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Comparison of the base catalytic activity of MgO prepared by thermal decomposition of hydroxide, basic carbonate, and oxalate under atmospheric conditions

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Abstract

To obtain highly active solid base catalyst of magnesium oxide (MgO) under atmospheric conditions, hydroxide ($Mg(OH)_2$), basic carbonate ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$), and oxalate ($MgC_2O_4{\cdot}2H_2O$) were examined as starting material for preparation, and the effect of heating temperature on base catalytic activity was studied. Diacetone alcohol decomposition, a retro-aldol reaction, was performed to compare the base catalytic activity of prepared MgO catalysts. The order of activity of MgO as starting material for the retro-aldol reaction was oxalate > basic carbonate > hydroxide. In a comparison of catalytic activity based on catalyst weight and surface area, MgO prepared from oxalate showed higher activity than did samples prepared from carbonate and hydroxide. Catalytic activity based on surface area was the highest in MgO prepared by thermal decomposition of oxalate at 1173 K. The starting material, which had higher decomposition temperature and formed a larger amount of evolving gas molecules accompanying decomposition, provided a solid base with higher activity under atmospheric conditions.

Keywords MgO · Starting material · Thermal decomposition · Solid base · Retro-aldol reaction

Introduction

Alkaline earth metal oxides are well known as solid bases. Among these catalysts, magnesium oxide (MgO) has received much attention. Many research papers concerning the preparation, active site structure, and application of MgO to numerous base-catalyzed organic reactions have been published [1–5]. Solid

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base catalysts have been applied to several C–C bond formation reactions, such as aldol reaction; these are important in the synthesis of fine chemicals.

A catalytically active MgO has been prepared by the decomposition of hydroxide or carbonate at higher temperatures under high vacuum or inert gas conditions. MgO, which shows the highest activity for 1-butene isomerization, was prepared by heating in vacuum at 773 K [2].

Active sites on prepared MgO surfaces are strongly poisoned by H_2O and CO_2 in the atmosphere [2, 3]. From these reports, it is expected that solid base catalysts cannot be used in air. However, some research has been conducted on MgO activated and used under atmospheric conditions [6–10]. In C–C bond formations catalyzed by a base, the reaction is initiated by a proton abstraction. The p*K*a of a proton activated by a carbonyl group is about 20. This p*K*a value means that base sites with moderate strength can eliminate protons in the α-position of the carbonyl group. Many organic reactions catalyzed by a base do not need very strong base sites, which are active in alkene isomerization [9]. A strong base site, prepared under vacuum or inert gas conditions, is not necessary for general organic reactions. MgO activated in air has shown sufficient activity for retro-aldol reactions [10]. A catalyst usable under atmospheric conditions is more desirable than one prepared and used under vacuum conditions. From the view point of the activation and handling of MgO in air, it is important to study preparation conditions that can obtain more highly active MgO under atmospheric conditions. In this study, we used hydroxide, carbonate, and oxalate as starting material for MgO, and compared the activity of MgO catalysts obtained by heating in air at various temperatures. Among these starting materials, it has been reported that MgO formed by thermal decomposition of oxalate shows higher activity [6, 8].

Experimental

Catalyst preparation

As the starting material for MgO preparation, $MgC_2O_4 \cdot 2H_2O$ (Wako Pure Chemical Industries), two kinds of $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ (Wako Pure Chemical Industries and Sigma Aldrich), and $Mg(OH)_2$ were used. Magnesium hydroxide was prepared as follows. Pure MgO (Merck) was placed in a beaker and heated for 1 h in distilled water. Suspended solids were collected by filtration and dried at 373 K [11]. All starting materials were pressed into a pellet and powdered through a 32–50 mesh.

Thermal decomposition of starting materials into MgO was carried out in a muffle furnace. The starting materials in a glass ampoule or mortar were then placed in the furnace. The furnace temperature was raised from room temperature to the desired temperature in 30 min and maintained for 3 h. The sample was kept in a sealed ampoule until use. MgO catalysts prepared from oxalate, basic carbonate of the Wako sample, basic carbonate of the Sigma-Aldrich sample, and hydroxide were denoted as MgO–O, MgO–W, MgO–S, and MgO–H, respectively.

