

Original Research

## Synthesis of a Solid Base Catalyst Formed from Zinc(II) Acetylacetonate and Consisting of MgO Modified with ZnO

Hiromi Matsuhashi \*

Department of Science, Hokkaido University of Education, 1-2 Hachiman-cho, Hakodate 040-8567, Japan; E-Mail: [matsuhashi.hiromi@h.hokkyodai.ac.jp](mailto:matsuhashi.hiromi@h.hokkyodai.ac.jp)

\* **Correspondence:** Hiromi Matsuhashi; E-Mail: [matsuhashi.hiromi@h.hokkyodai.ac.jp](mailto:matsuhashi.hiromi@h.hokkyodai.ac.jp)

**Academic Editors:** Michalis Konsolakis and George Marnellos

**Special Issue:** [Recent Advances on Metal Oxide \(Nano\)Catalysts](#)

*Catalysis Research*  
2022, volume 2, issue 2  
doi:10.21926/cr.2202015

**Received:** April 28, 2022  
**Accepted:** May 24, 2022  
**Published:** June 06, 2022

### Abstract

Solid base catalysts consisting of MgO modified with 10 mol% ZnO (ZnO/MgO) were prepared by depositing zinc(II) acetylacetonate ( $\text{Zn}(\text{acac})_2$ ) in polar and nonpolar organic solvents on the surface of MgO and  $\text{Mg}(\text{OH})_2$ . The process was followed by thermal decomposition in air at 773 K over a period of 3 h. The activity of MgO modified with  $\text{Zn}(\text{acac})_2$  for base-catalyzed retroaldol reaction (the decomposition of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) to acetone) at 299 K was higher than the activity of unmodified MgO prepared by thermal decomposition of  $\text{Mg}(\text{OH})_2$ . The activity of the catalysts prepared by depositing  $\text{Zn}(\text{acac})_2$  on  $\text{Mg}(\text{OH})_2$  was lower than that of unmodified MgO. Analysis of X-ray diffraction patterns revealed the presence of highly intense peaks, which were assigned to the ZnO units in the samples with high catalytic activity. ZnO was deposited in the form of large particles on the surface of MgO in the catalysts with high activity.

### Keywords

Magnesium oxide; zinc oxide; solid base; surface modification; retroaldol reaction



© 2022 by the author. This is an open access article distributed under the conditions of the [Creative Commons by Attribution License](#), which permits unrestricted use, distribution, and reproduction in any medium or format, provided the original work is correctly cited.

## 1. Introduction

Alkaline earth metal oxides are well-known solid bases. MgO, in particular, is a representative solid base catalyst [1-4]. Numerous reports that describe the structure of basic sites and the applications of many base-catalyzed reactions have been published over the years. Solid base catalysts have been used to conduct numerous C–C bond formation reactions, such as aldol reaction. These reactions are important for synthesizing fine compounds, and these bond-forming reactions are conducted to form large molecules.

Basic sites on the surface of MgO are poisoned by the H<sub>2</sub>O and CO<sub>2</sub> present in the atmosphere [1, 3]. Hence, the process of activation of alkaline earth metal oxides and base-catalyzed reactions are usually carried out under a vacuum or in an atmosphere of inert gas. This limits the application of these solid base catalysts in the field of organic synthesis. Thus, it is important to devise ways to prepare solid bases that can be used under normal atmospheric conditions.

Active MgO has been prepared by the thermal decomposition of hydroxide, carbonate, or oxalate species at high temperatures under a vacuum or in an atmosphere of inert gas. The most active MgO for base-catalyzed reactions was prepared by heat treatment at 973 K under vacuum. The carbonates of alkaline earth metals exhibit high thermal stability. The compounds are subjected to high-temperature treatment conditions (>773 K) to remove CO<sub>2</sub> from the active sites of the surface O<sup>2-</sup> groups.

Alkaline earth metal oxides are soluble in several polar solvents, such as methanol [5]. In many cases, oxide catalysts function as homogeneous catalysts. It is important to develop base catalysts that exhibit high tolerance against H<sub>2</sub>O and CO<sub>2</sub> and are insoluble in a polar solvent.

Previously, we have reported ways to cover the surface of a MgO-based base catalyst with various metal oxides to address the problems of poisoning by H<sub>2</sub>O and CO<sub>2</sub> and dissolution in a polar solvent. Aluminum isopropoxide dissolved in ethyl acetate was reacted with OH<sup>-</sup> groups in a double hydroxide layer of Mg(OH)<sub>2</sub>. The materials obtained were covered with a monolayer or bilayer of aluminum oxide. Among the base catalysts tested, MgO covered with ≥7 mol% of aluminum oxide exhibited excellent tolerance toward H<sub>2</sub>O and good reusability in the case of aldol reactions with acetone [6]. Base sites are expected to consist of O<sup>2-</sup> ions bonded to octahedral Al<sup>3+</sup> ions attached to the surface of MgO and/or Mg<sup>2+</sup> ions near the MgO surface [7].

