Catalytic and Physical Properties of Ca\(^{2+}\)-doped MgO

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Ca\(^{2+}\) ions loaded on MgO surface markedly promoted catalytic activities of MgO for isomerization of 1-butene, hydrocarbon gasification with CO\(_2\) or O\(_2\), and the reverse water-gas shift reaction, although MgO itself was almost inactive after treatment at 1273 K in air. Ca\(^{2+}\) ions also increased the basicity and basic strength of MgO. Strong basic sites catalyzed isomerization of 1-butene. In the course of impregnation with Ca(NO\(_3\))\(_2\), MgO (periclase) was completely transformed into hydrate (brucite) by the action of nitrate ions. It is considered that Ca\(^{2+}\) ions interfere with the transformation of surface arrangements accompanied with structural transformation from brucite (hcp) to periclase (fcc). It was found that most of Ca\(^{2+}\) ions aggregated to form particles of CaO on the surface of MgO while Ca\(^{2+}\) ions were highly dispersed on the surface of MgO when the MgO was prepared from basic carbonate salt involving calcium as an impurity.

1. Introduction

Alkaline earth metal oxides have been reported to catalyze certain reactions, such as isomerization of olefins,\(^{15-17}\) hydrogenation of conjugated dienes,\(^{18}\) and H\(_2\)-D\(_2\) exchange reaction\(^{19}\), after treatment in vacuo at proper temperatures. Although strong adsorption of CO\(_2\) and H\(_2\)O contained in the atmosphere causes deactivation of alkaline earth metal oxide catalysts for these reactions, we have shown that these oxide catalysts can activate CO\(_2\) at high temperatures, above 973 K, and thus catalyze CO\(_2\) gasification of hydrocarbons and the reverse water-gas shift reaction.\(^{20-22}\)

It is difficult to transform MgO into carbonate or hydrate by the absorption of CO\(_2\) or H\(_2\)O, whereas CaO, SrO, and BaO are easily transformed into carbonate or hydrate. Because of its high stability, MgO has frequently been selected as a representative for the investigation of catalysis by alkaline earth metal oxides. It has generally been accepted that the regular lattice of MgO, of which the surface has five-fold coordination, is of relatively low reactivity. The surface, however, possesses many kinds of defects such as Schottky defects, in addition of having sites of lower coordination at the corners, edges, and kinks. The catalytic function of the surface of MgO is frequently associated with such surface locations,\(^{10-15}\) although the relation between the catalytically active site and the local surface structure has not been sufficiently elucidated.

Increasingly, attention has been paid for segregation of isovalent large cations such as Ca\(^{2+}\), Ba\(^{2+}\), Ni\(^{2+}\), and Fe\(^{2+}\) on the surface of MgO.\(^{16-20}\) McCune and Wynblatt\(^{20}\) have pointed out that 200 ppm of calcium included in bulk segregates at the MgO surface and replaces 20% of surface Mg\(^{2+}\) ions under equilibrium at 1223 K. A computational approach by Tasker et al.\(^{21}\) has also shown that there are driving forces allowing large isovalent cations such as Ca\(^{2+}\) to segregate to the surface of MgO, for example, \(\Delta H_{\text{seg}}=-46.3 \text{ kJ mol}^{-1}\) for segregation of Ca\(^{2+}\) ions. These cations segregated to the surface of MgO cause reconstruction of the dopant-rich MgO surface into rumpled arrangements. These results prompted us to dope MgO with Ca\(^{2+}\) ions in order to improve the catalytic properties of MgO. The number of coordinatively unsaturated sites on MgO may be increased by doping with large isovalent cations.

In the present study, we shall demonstrate the pronounced effect of Ca\(^{2+}\) dopant on the catalytic and physical properties of MgO. Several methods of characterization were used to comprehensively grasp the surface properties of Ca\(^{2+}\)-doped MgO. For the purpose of comparison, we used MgO containing calcium as an impurity. In particular, we were interested in clarifying the effect of Ca\(^{2+}\) dopant on the morphological and structural features of MgO crystal, accompanied with an increase of the basicity.

2. Experimental

Magnesium oxide, represented as MgO(0), was prepared from a magnesium basic carbonate salt...
Ca$_2^+$-doped MgO samples were prepared by the impregnation method. MgO(0) was soaked in decationated water and an appropriate amount of Ca(NO$_3$)$_2$ aqueous solution was added to MgO(0)-water mixture. The resulting slurry was dried in air at 383K and then treated in a stream of N$_2$ at 1223K for 5h. The amount of Ca$_2^+$ loaded (wt% as oxide) will be represented in the parenthesis as: Ca$_2^+$(1.0)/MgO. The other type of Ca$_2^+$-containing (0.94wt% as oxide) MgO, represented as MgO(I), was prepared from a magnesium basic carbonate salt (Kanto) containing Ca$_2^+$ as an impurity in the same procedure with that for preparation of MgO(0). Ca$_2^+$ content was determined by means of inductively coupled plasma emission spectrometry.

Isomerization of 1-butene, O$_2$- or CO$_2$-gasification of benzene, and the reverse water-gas shift reaction were carried out to evaluate the catalytic activities of Ca$_2^+$-doped MgO. A continuous flow reactor with a fixed bed was used for each reaction. The experimental apparatus used in the latter two reactions was previously described.\textsuperscript{7)} O$_2$ gasification of benzene was also carried out in a similar apparatus. The experimental apparatus used in the latter two reactions was previously described.\textsuperscript{7)}