Retro-aldol reaction of diacetone alcohol

A retro-aldol reaction of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) into acetone, shown in Scheme 1, was performed in a batch-reaction system to compare the base catalytic activity of MgO catalysts. The reaction was carried out at 299 K for 3 h using 25 mg of catalyst and 100 mmol of diacetone alcohol in a round-bottom flask. Samples were taken every 30 min and analyzed using gas chromatography. The equilibrium conversion of this reaction is 88% at 299 K [12]. The reaction product was acetone. Dehydration product of mesityl oxide was not detected in this study. The catalytic activities of the prepared catalysts were compared using the rate constants calculated by applying a first-order reaction equation.

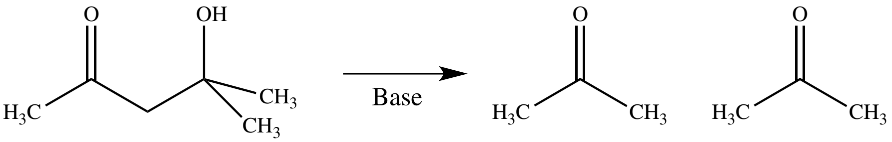
Catalyst characterization

Thermogravimetry–differential thermal analysis (TG–DTA) was performed on the sample before calcination to determine the decomposition temperature of starting material. TG–DTA experiments were performed in the temperature range from room temperature to 1073 K at the programmed rate of 2–10 K min^{-1}. The surface area was measured using N_2 adsorption amount at 77 K, the BET method. The sample was treated at 573 K for 2 h in vacuum after thermal treatment under atmospheric conditions. Powder X-ray diffraction (XRD) spectra were measured using Cu Kα radiation. The crystal size of the MgO particles was determined using Scherrer's equation on the (200) diffraction peak. The base strength of the samples (H_-) was determined using Hammett indicators. 4-Chloroaniline ($H_-=26.5$), diphenylmethane ($H_-=35.0$), and cumene ($H_-=37.0$), dissolved in cyclohexane at a concentration of 0.1%, were used as Hammett indicators. Approximately 20 mg of MgO sample, which was treated at 773 K for 3 h and kept in a sealed ampoule, was put in a cyclohexane solution of the Hammett indicator.

Results

TG–DTA

The results of TG–DTA are shown in Fig. 1. All measurements were performed in an N_2 atmosphere. Addition to those, measurement in air was performed on oxalate. In the TG–DTA of basic carbonate, three weight decreasing steps were observed (Fig. 1a, b). The lowest one, at 539 K, was attributed to the elimination of two



Scheme 1 Retro-aldol reaction of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)

