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Surface Active Sites for Dehydrogenation Reaction of Isopropanol on Manganese Dioxide

SADAO HASEGAWA, KAZUHIRO YASUDA, TOKUMI MASE,
AND TAKEO KAWAGUCHI

Department of Chemistry, Tokyo Gakugei University, Koganei-shi, Tokyo 184, Japan

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The existence of O_2^- or HOO^- has been observed by epr at $g = 2.008$ and 2.03 on samples of manganese dioxide pretreated between 100 and 400°C. The relative value of the epr absorption decreased with an increase in the pretreatment temperature. The concentration of surface traps determined by the DPPH method was nearly proportional to the relative value of the epr absorption on manganese dioxide. Furthermore, O_2^- or HOO^- on the surface of manganese dioxide acts as an active site during the dehydrogenation reaction of isopropanol.

INTRODUCTION

Recently, the relations between the amounts of surface active oxygen and the catalytic activities for the oxidation reaction of carbon monoxide (*1*, *2*) or the dehydrogenation reaction of cyclohexane (*3*, *4*) on manganese dioxide catalysts have been investigated. Since manganese dioxide has been used as a depolarizer of drycells, the surface properties of manganese dioxide have been studied by many investigators (*5*, *6*). Furthermore, the amount of surface active oxygen [according to Oei and Garnett (*7*)] on manganese dioxide was determined by measuring the concentration of 1,1-diphenyl-2-picryl hydrazil (DPPH) formed by the reaction between 1,1-diphenyl-2-picryl hydrazine ($DPPH_2$) and the surface of manganese dioxide. However, the species of active sites on manganese dioxide catalysts are insufficiently investigated.

In the present paper, the relation between the paramagnetic behavior or the surface properties of manganese dioxide ($Mn_{2-x} \cdot nH_2O$) and the rates of the dehydrogenation reaction of isopropanol on manganese dioxide is described.

EXPERIMENTAL METHODS

The surface excess oxygen and the total excess oxygen are the species of oxygen of surface and bulk of manganese dioxide obtained by KI method, respectively. Also, the surface trap is the species of surface of manganese dioxide determined by DPPH method. The experimental procedures of these methods are described in the following section.

Preparation of Samples

Manganese dioxide ($MnO_{1.94} \cdot 0.34H_2O$), a product from the electrolytic oxidation of manganous sulfate, was supplied by Hanshin Yohsetsu Co. It was preheated at 100–700°C for 1 hr in air and used for the experiments. The surface area was determined by BET method and the results are shown in Table 1.

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TABLE 1

The Change of Surface Area of Manganese Dioxide by Heat Treatment

Temp of heat treatment (°C)	Surface area (m^2/g)
Initial sample	23.0
100	25.1
150	26.7
200	26.0
300	27.1
400	27.0
500	27.2

Measurement of epr Spectra

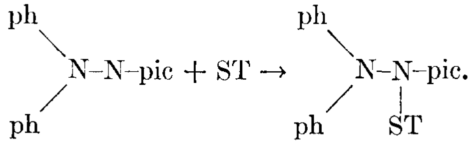
The epr measurements were performed with a JEOL-3ME X-band epr spectrometer with the magnetic field modulation of 100 kHz/sec. The magnetic field intensity measurements were made with a nuclear magnetic resonance gaussmeter. The spectra were obtained at room temperature and recorded as differential curves.

Determination of the Amount of Surface Excess Oxygen

The amount of surface excess oxygen was measured by the KI method (*2*, *8*, *9*) at five pH values in the range from 6.0 to 8.8. Also, the amouut of total excess oxygen of manganese dioxide was determined by applying the KI method to the solution which was obtained by dissolving manganese dioxide into 6*N* HCl.

Measurement of the Concentration of Surface Traps

The concentration of surface traps was determined by using the DPPH method (*7*, *10*, *11*). A weighed sample (10 mg) and 0.5 ml of 1×10^{-3} mol/liter DPPH benzene solution were introduced into a 4 mm i.d. epr sample tube. The decrease of DPPH by the reaction with surface traps (ST) was measured by epr after 48 hr at 20°C. The reaction between DPPH and the surface reaches its equilibrium state after 48 hr at 20°C. The concentration of surface traps was calculated from the decrease in the concentration of DPPH.