<table>
<thead>
<tr>
<th>Sample</th>
<th>1-Butene Isomerization</th>
<th>Propane Oxidation</th>
<th>CO$_2$-H$_2$ \textsuperscript{2}</th>
<th>CO$_2$ Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conversion (mol%)</td>
<td>Gas Yield (mol%)</td>
<td></td>
<td>CO$_2$ Conversion (mol%)</td>
</tr>
<tr>
<td>MgO(0)</td>
<td>2.7</td>
<td>0.9</td>
<td>1.1</td>
<td>10.7</td>
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<tr>
<td>MgO(1)</td>
<td>18.9</td>
<td>58.7</td>
<td>13.6</td>
<td>36.6</td>
</tr>
<tr>
<td>Ca$_2^+$(0.1)/MgO</td>
<td>18.8</td>
<td>6.2</td>
<td>----</td>
<td>29.7</td>
</tr>
<tr>
<td>Ca$_2^+$(0.5)/MgO</td>
<td>46.1</td>
<td>21.2</td>
<td>----</td>
<td>31.7</td>
</tr>
<tr>
<td>Ca$_2^+$(1.0)/MgO</td>
<td>25.2</td>
<td>33.5</td>
<td>7.9</td>
<td>35.9</td>
</tr>
</tbody>
</table>

a) reaction temperature, 323 K; W/F, 50 g-cat. min$^{-1}$; P$_{CO_2}$, 152 Torr.  
b) reaction temperature, 1173 K; W/F, 3.00×10^4 g-cat. min mol-CO$_2^{-1}$; P$_{CO_2}$, 30.4 Torr; P$_{CO_2}$, 182 Torr.  
c) reaction temperature, 873 K; W/F, 1.00×10^4 g-cat. min mol-CO$_2^{-1}$; P$_{CO_2}$, 7.60 Torr; P$_{CO_2}$, 22.8 Torr.  
d) reaction temperature, 1073 K; W/F, 7.10 g-cat. min mol-CO$_2^{-1}$; P$_{CO_2}$, 380 Torr; P$_{He}$, 50 Torr.

Table 1: Catalytic Activities of MgO(0), MgO(I), and Ca$_2^+$-doped MgO

(Kanto) by calcination in air at 1273 K for 5 h. Ca$_2^+$-doped MgO samples were prepared by impregnation method. MgO(0) was soaked in decationated water and an appropriate amount of Ca(NO$_3$)$_2$ aqueous solution was added to MgO(0)-water mixture. The resulting slurry was dried in air at 383K and then treated in a stream of N$_2$ at 1223K for 5h. The amount of Ca$_2^+$ loaded (wt% as oxide) will be represented in the parenthesis as: Ca$_2^+$(1.0)/MgO. The other type of Ca$_2^+$-containing (0.94wt% as oxide) MgO, represented as MgO(I), was prepared from a magnesium basic carbonate salt (Kanto) containing Ca$_2^+$ as an impurity in the same procedure with that for preparation of MgO(0). Ca$_2^+$ content was determined by means of inductively coupled plasma emission spectrometry.

Isomerization of 1-butene, O$_2$- or CO$_2$-gasification of benzene, and the reverse water-gas shift reaction were carried out to evaluate the catalytic activities of Ca$_2^+$-doped MgO. A continuous flow reactor with a fixed bed was used for each reaction. The experimental apparatus used in the latter two reactions was previously described.\textsuperscript{7)} O$_2$ gasification of benzene was also carried out in a similar apparatus. The reactor used for isomerization of 1-butene was a U-shaped tube made of quartz (i.d. 5 mm) in which a desired amount of the sample was packed. The sample was heated at a rate of 10 K min$^{-1}$ to 1173 K and maintained at that temperature for 2 h in a stream of Ar purified by a Mn/SiO$_2$ column. 1-butene was also purified by the same column before reaction. Reaction conditions for the probe reactions were described in Table 1.

X-ray diffraction (XRD, Rigaku RAD-C) with Cu-target and Ni-filter, and Scanning and Transmission electron microscopes (SEM Hitachi S-570, TEM Hitachi HU-11) were employed to observe the morphological and structural changes in the course of the preparation of the samples. Specific surface areas of the samples were determined by the BET method after heat treatment in vacuo at 1173 K.

Temperature-programmed desorption (TPD) for CO$_2$ adsorbed on the samples was carried out. An amount of the sample weighing 0.5 g was heated to 1173 K at a rate of 10 K min$^{-1}$ and maintained at that temperature for 2 h in flowing He. After cooling to room temperature, the sample was exposed to ca. 20 Torr of CO$_2$ for 0.5 h and then evacuated for 0.5 h. CO$_2$-TPD measurement was carried out at a heating rate of 10 K min$^{-1}$ up to 1173 K in a stream of He. The flow rate of He was 3.7×10$^{-3}$ mol min$^{-1}$ and the pressure of He carrier was kept to be 50 Torr. A part of the outlet gas was introduced into a mass spectrometer (NEVA TE-600). The sensitivity of the spectrometer was normalized by using 1020 ppm of Ar involved in He carrier. Temperature-programmed decomposition of CaCO$_3$ was carried out by following similar procedures without heat treatment.

The number of basic sites and basic strength were also investigated by volumetric measurements. CO$_2$ adsorption isotherms were measured at 313 K after evacuation at 1173 K for 2 h. The total amount of CO$_2$ adsorbed on the sample was determined by extrapolating the adsorption isotherm to 0 Torr of CO$_2$ pressure to eliminate the amount of physically adsorbed CO$_2$. After conducting these measurements, the sample was heated to 473 K in vacuo and maintained at that temperature for 2 h for the sake of allowing weakly adsorbed CO$_2$ to desorb. Then, the amount of CO$_2$ adsorbed at 313 K was again determined. The difference in the amounts of adsorbed CO$_2$ between the first and the second measurements, gives the number of the weaker basic sites adsorbing CO$_2$ which desorbed in the temperature range of 313-473 K. In similar procedures, the amounts of CO$_2$, desorbed in the temperature range of 313-473 K, were determined.
ranges of 473—673 and 673—873 K, were successively determined.

Infra-red (IR) spectra were recorded at room temperature on a JASCO IR-810 spectrometer. The sample weighing ca. 40 mg was pressed to form a disk. The sample disk was set in a cell, evacuated at 1073 K for 2 h, and then cooled. After these pretreatments, the sample disk was exposed to 20 Torr of CO₂ at a desired temperature. Then, the sample disk was evacuated at a desired temperature for 0.5 h.

The apparatus used for X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) was a Physical Electronics Model 545—548 combined XPS-AES system. XPS spectra were obtained by use of a Al Kα X-ray source at 15 kV, 300 W power and a base pressure better than 5×10⁻⁹ Torr. For calibration purpose, Au 4f(7/2 and 5/2) spectra of pure metal sample were recorded and contamination by the C 1s peak was measured to cancel charging-effects. Periodic checks were performed to ensure that a drift due to charging and instrumental instability was not affecting peak positions. All spectra were reproducible within ±0.2 eV. AES measurement was successively performed after the collection of XPS spectra. Primary beam energy was 2 keV.