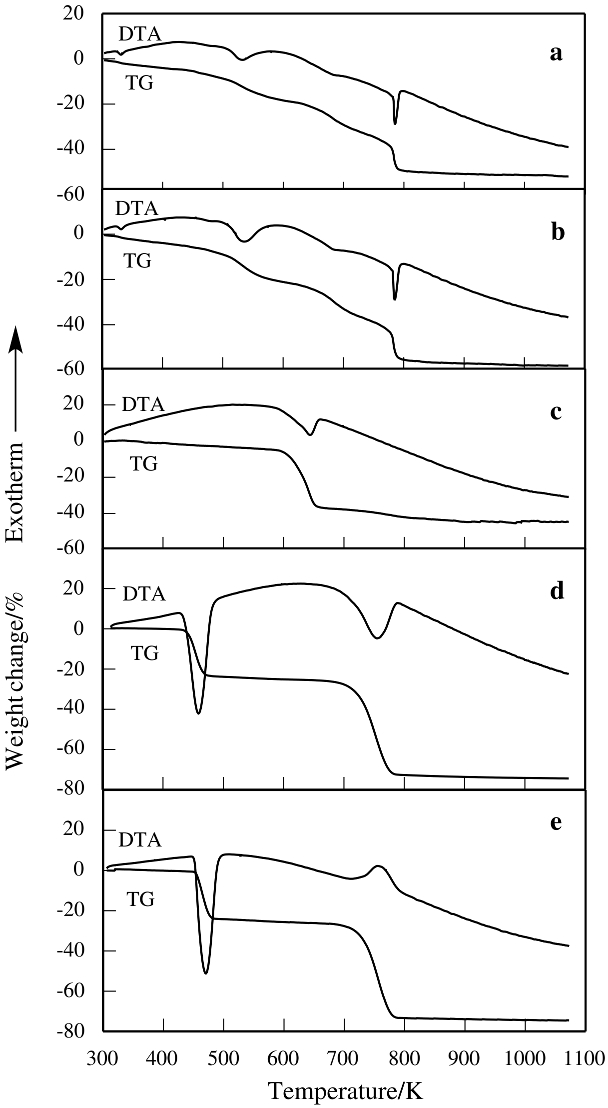


Fig. 1 TG–DTA profiles of starting materials of MgO for thermal decomposition. **a** $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ (Sigma-Aldrich), **b** $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ (Wako), **c** $Mg(OH)_2$, **d** $MgC_2O_4 \cdot 2H_2O$ in N_2, **e** $MgC_2O_4 \cdot 2H_2O$ in air

crystal water molecules. The hydroxide part of $Mg_5(CO_3)_4(OH)_2$ was decomposed at 695 K and converted into $MgCO_3$ and MgO. Finally, $MgCO_3$ was converted into MgO at 786 K [13]. The TG–DTA profiles of two kinds of basic carbonates, the Sigma Aldrich and Wako samples, were the same.

The prepared $Mg(OH)_2$ was converted into oxide at 648 K (Fig. 1c). Among the tested samples in this study, the decomposition temperature was the lowest in $Mg(OH)_2$. This temperature was lower than that of the hydroxide part in basic carbonate ($Mg_5(CO_3)_4(OH)_2$).

Magnesium oxalate hydrate ($MgC_2O_4 \cdot 2H_2O$) gave a two-step decomposition profile (Fig. 1d, e). The lower one was due to the elimination of crystal water molecules, and the higher one to oxalate decomposition into MgO, CO, and CO_2 [14]. The formation of CO and CO_2 occurred simultaneously at 754 K. This process was endothermic, as shown in Fig. 1d. This process was changed to an exothermic one when carried out in air because the exothermic reaction of CO oxidation by O_2 took place in air (Fig. 1e). The final decomposition temperatures were in the order of basic carbonate > oxalate > hydroxide. However, at 695 K, basic carbonate was partly converted into the catalytically active MgO. The order of decomposition temperature in which the active MgO was formed was oxalate > basic carbonate > hydroxide.

Plots of $2\ln T_m - \ln\beta$ versus $1/T_m$ [15], where T_m is peak temperature and β is the increasing temperature rate, are illustrated in Fig. 2. The slope of plots is E_a/R, where E_a is activation energy of thermal decomposition and R is gas constant. In hydroxide, the thermal decomposition temperature was the lowest, but the activation energy of decomposition was the largest (251 kJ mol^{-1}) among the studied samples. In basic carbonate, the activation energy of the decomposing hydroxide part was measured because catalytic activity was observed in the sample obtained by thermal treatment at 723 K in basic carbonate samples. The effect of heat treatment temperature on the base catalytic activity will be shown in next section. This temperature was lower than that of carbonate decomposition (786 K, Fig. 1a, b). The activation energy of the decomposing hydroxide part in basic carbonate was 124 kJ mol^{-1}, which was much smaller than those of the other samples.

In oxalate, the activation energy was measured in air and in an N_2 stream. As described above, the oxalate decomposition process was endothermic in N_2 and exothermic in air. The obtained activation energies were 237 kJ mol^{-1} and 221 kJ mol^{-1}, respectively. The decomposition temperatures were observed in a lower temperature range in the measurement in air. As shown in Fig. 2, the values