Here, ph and pic indicate a phenyl group and a picryl group, respectively.

Measurement of the Rate of Dehydrogenation of Isopropanol

The rate of reaction for the dehydrogenation of isopropanol on 1 g of manganese dioxide in 0.5 mol/liter of benzene solution at 30°C was examined by means of gas chromatography.

RESULTS AND DISCUSSION

1. Change of Chemical Composition

From the results of X-ray diffraction as shown in Fig. 1A, the samples preheated in air in the temperature range between 100 and 500°C were amorphous, and Mn_2O_3 was formed in the samples preheated above

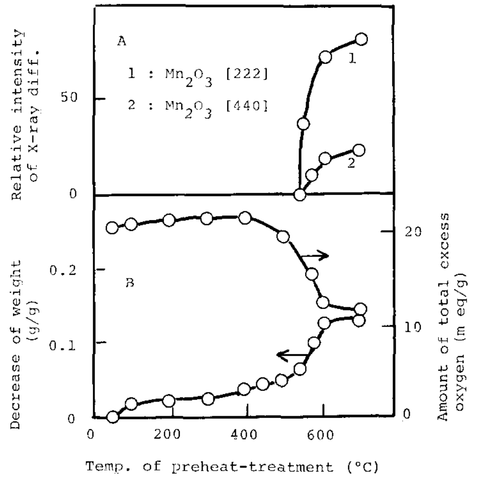


FIG. 1. The changes of the weight, the amount of total excess oxygen and the structure of manganese dioxide.

TABLE 2

The Change of Chemical Composition of Manganese Dioxide by Heat Treatment

	Condition of heat treatment	Composition
A	Initial sample	$MnO_{1.94} \cdot 0.34H_2O$
	100°C in air	$MnO_{1.95} \cdot 0.42H_2O$
	200°C in air	$MnO_{1.93} \cdot 0.19H_2O$
	300°C in air	$MnO_{1.91} \cdot 0.04H_2O$
	400°C in air	$MnO_{1.90} \cdot 0.02H_2O$
	500°C in air	$MnO_{1.75} \cdot 0.02H_2O$
B (12)	5 days at 60°C	$MnO_{1.96} \cdot 0.93H_2O$
	200°C in oxygen	$MnO_{1.98} \cdot 0.63H_2O$
	300°C in oxygen	$MnO_{1.92} \cdot 0.39H_2O$
	400°C in air	$MnO_{1.84} \cdot 0.4H_2O$
	450°C in air	$MnO_{1.74} \cdot 0.4H_2O$

550°C. The amounts of total excess oxygen in the amorphous samples of manganese dioxide preheated between 100 and 400°C slightly increased and the weights of the samples slightly decreased with elevating the temperature of heat treatment as shown in Fig. 1B.

From the results of the decrease in the amount of total excess oxygen, and the chemical analysis of manganese dioxide, it was ascertained that the chemical composition was changed by heat treatment in air as shown in Table 2A. Similar results as in Table 2B were reported by Moor and co-workers (*12*). These facts suggest that the adsorbed or structural water and the excess oxygen on or in manganese dioxide are removed from the initial sample by heat treatment at 100–300°C.

2. Surface Excess Oxygen and Surface Traps

The amount of surface excess oxygen as a function of the temperatures of heat treatment are shown in Fig. 2 for various pH values between 6.0 and 8.8. At any pH value, they decreased with elevating the temperature of heat treatment. This fact shows that the amounts of surface excess oxygen decreased with the dehydration of manganese dioxide as mentioned in the preceding section. The surface excess oxygen disappeared on the sample preheated at 600°C of which the chemical composition was Mn_2O_3.

According to Kobayashi and co-workers (*2*), the amount of surface excess oxygen on manganese dioxide catalysts measured by KI method, two linear regions giving a decrease in the amount of surface excess oxygen were found at pH 7.1 and 7.5, and no decrease was found at pH 8.6 or 9.7. In the present work, the linear regions in a decrease similarly were obtained at pH 6.0–7.5 and pH 7.5–8.8.

