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Author(s)	IIZUKA, Tokio; SAITO, Mitsuko; TANABE, Kozo
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THE DIFFERENCE IN SURFACE CRYSTAL FIELD STRENGTH AND CATALYTIC PROPERTIES OF TWO DIFFERENT MAGNESIUM OXIDES

By

Tokio IIZUKA^{*)}, Mitsuko SAITO^{*)} and Kozo TANABE^{*)}

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Abstract

Two kinds of adsorbed states of O_2^- ion were observed on the surface of MgO. The relative abundance of those adsorption sites were sensitive to the starting materials in preparation of MgO; hydroxide and basic carbonate. From the ESR parameters of O_2^- ion, the surface field strength of each oxide was estimated. Magnesium oxide prepared from the hydroxide was found to have stronger field than MgO prepared from the basic carbonate and the difference was ascribed to the different surface morphology of the particles obtained by the different routes. The catalytic activity and selectivity for the decomposition of 2-propanol were affected by the surface crystal field strength.

Introduction

Recently, it is well known that catalytic properties are strongly dependent on the preparation method of catalyst. Among various factors influencing the catalytic properties, the differences in starting materials of catalyst preparation and pretreatment condition give often remarkable effect on the activity and selectivity.

The catalytic properties of alkaline earth oxides are quite dependent on the starting material and the pretreatment temperature. Pines *et al.*¹⁾ observed that CaO prepared from $Ca(OH)_2$ by calcining at 900°C had little activity for the isomerization of 1-hexene, while CaO prepared from $CaCO_3$ by the same way showed a high catalytic activity. They speculated that the activity depended on the difference in dislocations of the crystals of the calcium oxides. Hattori *et al.* have reported the differences in catalytic properties of two kinds of MgO prepared from the hydroxide and from the basic magnesium carbonate for the isomerization of 1-butene and the alkylation of phenol with methanol.²⁾ In the case of 1-butene isomerization, the

^{*)} Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, 060 Japan.

activity and the selectivity of both magnesium oxides were not much different. However, for the isomerization of cis-2-butene, the maximum activity and the selectivity of MgO prepared from $\text{Mg}(\text{OH})_2$ were about four times higher than those of MgO from $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$.

The decomposition of 2-propanol is known as a model reaction for studying the principles of catalyst selectivity and reactivity of metal oxides.³⁾ The alkaline earth oxides are surprisingly active catalysts for the dehydrogenation reaction.³⁾ The selectivity seems to depend on the reaction conditions and the starting materials. De Vleeschauwer, who prepared the MgO by heating basic magnesium carbonate at temperatures above 550°C, reported the selectivity values of 0.92~0.96 for the dehydrogenation,⁴⁾ while Hoddless *et al.* reported the value of about 0.7 over MgO prepared from $\text{Mg}(\text{OH})_2$.⁵⁾

In this report, the authors wish to characterize the surface states of two magnesium oxides obtained from different starting materials by EPR and IR spectroscopies and to discuss the difference in catalytic activity and selectivity for the decomposition of 2-propanol.

Experimentals

Magnesium hydroxide was guaranteed reagent of Kanto Chemical Co. and magnesium basic carbonate was guaranteed reagent of Merck Co. To remove carbonate, $\text{Mg}(\text{OH})_2$ was heated at 900°C and rehydrated in boiling water or in boiling heavy water in some cases and dried. Before the reaction, 100 mg of catalyst (MgO) was supported by quartz wool in the reactor and heated at different temperatures in a vacuum for 1 hr. Reaction was carried out in a conventional pulse reactor at 380°C using He as a carrier gas. ESR spectra were recorded with JEOL ME-3X X band spectrometer at room temperature or liquid nitrogen temperature. Details of the experiments for the formation of O_2^- on MgO was described in a previous paper.⁶⁾ IR spectra were taken with JASCO-DS-701G spectrometer using an in situ cell.