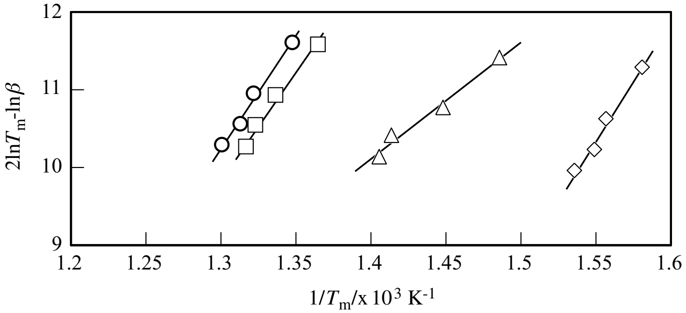


Fig. 2 Thermal decomposition activation energy of Mg compounds; plots of $2\ln T_m - \ln\beta$ versus $1/T_m$. Circle: $MgC_2O_4 \cdot 2H_2O$ in N_2, square: $MgC_2O_4 \cdot 2H_2O$ in air, triangle: $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ (Wako), diamond: $Mg(OH)_2$

of $1/T_m$ were plotted in a higher range when the DTA profile was measured in air, which indicates that T_m in the DTA profiles were in the lower temperature range. It was considered that the oxidation of CO by O_2 in air would promote oxalate decomposition.

Retro-aldol reaction

The effects of starting material and heat treatment temperature on the base catalytic activity for the retro-aldol reaction of diacetone alcohol (Scheme 1) are illustrated in Fig. 3. The retro-aldol reaction is the reverse of an aldol reaction. This reaction is catalyzed by acid and acid–base bifunctional catalysts as well as the base catalyst. The acid sites provide the dehydration product of mesityl oxide [2, 16]. Mesityl oxide was not detected in this study, which indicates that the contribution of acid sites for a retro-aldol reaction do not need to be considered in this study. Another representative solid base catalyst of CaO prepared by thermal decomposition of carbonate at 1123 K showed comparable activity for this reaction [17]. A higher temperature was applied for the aldol condensation on acid catalysts of proton–type zeolites, because of relatively lower activity [18]. Therefore, the retro-aldol reaction is convenience for the comparison of base catalytic activity.

Prepared catalysts showed activity in all activation temperatures ranging from 723 K to 1173 K (Fig. 3). The MgO–O sample obtained by thermal treatment of oxalate at 773 K was the most active for this reaction. Thermal treatment at 723 K provided MgO of relatively higher activity (ca. 70% of the highest one). The reaction rate was higher than that of CaO (1.16 mol g^{-1} h^{-1}) [17]. However, the decomposition of oxalate was not completed as expected based on the results of TG–DTA in Fig. 1. The applied heat treatment temperature (723 K) was lower than that of oxalate decomposition (756 K). As observed in the TG–DTA profile, the oxalate decomposition took place across a wide temperature range. It was expected that oxalate decomposition should be incomplete, but a partly formed MgO showed higher base catalytic activity. We have been reported that MgO prepared from hydroxide

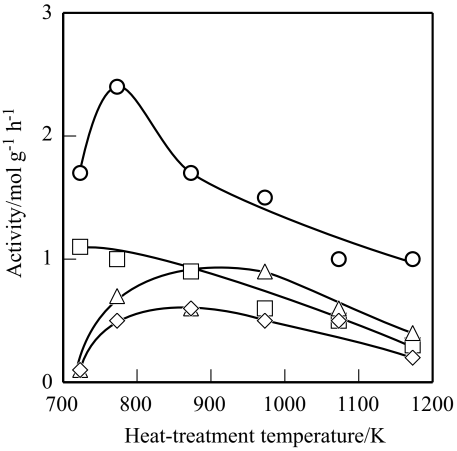


Fig. 3 Effects of starting material and heat treatment temperature on the catalytic activity of MgO catalysts for retro-aldol reaction of diacetone alcohol. Circle: MgO–O, square: MgO–S, triangle: MgO–W, diamond: MgO–H

that was decomposed and annealed in a short time, is more active compared with that of conventional long-time annealed MgO [10]. We can see similar behavior in the decomposition of $MgC_2O_4 \cdot 2H_2O$. MgO–O showed the highest activity by heat treatment at 773 K. The annealing effect would become small when the treatment temperature was close to that of decomposition.