From these results, it was deduced that a part of the surface excess oxygen on manganese dioxide was removed along with the adsorbed or structural water of the samples by the heat treatment. The concentration of surface traps on manganese dioxide as measured by the DPPH method (*7, 10, 11*) is also shown in Fig. 2. The concentration of surface traps gradually decreased with elevating the temperature of heat treatment in the same way as the

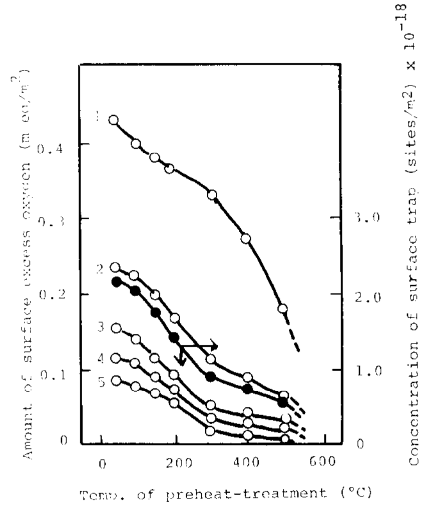


FIG. 2. The changes of the amount of surface excess oxygen and the concentration of surface traps of manganese dioxide. pH: (1) 6.0; (2) 6.9; (3) 7.5; (4) 8.0; (5) 8.8.

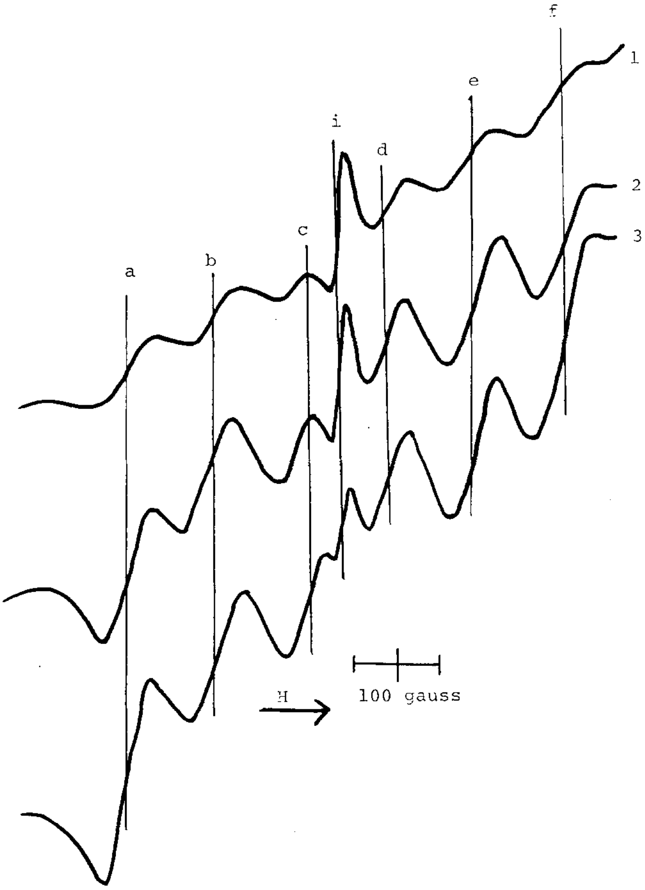


FIG. 3. The epr signals of Mn^{2+} in manganese dioxide. Temp of heat treatment (°C): (1) 400; (2) 500; (3) 530; g values: (a) 2.154; (b) 2.096; (c) 2.038; (d) 1.980; (e) 1.922; (f) 1.864; (i) 2.008.

change of the amount of surface excess oxygen and was nearly proportional to the amount of surface excess oxygen measured in the pH range between 6.9 and 8.8. These facts suggest that a part of the surface excess oxygen acts as surface traps, as reported on Co_3O_4 (*13*). Furthermore, the activation energy on the reaction between DPPH and the surface at 20–50°C was about 5 kcal/mol on the sample preheated at below 150°C, and about 10 kcal/mol on the sample preheated above 200°C.