Depth distribution of Ca was measured by means of secondary ion mass spectrometry (SIMS, Hitachi IMA-2) using O₂⁺ ion beam. A target sample was pressed to form a disk and stuck on a sample holder with an adhesive silver paste. Then, it was mounted in an UHV chamber which was evacuated to better than 10⁻⁸ Torr before beginning ion bombardment. The primary ion beam energy was 10 keV and the incident O₂⁺ ion beam flux was 1.2×10⁻² A cm⁻². Generally, SIMS measurements for insulating materials are difficult because of severe charging effects resulting from their low electron conductivity. In the present study, the incident beam was irradiated at the boundary between the sample disk and the silver paste to obtain sufficient electron conductivity.

3. Results

3.1 Catalytic Activities

Table 1 compares catalytic activities for some probe reactions. Catalytic activity of MgO was markedly improved by doping of Ca²⁺ ions, while increment of catalytic activity varied with the type of reaction. Product gases in 1-butene isomerization were cis- and trans-2-butenes. The cis/trans molar ratios were greater than unity, indicating that all these catalysts serve as base. Results shown in Table 1 reveal that these basic catalysts are capable of activating CO₂ at a high temperature and thus of catalyzing CO₂ gasification of benzene and the reverse water-gas shift reaction. We have reported the catalytic role of alkaline earth metal oxides and the reaction network for hydrocarbon gasification with CO₂.7)-9) These catalysts also facilitated O₂ gasification of benzene at 873 K.

3.2 Structural and Morphological Features

Structural change of MgO in the course of preparation of Ca²⁺-doped MgO was investigated by means of XRD. MgO(0) having a structure of periclase was completely transformed into brucite, Mg(OH)₂, when soaked in Ca(NO₃)₂ aqueous solution. Reflection peaks due to brucite, however, disappeared after heat treatment at 773 K for 2 h in a stream of N₂ and those due to periclase were solely observed. Fig. 1 shows variation in the (200) reflection peak of periclase with Ca²⁺ doping. The Ca²⁺-doped MgO samples were treated at 1223 K for 5 h in a stream of N₂. The (200) reflection peak was broadened by addition of a small amount of Ca²⁺ (0.1 wt%) accompanied by a decrease in intensity. An increase in the amount of Ca²⁺ dopant shifted the position of reflection toward a larger angle and reduced line width. We ascertained that other reflection peaks also changed in a similar manner. The (200) reflection peak of periclase from MgO(1), which is not shown in Fig. 1 to avoid overcrowding, was broadened but located at the position same with MgO(0).

It is generally known that line breadth of XRD reflection is influenced by both the crystallite size and the stress effect. Hall17) has given an equation to distinguish between them as follows:
\[
\frac{\beta \cos \theta}{\lambda} = \frac{1}{\varepsilon} + \frac{\sin \theta}{\lambda}
\]

where \( \beta \) represents line width, \( \theta \) Bragg angle, \( \lambda \) X-ray wavelength, \( \varepsilon \) crystallite size, and \( \eta \) strain. The Hall plots for Ca\(^{2+}\)-doped MgO are shown in Fig. 2. Judging from the slope of the Hall plots, the strain is estimated to be comparable for each sample. These results imply that broadening reflection peaks observed in Fig. 1 are indicative of decreasing crystallite size.

The morphological changes in the course of sample preparation were observed by means of scanning and transmission electron microscopes (SEM and TEM). Structural transformation from brucite to periclase phase accompanied change in morphology of the sample as shown in Fig. 3. It should be noted that the amount of Ca\(^{2+}\) dopant dramatically affects the morphology of resultant Ca\(^{2+}\)-doped MgO. As shown in Fig. 3(a), MgO(0) is structured of an assembly of large cubic crystals having flat faces. When MgO(0) was soaked into Ca(NO\(_3\))\(_2\) aqueous solution, the external shape changed into hexagonal flakes. This intrinsic shape exhibits the hexagonal characteristics of the hydroxide structure (hcp). The hydrated sample revealed a low contrast mottling as shown in Fig. 3(e).

We confirmed by means of XRD that heat treatment at 727 K resulted in the transformation from brucite to periclase, while no appreciable change of external shape was observed by TEM. These results mean that Ca\(^{2+}\)-doped MgO formed pseudomorph. In the case of Ca\(^{2+}\)(0.1)/MgO, the external shape of pseudomorph was preserved even after treatment at a higher temperature, 1223 K, as shown in Fig. 3(b) and (g). The SEM observation clearly shows that this stable pseudomorph after treatment at a high temperature was composed of tiny particles in the order of tens nm and of a number of voids. By means of TEM (Fig. 3(g)), we observed fine mottled or striped contrasts on Ca\(^{2+}\)(0.1)/MgO. The width between the arrow marks in this micrograph corresponds to ca. 5 nm. We observed by means of electron diffraction that plate-like crystal of pseudomorph tended to lie on the TEM carbon film with (111) direction parallel to the electron beam. Tiny particles forming pseudomorph of MgO possessed almost the same orientation such that the pseudomorph yielded an electron diffraction pattern coinciding with that of single crystals.

An increase in the amount of Ca\(^{2+}\) dopant led to a further morphological change: Ca\(^{2+}\)(1.0)/MgO after treatment at 1223 K consisted of assembly of cubic particles having rounded corners as shown in Fig. 3(d). However, TEM micrograph (Fig. 3(h)) shows that a cube observed by SEM was composed of many fine particles. On the other hand, MgO(I) was observed as assembly of cubic crystals, the size of which was smaller than that of MgO(0) as shown in Fig. 3(i). Small spot-like contrasts were obvious at grain boundaries in this TEM micrograph for MgO(I), indicating the presence of surface defects.

3.3 Basic Properties of Ca\(^{2+}\)-doped MgO Catalysts

Fig. 4(a) shows TPD spectra of CO\(_2\) adsorbed at room temperature. Each spectrum contained at least three types of discernible peaks, of which the maxima appeared at around 370 K (peak I), 500 K (peak II), and 770 K (peak III). As to MgO(0), CO\(_2\) desorption was completed at around 670 K and peak III was not perceivable. The amount of desorbed CO\(_2\) markedly increased with Ca\(^{2+}\) doping and peak III became appreciable, indicating formation of a different type of sites having stronger basicity.