MgO catalysts prepared using two kinds of basic carbonates, MgO–W and MgO–S, showed sufficient activity across all temperature ranges. The sample obtained by thermal treatment at 723 K, which was lower than that of carbonate decomposition (786 K), was sufficiently active. Basic carbonate is decomposed in two steps. The hydroxide and carbonate were decomposed at 695 K and 786 K, respectively. The decomposition of the hydroxide part was complete at 723 K, and the obtained MgO showed base catalytic activity. The catalytic activity of MgO–W sample heat-treated at 723 K was the highest in comparison with those obtained at higher temperatures.

The conventional starting material of $Mg(OH)_2$ provided the catalyst with the lowest activity among the MgO samples tested in this study. The MgO–H samples, which were treated in a wide temperature range, from 773 K to 1073 K, showed only small changes in catalytic activity.

The temperature of MgO formation from hydroxide was the lowest among the samples used in this study (Fig. 1). As reported, MgO annealed in a short time was more active that annealed in a long time [10]. In this report, $Mg(OH)_2$ was placed in a muffle furnace maintained at a desired temperature for a rapid increase in the activation temperature and short-time heating in the preparation of MgO. The effect of annealing would be the largest in the MgO–H sample.

The order of catalytic activity was oxalate > basic carbonate > hydroxide as the starting material. This order was the same as that for the decreasing decomposition temperatures of the starting material, which were 756 K, 695 K (the decomposing hydroxide part), and 648 K, respectively. The starting material, which has a higher decomposition temperature, gave MgO showing higher catalytic activity.

XRD analysis

To clarify the relation between the change of catalytic activity and phase transformation of the magnesium compound, XRD measurement was carried out on samples treated at various temperatures. As shown in Fig. 4a, MgO–O samples heat-treated at 773 K or higher gave a diffraction peak set of MgO. Increased peak heights and decreased peak widths were observed with increasing treatment temperatures.

The XRD profiles of all samples prepared by thermal decomposition at 723 K are shown in Fig. 4b. MgO–O activated at 723 K showed a magnesium oxalate peak set with small and wide MgO peaks. This temperature was not sufficiently high to decompose magnesium oxalate. This result regarding the partial formation of MgO coincided with the results of TG–DTA and catalytic activity testing shown in Figs. 1 and 3.

Samples prepared from hydroxide and basic carbonate gave an XRD profile of MgO. As shown in the TG–DTA section, the decomposition of the hydroxide

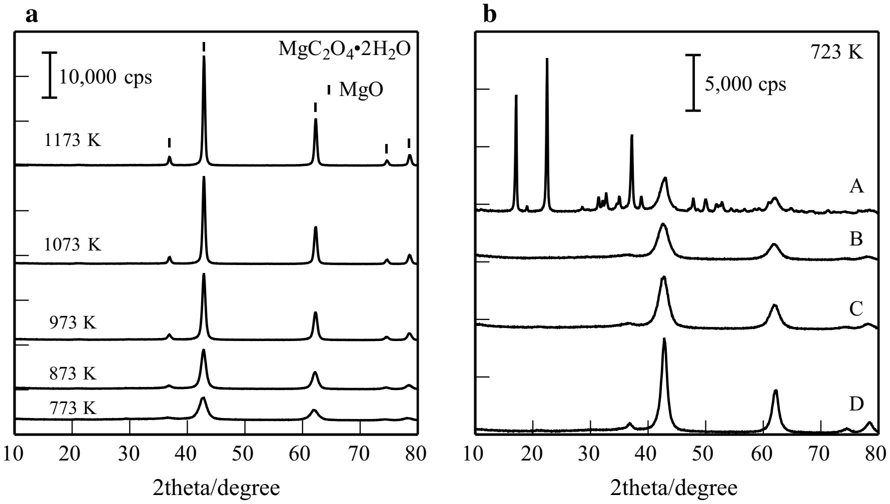


Fig. 4 Effects of heat treatment temperature and starting material on XRD profile of formed MgO. **a**: Effect of heat treatment temperature on XRD profile of MgO–O. **b**: Effect of starting material, A: MgO–O, B: MgO–S, C: MgO–W, D: MgO–H

part in basic carbonate was completed, and no carbonate decomposition occurred at 723 K. The carbonate decomposition took place at 786 K according to the TG–DTA results. It was expected that two samples obtained by heat treatment of basic carbonates at 723 K were composed of MgO and $MgCO_3$. However, no diffraction peak assigned to magnesium carbonate was observed in the measured XRD profiles of either sample. The carbonate part of the starting material would be highly dispersed in the formed MgO matrix.

