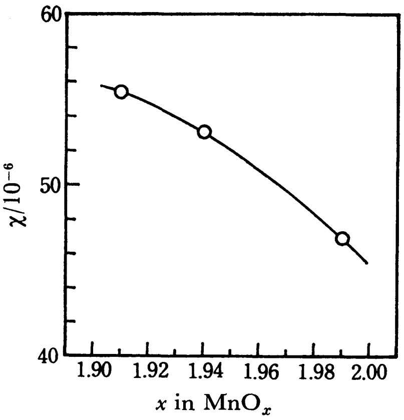


Fig. 7. Magnetic susceptibilities of the hydrous MnO_2 prepared by disproportionation as a function of x in MnO_x.

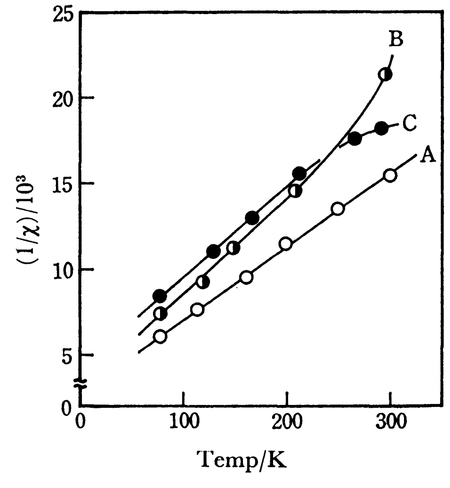


Fig. 8. Inverse magnetic susceptibilities of the hydrous MnO_2 prepared at various pH of suspensions as a function of temperature.

A: Sample No. 3 (pH 12.8), B: Sample No. 16 (pH 13.0), C: Sample No. 21 (pH 2.1).

magnetic moment because any hydrous MnO_2, Sample No. 3, appeared to follow the Curie-Weiss law. The moment for the manganese in this hydrous MnO_2 was 4.00 Bohr magneton compared with a theoretical moment of 3.87 Bohr magneton, while the Weiss constant was 63°. Two other hydrous MnO_2 substances, Samples Nos. 16 and 21, also appeared to follow the Curie-Weiss law in the temperature range from 77.4 to 220 K. The magnetic susceptibility of Sample No. 21 was higher than that of Sample No. 16 because of the increase in the number of unpaired electrons, but its temperature dependence was conversely small. The moments for the manganese of Samples Nos. 16 and 21 were 3.6 and 3.7 Bohr magneton, and the Weiss constants were 54 and 89°, respectively. This tendency can be explained by the mechanism by which the distribution of the manganese ion in the MnO_2 lattice becomes more regular during the removal of the chemically bound water and alkali by means of the decrease in the pH's of the suspensions.

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