Fig. 4(b) shows TPD spectra for CO\(_2\) adsorbed in the course of cooling after pretreatment at 1173 K. Another maximum at around 870 K (peak IV) appeared in the spectra upon exposure of Ca\(^{2+}\)-doped MgO to CO\(_2\) at higher temperatures. The height of peak IV was dependent on the amount of loaded Ca\(^{2+}\) ions. On the other hand, the spectra for MgO(0) and (I) were permanent irrespective of adsorption temperature. The peaks I, II, and III observed in the lower temperature region for Ca\(^{2+}\)-doped MgO were also similar to those shown in Fig. 4(a).

Temperature-programmed decomposition (TPDE) of CaCO\(_3\) and successive CO\(_2\)-TPD were carried out systematically at various temperatures.
Fig. 3 Electron Micrographs of MgO(0), MgO(I), and Ca²⁺-doped MgO samples. (a)-(d), SEM micrographs of the samples after heat treatment at 1223 K for 5 h; (e)-(i), TEM micrographs. (a), MgO(0); (b), Ca²⁺(0.1)/MgO; (c), Ca²⁺(0.5)/MgO; (d), Ca²⁺(1.0)/MgO; (e), MgO(0) before heat treatment; (f), Ca²⁺(0.1)/MgO after heat treatment at 727 K; (g), Ca²⁺(0.1)/MgO after heat treatment at 1223 K; (h), Ca²⁺(1.0)/MgO after heat treatment at 1223 K; (i), MgO(I).
out to investigate chemical properties of the Ca dopant itself on MgO surface. As shown in Fig. 5, decomposition of CaCO₃ started at around 790 K and the rate of decomposition reached a maximum at around 970 K. Two shoulder peaks were observed at lower temperatures (ca. 870 and 940 K).

After we ascertained that CaCO₃ had completely transformed into CaO in the TPDE experiment, CO₂ was adsorbed on CaO and a TPD experiment was successively performed. We observed that CO₂ had started to desorb at higher temperatures than in case of CO₂ adsorption on MgO (Fig. 4), when CO₂ was absorbed on CaO at room temperature. CO₂ was mainly desorbed from CaO in the temperature range of 670—900 K with a small peak of CO₂ desorption in the higher temperature range of 900—1070 K. Compared with decomposition of CaCO₃, the amount of desorbed CO₂ was smaller by a factor of 100. On exposure of CaO to CO₂ in the course of cooling from 1173 K after preceding TPD measurement, CO₂ desorption was manifested at around 870 K at which a shoulder peak had been observed in the TPDE spectrum.

Table 2 compares the basic property and the specific surface area of each sample. Specific surface area increased on doping with 0.1 wt% of Ca²⁺ ions. A further increase in the amount of Ca²⁺ dopant, however, led to a decrease in surface area. The amount of adsorbed CO₂ was measured and classified into three kinds by using temperature ranges where CO₂ was desorbed (313—473, 473—673, and 673—873 K). This classification was done to obtain information on distribution of basic strength. When the sample after measurements of the uptake of CO₂ was re-treated in vacuo

Table 2 Quantitative Basicity Measurements Using CO₂ as a Probe Molecule and Specific Surface Area

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ uptake ×10⁹ mol m⁻²</th>
<th>Specific surface area m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>313—473 K; 473—673 K; 673—873 K</td>
<td></td>
</tr>
<tr>
<td>MgO (0)</td>
<td>3.2</td>
<td>30.0</td>
</tr>
<tr>
<td>MgO (1)</td>
<td>24.5</td>
<td>23.3</td>
</tr>
<tr>
<td>Ca²⁺(0.1)/MgO</td>
<td>22.1</td>
<td>35.4</td>
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<tr>
<td>Ca²⁺(0.5)/MgO</td>
<td>21.8</td>
<td>50.8</td>
</tr>
<tr>
<td>Ca²⁺(1.0)/MgO</td>
<td>32.9</td>
<td>47.9</td>
</tr>
</tbody>
</table>

Fig. 4 TPD Spectra for CO₂ Adsorbed (a) at Room Temperature and (b) during Cooling from 1173 K to Room Temperature. Sample: (i), Ca²⁺(1.0)/MgO; (ii), Ca²⁺(0.5)/MgO; (iii), Ca²⁺(0.1)/MgO; (iv), MgO(I); (v), MgO(0).

Fig. 5 TPDE Spectrum (a) for CaCO₃ (-----) and TPD Spectra for CO₂ Adsorbed on CaO (a) at Room Temperature (-----) and (c) during Cooling from 1173 K to Room Temperature (-----).
at temperatures above 873 K, no appreciable amount of CO₂ was desorbed, being in agreement with the results of TPD. From the results listed in Table 2, and increase in the amount of loaded Ca²⁺ ions obviously increases the number of three types of basic site per unit surface area.

Ca²⁺ (0.1)/MgO adsorbed 1.7×10⁻⁴ mol g⁻¹ of CO₂, whereas it contained 1.8×10⁻⁵ mol g⁻¹ of Ca²⁺ ions. As MgO(0), which was the starting material to prepare Ca²⁺ (0.1)/MgO, adsorbed 1.9×10⁻⁵ mol g⁻¹ of CO₂, one can evidently conclude that Ca²⁺ ions act to increase the number of basic sites on MgO surface. Furthermore, the number of basic sites on MgO(1) was 14 times that on MgO(0).

The structure of adsorbed CO₂ species was obtained by means of IR. Fig. 6(a) and (b) show the spectra for CO₂ adsorbed on MgO(1) and (0), respectively, after CO₂ was adsorbed at room temperature and then evacuated at different temperatures. Broad and large absorption bands were observed at around 1560 and 1400 cm⁻¹ after MgO(1) was exposed to CO₂ and successively evacuated at room temperature. Weaker bands were also observed at 855 and at ca. 1000 cm⁻¹ with a discernible shoulder around 1560 cm⁻¹. MgO(0) gave different spectra of adsorbed CO₂ from MgO(1). The bands for CO₂ adsorbed on MgO(0) appeared at 1650, 1410, 1200, and 830 cm⁻¹ on evacuation at room temperature as shown in Fig. 6(b). The intensities of all absorption bands for CO₂ adsorbed on both MgO(1) and (0) decreased with increasing evacuation temperature, being obscure after evacuation at 873 K. These results are in good agreement with those of CO₂-TPD and volumetric measurements.