3. EPR Behavior

Electron paramagnetic resonance spectra of manganese dioxide are shown in Figs. 3 and 4. Seven epr signals at $g = 2.154, 2.096, 2.038, 2.008, 1.980, 1.922$ and 1.864 as in Fig. 3 were observed in the samples preheated at 400–530°C. The six signals (a, b, c, d, e and f in Fig. 3) were due to the hyperfine interaction between the electron and the nuclear spin in a Mn^{2+} ion ($I = \frac{5}{2}$ and $S = \frac{5}{2}$). According to Allen (*14*), the zero-field splitting parameter (D) is correlated to the ratio of signal intensity, $I_{\frac{5}{2}}/I_{\frac{1}{2}}$. The D-value of Mn^{2+} in MgO increased with elevating the temperature of heat treatment in the temperature range between 100 and 1000°C. From the results in Fig. 3, the D-values of Mn^{2+} ion in manganese dioxide preheated at 400, 500 and 530°C

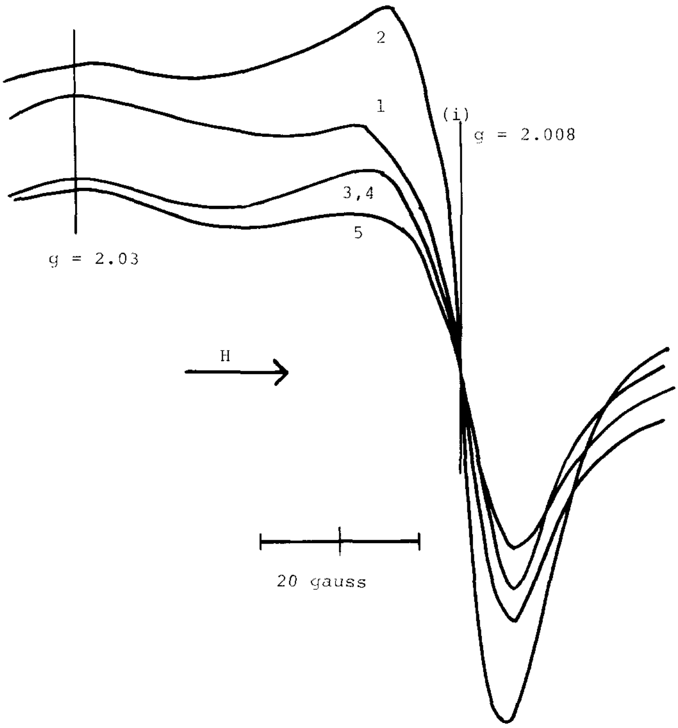


Fig. 4. The epr signals of manganese dioxide at $g = 2.03$ and $g = 2.008$. Temp of heat treatment (°C): (1) initial sample; (2) 100; (3) 200; (4) 300; (5) 400.

are 100, 98 and 96 G, respectively. Therefore, the samples preheated between 400 and 530°C should be amorphous which is consistent with the results of X-ray diffraction.

Asymmetic epr signals at $g = 2.03$ and 2.008 as shown in Figs. 4 and 3 were observed in any sample preheated at 100–530°C. Asymmetric signals are generally observed in polycrystalline samples (*16*). The intensities of these signals decreased with elevating the temperature of heat treatment and became zero above 580°C.

The shapes of the epr signals and the dependency of the microwave power on the intensities of the epr signals at $g = 2.03$ and 2.008 are similar to those of some metal peroxide (e.g., $BaO_2 \cdot 2H_2O_2$, ZnO_2 and CdO_2) (*13*). Therefore, the asymmetric epr signals of manganese dioxide at $g = 2.03$ and 2.008 are suggested to have come from O_2^- or HOO^-.

The relative value of the epr absorption (Ab) is calculated by the following equation:

$$\mathrm{Ab} \approx I \times (\Delta H_{\mathrm{msl}})^2,$$

where, I and ΔH_{msl} indicate the peak height and the line width of epr signal at $g = 2.008$.

TABLE 3

The Changes of the Amount of Surface Excess Oxygen and the Concentration of Surface Traps of Manganese Dioxide Caused by the Dehydrogenation Reaction of Isopropanol at 30°C

	Amount of surface excess oxygen (meq/g)	Concn of surface traps (sites/g)
Before reaction	0.23	2.20×10^{18}
After reaction	0.17	1.04×10^{18}
Decrease	0.06	1.16×10^{18}