The treatment temperature of 723 K was sufficiently high to complete $Mg(OH)_2$ decomposition. The hydroxide sample showed a diffraction peak in the MgO phase, as shown in Fig. 4b, D. The diffraction peaks of MgO in MgO–H sample became larger and narrower with further higher temperature treatment.

A relation was seen between heat treatment temperature and crystal size as calculated from an XRD peak width of (200) diffraction applying Scherrer's equation. As shown in Fig. 5, the crystal sizes of four kinds of MgO were similarly increased with increasing heat treatment temperature. No relation was seen in the changes of the crystal size of prepared MgO and the base catalytic activity shown in Fig. 3.

Surface area measurement

The relation between the surface area of prepared MgO and the base catalytic activity was studied. Adsorption isotherms of MgO samples treated at 773 K are illustrated in Fig. 6, and obtained surface area and pore volume are listed

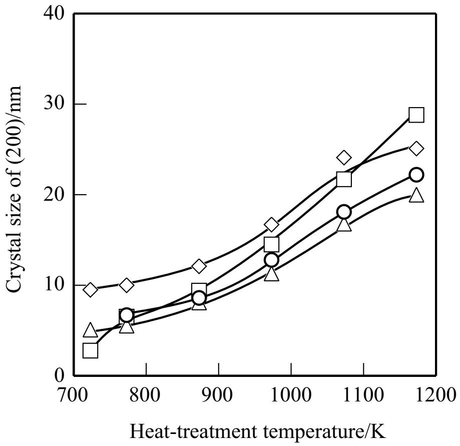


Fig. 5 Relation between heat treatment temperature and crystal size. Circle: MgO–O, square: MgO–W, triangle: MgO–S, diamond: MgO–H

in Table 1. The surface area of MgO–O prepared at 723 K was 304 m^2 g^{-1} and decreased with increasing treatment temperature. Finally, it was reduced to 46 m^2 g^{-1} at 1173 K. This result agreed well with the increasing crystal size shown in Fig. 5.

A hysteresis of adsorption–desorption isotherm was observed in prepared MgO samples as shown in Fig. 6. These results expected that an existence of mesopore in MgO samples. However, as for as concerned with the pore volume of a mesopore, the data of volume listed in Table 1 were much smaller. These results would mean that the capillary condensation in the space between MgO particles was measured as the hysteresis of adsorption–desorption isotherm.

The surface area and base catalytic activity on MgO–O sample activated at various temperatures are shown in Table 1. These of other MgO samples prepared by thermal treatment at 773 K were compared. The unit of catalytic activity was converted into those per surface area in this table.

The surface area-based activity of MgO–O activated at 773 K was about two or three times larger than those of the carbonate samples, MgO–S and MgO–W, and about five times larger than that of MgO–H (Fig. 3). The higher surface area-based activity would be the result of a large number of active sites on its surface. The difference in the base strength of active sites between MgO samples is not considered, because active sites constructed on MgO samples should have the same structure. The strong base sites, which are active in 1-butene isomerization under vacuum conditions, seemed to be poisoned by CO_2 and H_2O in air [2, 3]. It can therefore be concluded that MgO prepared from oxalate shows higher catalytic activity and has a large number of active sites on the surface.

Base strength measurement

The base strength of the samples was determined using Hammett indicators. Results are summarized in Table 2. A color change of 4-chloroaniline was observed on MgO–O, MgO–S, and MgO–H. No sample showed color changing of