Results

1. Decomposition of 2-propanol

Catalytic activity and selectivity of two magnesium oxides are shown in Table 1. Acetone and propylene were obtained as primary products. A small amount of mesityl oxide (<2%) formed from produced acetone. Basic magnesium carbonate evacuated at the temperature lower than 500°C showed high catalytic activity and good selectivity for the formation of propylene,

Surface Crystal Field Strength and Catalytic Properties of MgO

TABLE 1. Catalytic Activity and Selectivity for the Decomposition of 2-Propanol

Catalyst	Evacuation Temp. (°C)	Conversion (%)	Propylene (%)	Acetone (%)	Dehydrogenation Selectivity (%)
Mg(OH) ₂	500	55.9	14.4	40.1	73.5
↓	600	45.3	11.4	32.6	74.1
MgO	700	35.0	9.5	24.6	72.1
4MgCO ₃ ·Mg(OH) ₂ ·4H ₂ O	400	88.8	58.9	29.9	33.7
↓	500	30.9	8.1	22.6	73.6
MgO	600	23.6	4.1	18.9	82.2
	700	11.8	2.1	9.3	81.6
	900	12.4	2.1	9.9	82.5

Reaction temperature; 380°C, Catalyst weight; 100 mg as MgO.

but over magnesium oxide obtained by evacuating at higher temperature, the activity decreased and the selectivity to acetone increased. In the case of magnesium hydroxide, the selectivity was always favorable to acetone formation and was not sensitive to evacuation temperature.

2. IR spectra of adsorbed 2-propanol

After the evacuation of basic carbonate at 600°C, the carbonate bands at 1570 and 1390 cm⁻¹ disappeared almost completely. Upon the adsorption of 2-propanol at room temperature, typical alcoholate adsorbed species⁷⁾ appeared as shown in Fig. 1 (O-H and C-H stretching region was not shown). The peaks of C-H bending region (1470 and 1370 cm⁻¹) and C-O stretching band at 1165 cm⁻¹ were almost disappeared after evacuation at 250°C. In the case of MgO prepared from Mg(OH)₂, as shown in Fig. 2, the band intensities of the adsorbed species were stronger than those on MgO from basic carbonate. Those bands decreased remarkably after evacuation at 200°C. Upon evacuation at 250°C, new bands appeared at 1585 and 1410 cm⁻¹ which have been ascribed to carboxylate species.⁷⁾

3. ESR spectra of adsorbed O₂⁻ ion

ESR spectra of O₂⁻ adsorbed on MgO are shown in Fig. 3. In those spectra, the *g*-values of *x* and *y* directions were not changed in any cases (*g_x*=2.001, *g_y*=2.008). However, two *g_z* values were observed and the relative heights of those peaks were sensitive to the starting materials. In the case of MgO prepared from Mg(OH)₂ at 500°C, the peak at *g_z*(I)=2.061 was main and *g_z*(II)=2.076 was observed as a shoulder peak. The shape

T. IZUKA, M. SAITO and K. TANABE

of g_z peaks was not changed on the surface of MgO obtained from Mg (OD)₂. On the other hand, the peak at $g_z(\text{II})=2.076$ was main and a small peak at $g_z(\text{I})=1.061$ appeared as a shoulder in the case of MgO prepared