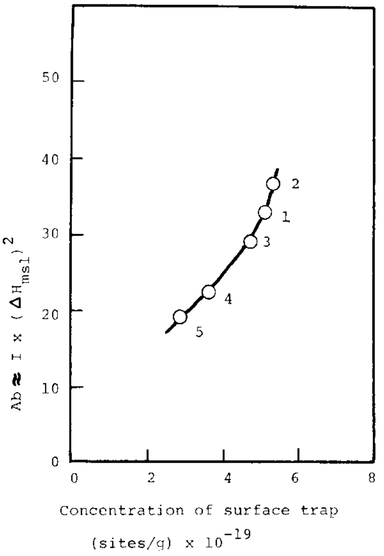


FIG. 5. The relation between the relative value of epr absorption (Ab) and the concentration of surface traps of manganese dioxide. Temp of preheat treatment (°C): (1) initial sample; (2) 100; (3) 150; (4) 200; (5) 300.

It was ascertained that Ab was nearly proportional to the concentration of surface traps as in Fig. 5.

Therefore, it is suggested that an anionic radical O_2^- or HOO^- on the surface of manganese dioxide acts as a surface trap or an active oxygen.

4. Rate of Reaction of Dehydrogenation

When benzene solution of isopropanol or *sec*-butanol is dehydrogenated on manganese dioxide at 30°C, only acetone or methyl ethyl ketone is formed. However, aldehyde, carboxylic acid, aldols and esters were formed by the dehydrogenation reaction of *n*-propanol, *n*-butanol and isobutanol on manganese dioxide at 30°C. In the present work, only the dehydrogenation reaction of isopropanol is described.

The amount of surface excess oxygen and the concentration of surface traps of manganese dioxide decreased appreciably by the dehydrogenation reaction of isopropanol as in Table 3.

In the previous reports (*3*, *4*), cyclohexane was dehydrogenated by the surface of manganese dioxide and benzene and water were formed in the following way:

$$C_6H_{12} + O^{2-} \rightarrow C_6H_{10} + H_2O + 2e^-,$$
$$C_6H_{10} + O^{2-} \rightarrow C_6H_8 + H_2O + 2e^-,$$
$$C_6H_8 + O^{2-} \rightarrow C_6H_6 + H_2O + 2e^-.$$

The rate of the dehydrogenation reaction of isopropanol was generally larger than that of *sec*-butanol in the gaseous phase (*3*). In the present work, the rate of the dehydrogenation reaction of isopropanol in benzene was nearly equal to that of *sec*-butanol. The rate of the reaction, v, was represented by the following equation:

$$v = k[C_{\mathrm{Pr}}][C_{\mathrm{ST}}],$$

where, k, C_{Pr} and C_{ST} are the rate constant, the concentration of isopropanol and the concentration of surface traps on manganese dioxide. Dehydrogenation was not observed on manganese dioxide preheated above 500°C.

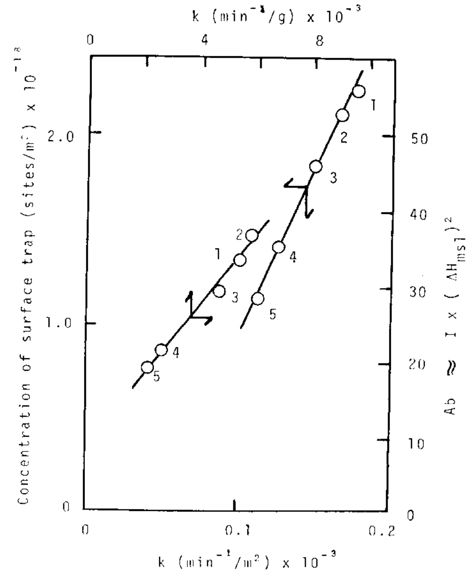


FIG. 6. The relation between the rate constant (k) and the concentration of surface traps or the relative value of epr absorption (Ab) of manganese dioxide. Temp of preheat treatment (°C): (1) initial sample; (2) 100 (3) 150; (4) 200; (5) 300.

The relation between the rate constant, k, and the concentration of surface traps, C_{ST}, or the relative value of epr absorption at $g = 2.008$, Ab, is illustrated in Fig. 6. C_{ST} or Ab is proportional to k. Bickley and co-workers (*17*) already reported that O_2^- and HOO^- acted as the active sites on rutile during the photocatalytic oxidation of isopropanol. Therefore, O_2^- or HOO^- which may be included in surface excess oxygen or surface traps behaves as an active site during the dehydrogenation reaction of isopropanol.

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