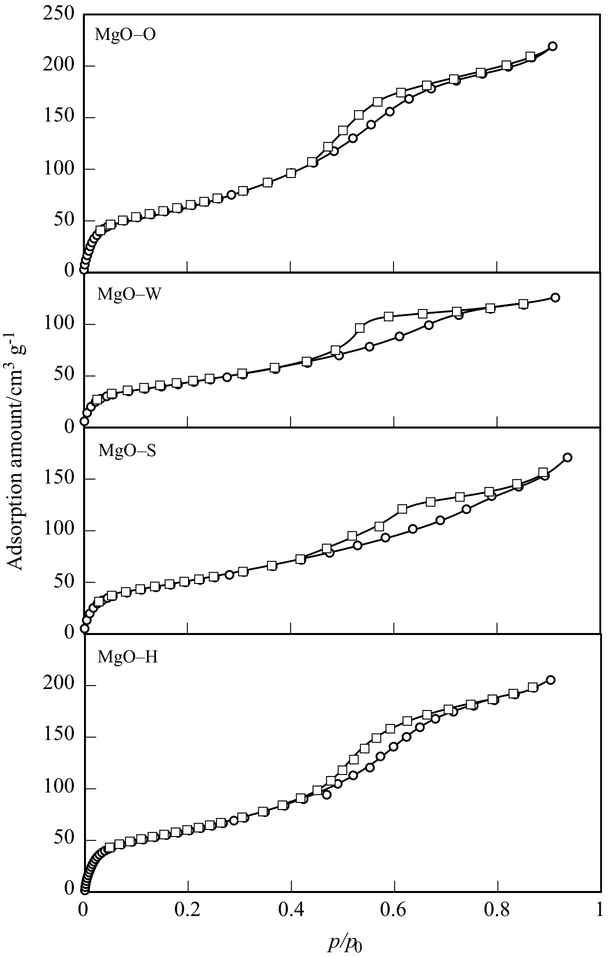


Fig. 6 Adsorption isotherms of MgO samples prepared by heating at 773 K for 3 h in air. Circle: Adsorption, square: desorption

diphenylmethane. Therefore, the base strength of MgO–O, MgO–S, and MgO–H was stronger than 26.5, and weaker than 35.0 in Hammett function scale. The base strength of MgO–W was determined to <26.5 in this method. It was expected that the base strength of MgO–W was close to 26.5, because of comparable catalytic activity of MgO–W shown in Fig. 3. The MgO samples used in this study were prepared and applied to a retro-aldol reaction under atmospheric conditions. As described above, the strong base sites seemed to be poisoned by CO_2 and H_2O in air. These molecules were adsorbed irreversibly on the strong base sites under the reaction conditions used in this study. The weak base sites, which can withdraw protons in the α-position of the carbonyl group, should be considered when applying a catalyst under atmospheric conditions. For this reason, a qualitative discussion on

Table 1 Surface area, pore volume, and catalytic activity of prepared MgO samples

Catalyst	Treatment temperature/K	Surface area/m^2 g^{-1}	Pore volume/ mL g^{-1}	Activity/ mmol m^{-2} h^{-1}
MgO–O	723	304	0.28	5.7
	773	235	0.20	10.0
	873	149	0.12	11.5
	973	83	0.07	17.7
	1073	47	0.03	22.3
	1173	46	0.04	22.7
MgO–H	773	218	0.16	2.1
MgO–W	773	158	0.14	6.7
MgO–S	773	185	0.16	3.5

Table 2 Base strength of MgO catalysts determined using Hammett indicators

Catalyst	4-Chloroaniline $H_{-}=26.5$	Diphenylmethane $H_{-}=35.0$	Cumene $H_{-}=37.0$
MgO–O	+	−	−
MgO–W	−	−	−
MgO–S	+	−	−
MgO–H	+	−	−

Catalysts were prepared by heating at 773 K for 3 h

(+): Color change was observed, (−): color change was not observed

the base strength of active sites would not be appropriate. Thus, it can be concluded that the surface area-based higher activity in MgO prepared from oxalate and heat-treated at 1073 K and 1173 K are attributable to the higher concentration of active sites.

Discussion

The retro-aldol reaction is catalyzed by acid and acid–base bifunctional catalysts as well as the base catalyst. The dehydration of diacetone alcohol into mesityl oxide takes place on acid sites. However, mesityl oxide was not detected in this study. The high selectivity of acetone indicates that the contribution of acid sites was negligible. The retro-aldol reaction is suitable for the comparison of base catalytic activity.