It has been shown¹⁸⁻²⁰ that the splitting of the asymmetric stretching band of surface carbonate group is about 100 cm⁻¹ for unidentate carbonate and about 300 cm⁻¹ for bidentate carbonate.

Accordingly, the bands observed at ca. 1560 and 1400 cm⁻¹ for CO₂ adsorbed on MgO(1) could be assigned to unidentate carbonate because of their small splitting of the asymmetric stretching band. On the other hand, bidentate carbonate of which the absorption bands were located at 1650 and 1410 cm⁻¹ was predominantly formed on MgO(0).

Fig. 7(a) shows IR spectra for CO₂ which was adsorbed on Ca²⁺ (0.5)/MgO at room temperature followed by evacuation at different temperatures. On evacuating at room temperature, adsorption bands were observed at 1695 (shoulder), 1650, 1620, 1375, 1305 (shoulder), ca. 1000, and 850 cm⁻¹. On the basis of considerations described above, the shoulder bands at 1695 and 1305 cm⁻¹ could be assigned to bidentate carbonate and the bands at 1620 and 1375 cm⁻¹ to unidentate carbonate. Although the band at 1650 cm⁻¹ could not be assigned, it disappeared after evacuation at 373 K. As in the case of MgO(1), all the absorption bands disappeared on evacuation at 873 K.

Fig. 7(b) shows IR spectra for CO₂ adsorbed on Ca²⁺ (0.5)/MgO in the course of cooling after evacuation at 1073 K. The most pronounced feature is appearance of double new bands at 1415
and 880 cm$^{-1}$, in harmony with appearance of peak IV on the TPD spectra (Fig. 4(b)), with no other bands being changed from Fig. 7(a). These two bands could be assigned to carbonate ion, CO$_3^{2-}$[18,19].

3.4 XPS, AES, and SIMS Measurements

MgO(I) contained Ca$^{2+}$ ions as Ca$^{2+}$-doped MgO, whereas these two showed different surface property, as described above. XPS was employed to investigate the difference in the surface structure between MgO(I) and Ca$^{2+}$-doped MgO. For this purpose, Ca$^{2+}$(1.0)/MgO was used because this contained a comparable amount of Ca$^{2+}$ ions with MgO(I). As shown in Fig. 8, Mg 2s and 2p, and Ca 3p peaks for both MgO(I) and Ca$^{2+}$(1.0)/MgO were located at binding energies of 94.0, 55.5, and 26.0 eV, respectively. Comparable intensities of Mg 2s and 2p peaks were attained both by MgO(I) and by Ca$^{2+}$(1.0)/MgO, whereas MgO(I) apparently gave a higher intensity of the Ca 3p peak than Ca$^{2+}$(1.0)/MgO. These results suggest a higher overage of the surface of MgO(I) with Ca$^{2+}$ ions as compared with Ca$^{2+}$(1.0)/MgO.

The surface coverage of Ca$^{2+}$ was also studied by means of AES. AES analysis of insulators may generally produce spurious results due to charging effects. However, in the present study, charging effects were not so serious to the extent that AES data were sufficiently reproducible to measure surface composition. As shown in Fig. 9, the relative intensity of LMM AES signal of Ca to that of LMM AES signal of Mg (I$_{Ca}$/I$_{Mg}$) linearly correlated to the amount of Ca$^{2+}$ dopant in the case of Ca$^{2+}$-doped MgO. These results are in good agreement with those of XPS study reported by Cunningham et al.[21]. Their XPS data have shown that there exists a linear relationship between the surface coverage of Ca$^{2+}$ and the level of doping of MgO with Ca$^{2+}$ ions, while their samples were prepared by use of methanol solutions of Ca(NO$_3$)$_2$. Nevertheless, in our AES measurements, MgO(I) gave a greater I$_{Ca}$/I$_{Mg}$ ratio.

Fig. 7 IR Spectra for CO$_2$ Adsorbed on Ca$^{2+}$(0.5)/MgO (a) at Room Temperature (b) during Cooling from 1073 K to Room Temperature. Evacuation temperature (K): (i), room temperature; (ii), 373; (iii), 473; (iv), 573; (v), 673; (vi), 773 (vii), 873.

Fig. 8 XPS Spectra of the Mg 2s and 2p and the Ca 3p Regions for (a) MgO(I) and (b) MgO(0)
than Ca\(^{2+}\)(1.0)/MgO, in agreement with the results of XPS.

On the other hand, SIMS gave opposite results to those of XPS and AES. Fig. 10 clearly shows that Ca\(^{2+}\) ions loaded on Ga\(^{2+}\)(1.0)/MgO were considerably concentrated in the surface layers compared with MgO(I).

4. Discussion

4.1 The Effect of Doping of MgO with Ca\(^{2+}\) Ions on the Structural and Basic Properties

Firstly, we discuss the effect of Ca\(^{2+}\) doping on the structural and chemical features of MgO.

Holt et al.\(^{20}\) have recently reported that Cl\(^{-}\) ions in the RuCl\(_3\) aqueous solution catalyze hydration of periclase to give brucite. In the present study, the structural transformation of MgO(0) from the periclase to the brucite phase in the course of impregnation with an aqueous solution of Ca(NO\(_3\))\(_2\) was observed. When MgO(0) was soaked in decactionated water in the absence of Ca(NO\(_3\))\(_2\), the partial transformation of MgO(0) from the periclase to the brucite phase was observed, being in agreement with the results by Holt et al.\(^{20}\). These results suggest that NO\(_3^{-}\) ions also catalyze hydration of the periclase phase.

On heating at 773 K, the brucite structure of Ca\(^{2+}\)-doped MgO was completely transformed into periclase exhibiting pseudomorph. After heat treatment at 1223 K, we found a remarkable effect of Ca\(^{2+}\) doping on the morphological and structural features. In general, treatment at high temperatures causes sintering of MgO crystals to give large cubic crystals. We observed that the external shape of pseudomorph composing Ca\(^{2+}\) (0.1)/MgO was preserved even after treatment at 1223 K. A pseudomorph consisting of tiny particles has a number of voids, leading to the increase of specific surface area, as shown in Table 2. The broadening of XRD reflections accompanied by doping with 0.1 wt% of Ca\(^{2+}\) ions as shown in Fig. 1 reveals a decrease in the particle size, being in also good agreement with the results of SEM observation.