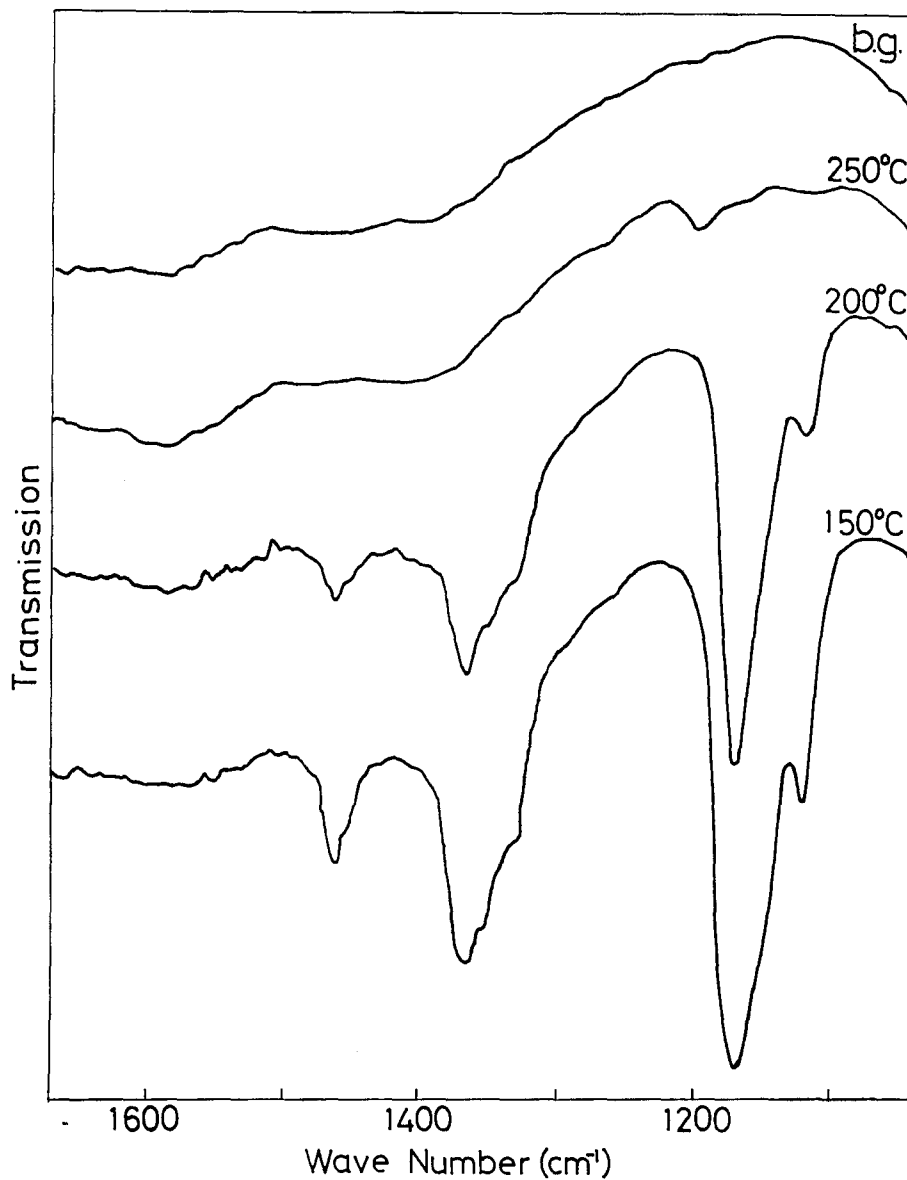


Fig. 1. IR spectra of adsorbed 2-propanol heated at different temperature on $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ evacuated at 600°C.

Surface Crystal Field Strength and Catalytic Properties of MgO

from basic carbonate. On the sample prepared from $\text{Mg}(\text{OH})_2$ obtained by the rehydration of heated basic carbonate, $g_2=2.061$ became dominant as shown in Fig. 3(g).