The order of activity based on weight in MgO catalysts activated at 773 K was as follows, MgO–O > MgO–S > MgO–W > MgO–H, as shown in Fig. 3. The active catalyst of MgO–O showed large surface area and higher activity. From the result of base strength measurement, the higher activity was attributed to the large number of active sites. The activity based on surface area was increased with increasing the treatment temperature. This was the highest in MgO–O treated at 1173 K. The activity based on surface area of MgO–O activated at 773 K was lower in comparison with those of higher temperature activated ones. The higher activity based on weight of MgO–O was caused by larger surface area.

In the differential thermal analysis shown in Fig. 1, it was clarified that the order of temperature in which active MgO was formed was oxalate > basic carbonate > hydroxide. The order of activation energy of decomposition was hydroxide > oxalate > basic carbonate. The activation energy is measured as a change in the reaction rate against the reaction temperature. A starting material having large activation energy of decomposition is converted into the product at once within a narrow temperature range in the temperature-increasing process accompanying a large amount of CO_2 and H_2O generation. The morphology of the obtained MgO is influenced by that of the starting material and annealing after the formation of MgO [10]. In addition, it can be expected that a large amount of desorption molecule generation during decomposition would provide a large surface area because of the formation of a desorption route of molecules from inside the bulk to outside [13, 19]. From this point of view, it can be said that starting material with a higher decomposition temperature and high activation energy of decomposition gives a higher surface area. These conditions were satisfied with magnesium oxalate. The annealing effect is small when starting material has a higher decomposition temperature. A short time heating in higher temperature also provides small annealing effect. High activation energy of decomposition means the reaction is completed in a short period in the temperature-increasing process. We have reported that MgO catalyst which has higher activity and larger surface area was obtained by the thermal decomposition and heating of $Mg(OH)_2$ for shorter time treatment [10]. In this case, rapid increase of treatment temperature provides generation of a large amount of desorption molecule in a short time. This experimental condition is coincident with that of sample preparation with lager surface area. Additionally, annealing effect was much smaller.

Magnesium hydroxide gives one H_2O molecule when it is decomposed. In basic carbonate, one H_2O or CO_2 molecule is evolved for one MgO molecule formation. Magnesium oxalate releases two CO_2 molecules for one MgO molecule formation. Among the studied samples, this starting material gave the most active MgO with the largest surface area. Basic carbonate showed a higher decomposition temperature, but the lowest activation energy of decomposition. The generation of H_2O by thermal decomposition takes place gradually. The formation of H_2O by degrees in the increasing temperature step of preparation would be a reason for the smaller surface area of MgO from basic carbonate.

Comparing the catalytic activity of catalysts heat-treated at 773 K, the surface areas were 235, 218, 185, and 158 $m^2 g^{-1}$ for MgO–O, MgO–H, MgO–S, and MgO–W, respectively, which differed from the order of the catalytic activity based on surface areas. In the MgO–H sample, the annealing effect by further heat treatment after decomposition on decreasing catalytic activity would be larger. An unstable MgO surface, including coordinative unsaturated surface ions formed by decomposition of the starting material in a lower temperature region, would be converted into a stable surface with low concentration active sites by further heat treatment. MgO–H sample showed a larger surface area because of a higher activation energy of decomposition, as shown in Fig. 2. However, catalytic activity was reduced by the annealing effect of thermal treatment.

In the thermal decomposition of oxalate, the reaction occurs at a higher temperature in a narrow temperature range, and a large amount of CO_2 molecules are generated. This is the reason to obtain a catalyst with higher activity and a larger surface area.

Conclusions

To obtain an active MgO under atmospheric conditions, $Mg(OH)_2$, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, and $MgC_2O_4 \cdot 2H_2O$ were used as starting material for thermal decomposition. Catalyst preparation and base-catalyzed reaction were performed under atmospheric conditions. The order of activity of prepared MgO for the retro-aldol reaction was MgO–O > MgO–S and –W > MgO–H. The highest activity was obtained by heating at 773 K in all starting materials and decreased gradually in a higher temperature range. The starting material, which was decomposed at a higher temperature and formed a larger amount of evolving gas molecules accompanying decomposition, tended to provide the MgO showing higher activity. No clear relation was observed between surface area or crystal size and catalytic activity. MgO prepared by thermal decomposition of oxalate at 1073 K and 1173 K had a higher concentration of active sites on the surface.

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