The fine mottled and striped contrasts observed by TEM for Ca\(^{2+}\)(0.1)/MgO imply rumpled arrangements of the resulting surface. Moodie and Wardle\(^{24}\) have recently reported similar observations on MgO morphology. Referring to the TEM observation, they have called these fine striped contrasts "morphological moiré". It is known that MgO cubes tend to stick together by overlapping on (100) faces, often over small areas; typically by 25% overlapping on (100) faces. The aggregation of MgO cubes in such a manner leads to building up pseudomorph having approximately (111) axes perpendicular to the surface of the sheet, as shown in TEM micrograph for Ca\(^{2+}\)(0.1)/MgO. However, the imperfect intergrowth very frequently occurs, resulting in the formation of twist grain boundaries observed as "morphological moiré". From the results of XRD, SEM, and TEM observations, we consider that Ca\(^{2+}\) ions loaded on MgO surface inhibit the transformation of surface arrangements accompanied by structural transformation from brucite (hcp) to periclase phase (fcc). We believe that Ca\(^{2+}\) ions act to relieve the lattice strain arising from surface rumpling as twist grain boundaries are formed, and to stabilize such rumpled arrangements even at higher temperatures.

There has been reliable prediction\(^{19,18}\) that Ca\(^{2+}\) ions segregated at the MgO surface inhibit the transformation of surface arrangements accompanied by structural transformation from brucite (hcp) to periclase phase (fcc). We believe that Ca\(^{2+}\) ions act to relieve the lattice strain arising from surface rumpling as twist grain boundaries are formed, and to stabilize such rumpled arrangements even at higher temperatures.

The reconstruction of the regular MgO lattice is driven by the strain resulting from the incorpora-
tion of high concentrations of impurity. This function of Ca\textsuperscript{2+} dopant to undulate the MgO surface is essentially similar to the function of Ca\textsuperscript{2+} ions, which was found in the present study, to stabilize rumpled surface resulting from the structural transformation from brucite to periclase phase.

With increasing amount of doped Ca\textsuperscript{2+} ions, sintering of the MgO particles was observed by means of SEM, in agreement with increasing intensities of reflection peaks in the XRD patterns and with decreasing specific surface area. Another feature is the shrinkage of the MgO lattice with doping with Ca\textsuperscript{2+} ions, as indicated from XRD results. This feature may be explained by formation of CaO-MgO solid solution. According to the phase diagram for the CaO-MgO system reported by Doman et al., CaO-MgO solid solution is formed at temperatures above 1870 K and, furthermore, the lattice constant of MgO should be expanded with formation of solid solution. The formation of CaO-MgO solid solution in the present study is denied because of heat treatment at temperature as high as 1123 K, and of the shrinkage of the MgO lattice. Then, we conclude that the shrinkage of MgO lattice is caused by the action of Ca\textsuperscript{2+} ions.

TPD measurements provided valuable information about the effect of Ca\textsuperscript{2+} ions on surface properties of MgO. In the TPD spectra for adsorbed CO\textsubscript{2}, we observed increment of peaks I and II, and appearance of peak III with Ca\textsuperscript{2+} doping. These features indicate the enhancement of basic property of MgO with Ca\textsuperscript{2+} doping. Another feature was appearance of peak IV when CO\textsubscript{2} was adsorbed in the course of cooling at 1173 K after heat treatment. To understand the mechanism for the formation of the species to give the peak IV, TPD results for CO\textsubscript{2} adsorbed on Ca\textsuperscript{2+}-doped MgO should be discussed in comparison with TPD spectra for CO\textsubscript{2} adsorbed on CaO itself, because Ca\textsuperscript{2+} ions may be adsorbed on CaO particles on the MgO surface.

The desorption peak in the lowest temperature region shown in Figs. 5(b) and (c) should be due to desorption of CO\textsubscript{2} which has been adsorbed on surface basic sites of CaO. On the other hand, CO\textsubscript{2} adsorbed on CaO in the course of cooling after evacuation at 1123 K, was mainly desorbed at higher temperatures than when CO\textsubscript{2} adsorbed at surface basic sites. The bands, which appeared at 1415 and 880 cm\textsuperscript{-1} in IR spectra on exposure of Ca\textsuperscript{2+}-doped MgO to CO\textsubscript{2}, in the course of cooling after pretreatment, could be assigned to CO\textsubscript{3}\textsuperscript{2-} ions, indicating the formation of CaCO\textsubscript{3}. In addition, CO\textsubscript{2} evolution due to decomposition of bulk CaCO\textsubscript{3} mainly occurred in the highest temperature region as shown in Fig. 5. As a result, we conclude that desorption of CO\textsubscript{2} in the higher temperature region is attributed to the decomposition of CaCO\textsubscript{3} phase formed in the surface layer of the CaO. Peak IV appeared at similar temperatures, around 873 K, where the CaCO\textsubscript{3} phase in the surface layers was decomposed. Consequently, we consider that the appearance of peak IV indicates the presence of CaO particles on the MgO surface. We therefore conclude that Ca\textsuperscript{2+} ions aggregate to form CaO particles on the MgO surface.

A combination of TPD and IR results permits us to conclude that no appreciable amount of CaCO\textsubscript{3} is formed when Ca\textsuperscript{2+}-doped MgO is exposed to CO\textsubscript{2} around room temperature, while CaO particles are transformed into CaCO\textsubscript{3} on exposure to CO\textsubscript{2} at higher temperatures.

4.2 Structural Features of MgO(I)

Despite the presence of Ca\textsuperscript{2+} ions in MgO(I), we observed some different structural and chemical features from those of Ca\textsuperscript{2+}-doped MgO. The most pronounced difference in surface properties between MgO(I) and Ca\textsuperscript{2+}-doped MgO is that peak IV did not appear in the TPD spectrum of MgO(I) when CO\textsubscript{2} was adsorbed in the course of cooling after treatment at 1173 K. If CO\textsubscript{3}\textsuperscript{2-} ions had been formed, the absorption bands would have appeared at around 1415 and 880 cm\textsuperscript{-1}. Being lack of these bands, it is implied that CO\textsubscript{3}\textsuperscript{2-} ions were not formed on MgO(I). From these results, it is hard to conclude that there exist large CaO particles on the surface of MgO(I): Ca\textsuperscript{2+} ions should be highly dispersed on the surface of MgO prepared from a basic carbonate containing Ca\textsuperscript{2+} ions as an impurity.