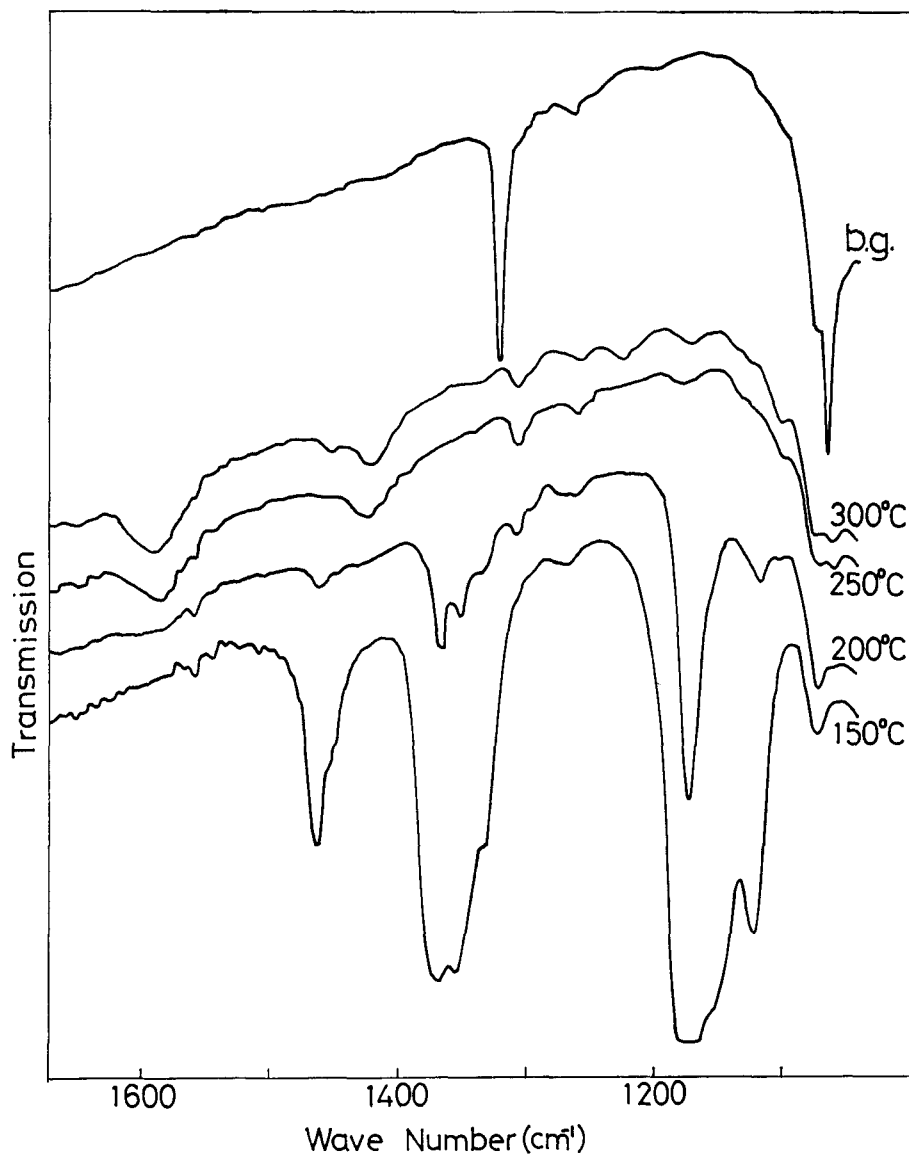


Fig. 2. IR spectra of adsorbed 2-propanol heated at different temperatures on $\text{Mg}(\text{OH})_2$ evacuated at 600°C.

T. IZUKA, M. SAITO and K. TANABE

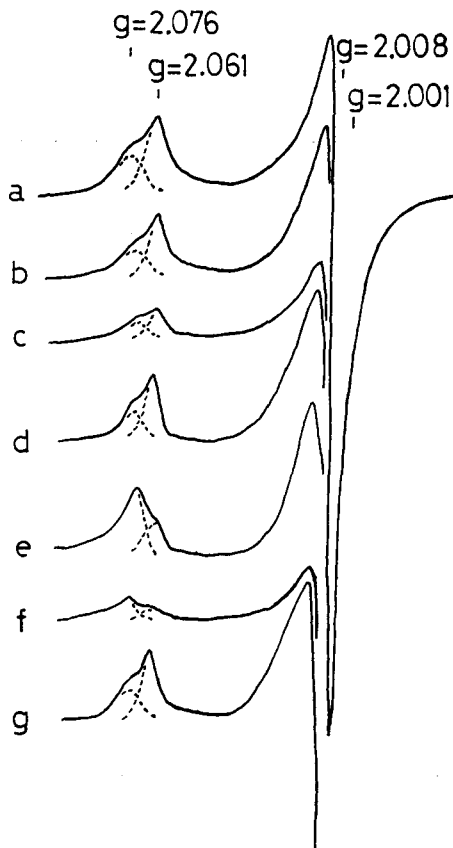


Fig. 3. ESR spectra of O_2^- adsorbed on MgO prepared from different materials.

a: $Mg(OH)_2$ evacuated at $500^\circ C$, b: $Mg(OH)_2$ evacuated at $600^\circ C$, c: $Mg(OH)_2$ evacuated at $700^\circ C$, d: $Mg(OD)_2$ evacuated at $600^\circ C$, e: $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ evacuated at $600^\circ C$, f: $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ evacuated at $900^\circ C$, g: sample f after rehydration and evacuation at $600^\circ C$.

Discussion

The ESR spectra of O_2^- on the surface of metal oxides are well known. The qualitative correlation between the g_z value of O_2^- ion and the oxidation state of cation caused by the difference in surface crystal field interactions has been reported.⁹⁾ Kasai reported that the crystal field strength estimated from the g_z value of O_2^- was twice for divalent Ba-Y zeolite as large as for monovalent Na-Y.⁹⁾ In certain systems, O_2^- is held at different types of adsorption sites and two or more overlapping spectra which result from the