The cubic crystals composing MgO(I) were much smaller than those composing MgO(0), as observed in the TEM micrograph. Then, it is reasonable that MgO(I) gave the broader XRD reflection peaks than MgO(0). Thus, we consider that Ca\textsuperscript{2+} ions contained in MgO(I) inhibit sintering of MgO crystals in the course of heat treatment, which is similar to the action of Ca\textsuperscript{2+} ions loaded on MgO(0).

We expect that a comparison among the results of XPS, AES, and SIMS measurements is valuable to further account for geometrical arrangement of Ca\textsuperscript{2+} ions on the surface of MgO. SIMS measurements revealed that the concentration of Ca\textsuperscript{2+} ions in the surface layer of Ca\textsuperscript{2+}(1.0)/MgO is higher than in the case of MgO(1), whereas both XPS and AES experiments gave opposite results. These conflicting results must be derived from the
differences in the manner of signal production from surface among these spectroscopies. Taking the results of the TPD, IR, and volumetric adsorption studies by use of CO₂ as a probe molecule into consideration, we propose models illustrated in Fig. 11 to reasonably explain these discrepancies.

As the starting material to prepare MgO(I) contains Ca²⁺ ions, it seems that a part of Ca²⁺ ions existed in the interior of crystals. Thus, we consider that the amount of Ca²⁺ ions at the surface of MgO(I) was smaller than that at the surface of Ca²⁺(1.0)/MgO. The results of SIMS measurements are in good agreement with this consideration. On the other hand, if Ca²⁺ ions are highly dispersed on the surface of MgO(I) as illustrated in Fig. 11, the coverage of Ca²⁺ ions at the surface of MgO(I) would be greater than that at the surface of Ca²⁺(1.0)/MgO.

The linear relationship between the amount of Ca²⁺ dopant and the ICa/IMg ratio obtained by AES measurements resembles the results of a XPS study reported by Cunningham et al.21) As shown in Fig. 9, however, the ICa/IMg ratio for MgO(I) was greater than expected from the linearity. This may also be attributed to smaller dispersion of Ca²⁺ ions in Ca²⁺-doped MgO than in MgO(I) as discussed above. It has not been mentioned by Cunningham et al.20) whether or not Ca²⁺ ions aggregate to form CaO particles on the surface of their samples. We show in the present study that results of the AES study do not provide information about the absolute amount of Ca²⁺ ions on the surface, but they indicate that Ca²⁺ coverage increases with increasing amount of Ca²⁺ dopant.

4.3 Enhancement of Basicity and Basic Strength

As discussed above, CaO particles on the MgO surface are not transformed into CaCO₃ when Ca²⁺-doped MgO is exposed to CO₂ at lower temperatures. Therefore, results of volumetric measurements provide information on the number of basic sites active for adsorption of CO₂. As shown in Table 2, the total number of basic sites per unit surface area was markedly increased with increasing amount of Ca²⁺ dopant. Similarly, the numbers of basic sites of every types increased with increasing amount of Ca²⁺ dopant.

The rumpled arrangements of the MgO surface owing to Ca²⁺ loading are probably responsible for the increment of basic sites, i.e. coordinatively unsaturated sites located at corners, steps and so on. A pronounced feature in TPD spectra for CO₂ adsorbed on the CaO surface is a fact that CO₂ was desorbed at temperatures above 590 K. As peaks I and II appeared at temperatures below 590 K in the TPD spectra both of MgO and of Ca²⁺-doped MgO, CaO particles on the MgO surface are considered not to be cause for the peaks I and II. Consequently, we consider that weak basic sites causing peaks I and II exist on the MgO surface itself.

Ca²⁺(0.1)/MgO contained 1.8×10⁻⁵ mol g⁻¹ of Ca²⁺ ions, whereas there are 3.1×10⁻⁵ mol g⁻¹ of strong basic sites where CO₂ was desorbed above 673 K. Taking it into consideration that Ca²⁺ dopant tends to aggregate to form CaO particles on the MgO surface, we consider that most of the strong basic sites are also located, not on the surface of CaO particles, but, on the MgO surface. There is a possibility that Ca²⁺ ions dispersed on the MgO surface enhance the basic strength of neighboring O²⁻ ions. The generation of strong basic sites on MgO(I), on which there was no CaO particle, supports this consideration. If this is so, the strong basic sites may not necessarily be located at coordinatively unsaturated sites.

Unidentate carbonate was predominantly formed on MgO(I), although bidentate carbonate was mainly formed on MgO(0). No spectral change indicative of the structural transformation of the carbonate group was observed with MgO(I) and (0) when evacuation temperature was raised. Fukuda and Tanabe20) have reported that the structure of carbonate group formed on the MgO surface depends on the coverage of CO₂, unidentate carbonate groups being predominantly formed at higher CO₂ coverages on the MgO surface. Since there are a greater number of basic sites to adsorb CO₂ on MgO(I) than on MgO(0), we consider that predominant formation of unidentate carbonate on MgO(I) is reasonable. Once a carbonate group is formed on the MgO surface, the structure of the carbonate group does not change even after adsorbed CO₂ is partly desorbed by evacuation at high temperatures, in spite of decreasing CO₂ coverage.
4.4 Catalytically Active Sites

It is known that the surface of MgO treated at high temperatures is almost inactive for double-bond migration of 1-butene. Ca$^{2+}$ ions loaded on MgO are capable of functionalizing the surface, leading to the enhancement of the catalytic activities for several kinds of reactions even after high temperature treatment. There was no relation between the reaction rate and the number of weak basic sites from which CO$_2$ was desorbed up to 673 K. Fig. 12 shows the rates of 1-butene isomerization as a function of the uptake of CO$_2$ per gram of catalyst. We calculated the CO$_2$ uptake as shown in this figure on the basis of the amount of CO$_2$ uptaken above 673 K. Because of the linearity shown in Fig. 12, we can conclude that the strong basic sites are responsible for 1-butene isomerization.

Both the reverse water-gas shift reaction and C$_6$H$_6$-CO$_2$ reaction catalyzed by alkaline earth metal oxides involve the activation of CO$_2$ molecules. As these oxides strongly absorb CO$_2$ on basic sites on their surface, the basic sites may be the cause for these two reactions, whereas the increment of catalytic activity due to Ca$^{2+}$ doping varied with the type of reaction. These suggest that there are some structurally and/or energetically different types of active site. Since the activation of CO$_2$ occurs at higher temperatures and CO$_3^{2-}$ ions are formed at these temperatures, the sites causing the formation of CO$_3^{2-}$ ions may also be catalytically active for CO$_2$ gasification and the reverse water-gas shift reaction. The mechanism of activation of CO$_2$ or O$_2$ and the active site are under investigation.

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References

Ca²⁺イオンをMgOに添加することにより、塩基性、触媒活性の向上を試みた。塩基性炭酸塩（特級品）を1123 Kで空気焼成して得たMgO（0）は1-ブテニン異化、炭化水素のCO₂、O₂ガス化、還元CO₂シフト反応には不活性であったが、Ca²⁺イオンを添加すると顕著な活性を示した（Table 1）。
Ca(NO₃)₂水溶液にMgO（ペリクリーズ）を含浸するとNO₃⁻イオンによりMgOの水和が促進され、完全にMg(OH)₂（ブルーサイド）となることがXRDにより確認された。これらを1123 Kで処理すると再び全てペリクリーズとなったが、Ca²⁺添加量が増加するとMgOの格子定数が0.00 Å大きくなった（Fig. 1）。これは、固溶体を形成したのではなく、Ca²⁺イオンとMgO結晶格子の相互作用の結果と思われる。
Ca²⁺イオンの添加はMgOの結晶形態にも大きく影響することがSEM、TEM観察により明らかであった（Fig. 3）。MgO（0）は立方体であったが、Ca²⁺イオンを酸化物として0.1 wt%添加したCa²⁺(0.1)/MgO（以下添加量は軽質側で示す）は小さな粒子の集合体よりなる偏平な六角柱（SEM）であり、結晶軸位あるいは粒界の存在を示すと思われる微細なコントラストが多数見られた。また、熱処理後の試料のTEM観察から、この六角柱の形態は酸化物のhcp構造に由来することがわかった。担持量の増加によりさらに形態の変化がみられ、TEM写真からこれらは六角柱状を構成する微細な結晶が凝集し成長したものであることがわかった。この六角柱状の結晶形態はpseudomorphとして知られており、一般に不安定で高温で処理すると立方体へと変化するが、本研究では1123 Kで処理後もその形態が維持されていた。添加されただけCa²⁺イオンは酸化物を脱水する際のhcpからfccに結晶構造の変化に伴い表面構造の変化を伴って、すなわちMgO表面の凹凸を安定化すると考えられる。一方、Ca²⁺イオンを不純物として含む塩基性炭酸塩より調製したMgO(1)（Ca²⁺含有量0.94 wt%）では、一方の軽質の立方体が凝集しているが、その粒径には表面欠陥によると思われる粒径のコントラストが見られた。
CO₂-TPD（Fig. 4）の結果から、Ca²⁺イオンの添加により塩基性が増加し、763 K以上でCO₂が脱離する強塩基点が生成することがわかった。1173 Kから冷却しながらCa²⁺添加MgO上にCO₂を吸着させた場合には870 K付近に新たな脱離ピークが現れたが、MgO(1)にはみられなかった。CaO単味を用いたTPDの結果（Fig. 5）から、新たな脱離ピークはCaOの表面層付近に生成したCaCO₃の分解温度に対応して現れることがわかった。IR測定より、873 Kから冷却しながらCO₂を吸着させた場合にはCa²⁺(0.5)/MgO上に炭酸イオンの吸収が現れ、これはMgO表面にパルクのCaCO₃が生成したためと考えられる。以上の結果よりMgO表面に添加されたCa²⁺イオンは凝集しCaO粒子となると考えられる。
MgO(1)を用いたIR測定では炭酸イオンの吸収はみられなかったので、MgO(1)の表面ではCa²⁺イオンは非分散していると考えられる。
Table 2には表面吸着実験の結果を示した。CO₂の吸着量はCaが存在することにより顕著に増大した。TPDの結果から考え232 Kの吸着温度でパルクのCaCO₃の生成は無視できないので、本結果は表面の塩基性度を示していると考えられる。例えばCa²⁺(0.1)/MgOの場合添加したCaO量のおよそ10倍の吸着量の増加を示しており、塩基量の増加分が添加したCaOに直接依存するとは考えにくい。先に述べたように、Ca²⁺イオンがMgOの表面構造の凹凸を安定化するためにMgO上に新たな塩基点を生じたものと結論できる。
Fig. 8にMgO(1)およびCa²⁺(1.0)/MgOのXPSスペクトルを示した。Ca(3p)/Mg(2p)比はMgO(1)の方が大きい。つまり、Caの表面被覆率はMgO(1)の方が大きい。AES（Fig. 9）によっても同様な結論が得られた。Fig. 10にはSIMSにより両試料の深さ方向分析を行った結果を示した。明かにCa²⁺(1.0)/MgOの表面にはCaがより凝集していることがわかり、両試料はほぼ同じCa担持量であるので、表面に存在するCa量はMgO(1)よりCa²⁺(1.0)/MgOの方が多いことがわかる。同一担持量で考えた場合、XPS、AESで分析したときに測定されるCaの表面被覆率はCaが高分散に存在する試料の方が粒子状に凝集している試料よりも大きくなると考えられ、このような分散性の違いがSIMSによる一見相反する結果の原因と思われる。
以上の実験結果より、Ca²⁺イオンのMgO表面での分散状態についてFig. 11に示したモデルを提案する。すなわち、Caを硝酸塩水溶液から添加した試料では表面に存在するCaの多くは凝集し粒子状のCaOとなっているのに対し、MgO(1)の場合にはCa²⁺が表面に高分散している。
673 K以上の温度でCO₂が脱離する強塩基点の量と1-ブテニン異化反応速度には良い直線関係がみられた（Fig. 12）。1-ブテニン異化反応は塩基塩基上で進行すると考えられる。しかし、Ca²⁺イオン添加による触媒活性の増加は反応の種類によって一様ではなく、さらに検証が必要である。

Keywords
Basicity, Calcium dopant, Catalyst preparation, Magnesium oxide, Solid base catalyst

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表2

Table 1

Table 2

Fig. 8

Fig. 10

SIMS

AES

AES

AES

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