Surface Crystal Field Strength and Catalytic Properties of MgO

ion in different environments were observed. The existence of a variety of adsorption sites in the cationic form of Y-type zeolites is a typical case of such a system. Three different adsorption sites were observed for the alkaline earth cationic zeolites and those corresponded to the different site location in zeolite framework.⁹ On MgO, several g_z values has been observed,¹¹ but the difference in the g_z values due to the difference in starting materials has never been reported. In this experiment, two kinds of the g_z values exist apparently and the relative abundance is sensitive to starting materials. From the experiment on deuterated sample, hydrogen hyperfine splitting was excluded for two g_z values. The SO_2^- species adsorbed on MgO also showed two different sites on the surface and Lunsford *et al.* ascribed those sites to edge or corner Mg^{2+} and normal lattice Mg^{2+} .¹² However, considering that the spectra is very sensitive to starting materials, we inclined to think that the change of sites could be ascribed to the difference in surface crystal plane exposed preferentially depending on the starting materials. Many morphological studies of MgO has been done with electron microscopy and electron diffraction method. Boudart *et al.* found that MgO prepared from $\text{Mg}(\text{OH})_2$ showed particles with (111), (211), and (210) orientations in order of decreasing importance.¹³ On the other hand, MgO prepared from basic carbonate showed the dominant orientation of (100), (110) and (111) planes.¹⁴ In (111) and (211) planes, Mg^{2+} ion has a coordination of three O_2^- and the crystal field would be strongest.¹¹ The weaker crystal field will appear in the planes of (210), (110) and (100), because the coordination numbers were four or five. The crystal field strength can be calculated from the g_z value of O_2^- ion from the equation of Känzig and Cohen.¹⁵ The calculated values were shown in Table 2. The stronger crystal field strength

TABLE 2. Crystal Field Strength

Oxides	g_z value	Crystal field strength (eV)	Reference
$\text{Mg}(\text{OH})_2 \rightarrow \text{MgO}$	$g_z = 2.061_0$	0.477	this work
	$(g_z = 2.076_1)$	(0.380)	
$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgO}$	$g_z = 2.075_8$	0.380	this work
	$(g_z = 2.061_0)$	(0.477)	
CaO	$g_z = 2.082$	0.351	ref. (6)
	$g_z = 2.093$	0.31	ref. (16)
SrO	$g_z = 2.102$	0.28	ref. (16)

of MgO prepared from $\text{Mg}(\text{OH})_2$ would correspond to the preferential growth of low coordinated (111) and (211) planes.

The alcohol dehydration and dehydrogenation reactions are known to correlate with acidic and basic properties, respectively.⁸⁾ Acidic catalyst such as Al_2O_3 has a tendency to produce olefin as a main product. Basic oxides such as CaO, SrO, BaO showed high dehydrogenation selectivities of 0.93, 0.99 and 0.99, respectively.¹⁶⁾ Beryllium oxide which is more acidic catalyst has been reported to have a selectivity of 0.41.¹⁷⁾ Magnesium oxide showed an intermediate property and the selectivity was between 0.7 and 0.96. Only MgO that was contaminated with CO_2 (or carbonate) which resulted from an incomplete decomposition of the carbonate appears to be active for the dehydration.¹⁸⁾ This phenomenon was also confirmed in this experiment. Partially decomposed basic carbonate evacuated at the temperature lower than 500°C showed a clear tendency for the dehydration (Table 1). The reason for the selective dehydration of basic carbonate is not so clear at this time. When basic carbonate was evacuated at 600°C , IR bands at 1570 and 1390 cm^{-1} of carbonate species disappeared and high selectivity for dehydrogenation was achieved. In the case of MgO prepared from $\text{Mg}(\text{OH})_2$, the selectivity for the dehydrogenation was always around 0.75. Though MgO is a selective catalyst for the dehydrogenation reaction, it can be concluded that MgO prepared from $\text{Mg}(\text{OH})_2$ is more selective for the dehydration than MgO from basic carbonate. Since MgO prepared from $\text{Mg}(\text{OH})_2$ had a stronger crystal field (stronger Lewis acid) than MgO from basic carbonate, the reaction for the dehydration would have been facilitated. On the other hand, lattice oxygen anions also have low coordination numbers in (111) or (211) planes. Tench *et al.* reported that the low coordinated O^{2-} decreased in the order of MgO from $\text{Mg}(\text{OH})_2$, MgO from basic carbonate, MgO smoke.¹⁹⁾ Thus, the basic strength of MgO from $\text{Mg}(\text{OH})_2$ would be stronger. In IR experiments, the formation of carboxylate species on this sample indicates the existence of stronger anion cation pairs on the surface. It is clear that the acid and base sites of MgO prepared from basic carbonate were too weak to stabilize the adsorbed alcohol. The high catalytic activity on MgO for $\text{Mg}(\text{OH})_2$ for the isomerization of 2-butene²⁾ also can be ascribed to the formation of strong cation anion pairs in low coordination index plane.

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