Surface modification processes are conducted in organic solvents to deposit chemicals on the surface of metal oxides which are unstable in water. During various impregnation procedures, water is used as a solvent to dissolve chemicals to be deposited on a metal oxide surface. A mixture of Mg(OH)<sub>2</sub> and the dissolved material is finally deposited on the surface, and it has been observed that a small portion of MgO dissolves in water. Furthermore, MgO can be readily converted to hydroxide by soaking it in water (Section 2.1; catalyst preparation). Here, an organic solvent such as ethyl acetate is used for the surface modification of materials that are unstable in the presence of water.

Metal alkoxides are sensitive to moisture in the air. They easily decompose to the corresponding metal hydroxides and alcohols under conditions of hydration. Often, a portion of a commercial reagent decomposes into hydroxides or oxides. Therefore, it is important to identify a compound that can be used to substitute metal alkoxides to prepare an alkaline earth metal oxide-based catalyst covered with a metal oxide.

The structure of a metal acetylacetonate is similar to the structure of an alkoxide: it consists of a metal cation and an organic anion. A covalent bond is formed between the metal and the O atom, and this is similar to the case of a metal alkoxide. Unlike metal alkoxides, metal acetylacetonates are stable in moisture in the air. Furthermore, metal acetylacetonates dissolve in nonpolar organic solvents. Hence, metal acetylacetonates might be suitable reagents for the surface modification of MgO.

It is well known that the surface properties of ZnO are similar to those of MgO [8, 9]. Both oxides have been used as base catalysts and are used for the heterogeneous dissociation of H<sub>2</sub> into H<sup>+</sup> and H<sup>-</sup>. The formation of O–H and Mg–H following the process of H<sub>2</sub> dissociative adsorption has been observed using the infrared (IR) spectroscopy technique. Consequently, ZnO can be effectively used for covering the surface of MgO.

We used zinc(II) acetylacetonate (Zn(acac)<sub>2</sub>) to prepare MgO-based base catalysts modified with ZnO. Herein, we report the method of synthesis of ZnO-modified MgO, a solid base catalyst formed from Zn(acac)<sub>2</sub>, and the application of the catalyst in retroaldol reactions. The catalyst was characterized using various analytical techniques, thermogravimetry-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), and IR, and the results have been reported.

## 2. Materials and Method

### 2.1 Preparation of MgO Modified with ZnO

Mg(OH)<sub>2</sub> used to conduct the experiments was prepared by hydrating MgO (Merck). MgO was treated with warm distilled water (approximately 343 K) over a period of 1 h to afford Mg(OH)<sub>2</sub>, characterized by the presence of small crystals [10, 11].

The process followed for the preparation of MgO modified with ZnO has been presented herein. Zinc(II) acetylacetonate (Zn(acac)<sub>2</sub>, Merck) was dissolved in a suitable solvent. Mg(OH)<sub>2</sub> was dried at 373 K. An alternative way involved the thermal treatment of Mg(OH)<sub>2</sub> at 773 K in the air over a period of 3 h to afford MgO. MgO was added to the solution of Zn(acac)<sub>2</sub>. Ethyl acetate (AcOEt), acetone, ethanol, toluene, dioxane, or tetrahydrofuran (THF) was used as the solvent. The solution was stirred for 1 h at room temperature, following which the solvent was removed by evaporation under a vacuum. Subsequently, the sample was dried at 373 K in the air for 12 h. The product was then heated in the air at 773 K over 3 h. Samples were stored in glass ampoules for further use. The Zn content in Zn/(Zn+Mg) was fixed to 0.1 (10 mol%).

A ZnO supported on MgO sample was prepared following a conventional impregnation method using an aqueous solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Wako) and MgO (prepared by thermally treating Mg(OH)<sub>2</sub> at 773 K in the air for 3 h). The Zn content in the impregnated sample was the same as the Zn content in the modified catalysts.

ZnO was prepared, for comparison of activity, following a conventional preparation method. Hydrated ZnO was obtained by adding NH<sub>3</sub> (28%, Wako) to an aqueous solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (100 g in 3 L). The precipitate was washed 5 times with 1 L of distilled water, collected under conditions of suction, dried at 373 K, and heated at 773 K in the air over a period of 3 h.

## 2.2 Retroaldol Reaction

All catalysts were handled under atmospheric conditions. As a test reaction, a base-catalyzed retroaldol reaction (the decomposition of diacetone alcohol to acetone) was conducted in a batch reaction system to determine the base catalytic activity of the prepared catalysts. The reaction was carried out with 100 mg of the catalyst and 100 mmol of the diacetone alcohol at 299 K over a period of 3 h. The products were analyzed using the gas chromatography technique. Under the applied reaction conditions, the maximum conversion of diacetone alcohol was 88% [12].

On completion of the reaction, the presence of any eluted metal cations in the product mixture was checked by adding a few drops of Eriochrome Black T.

## 2.3 Catalyst Characterization

For sample characterization, the thermogravimetry-differential thermal analysis (TG-DTA; Rigaku TG8120 instrument) technique was used. The experiment was conducted prior to heat treatment of the sample to analyze the thermal reaction and analyze the process of combustion of the residual organic compounds on the surface of MgO at elevated temperatures. Powder X-ray diffraction (XRD) spectra of the prepared samples were recorded using CuK $\alpha$  radiation. IR spectra were recorded on a JASCO FT/IR-4000 Fourier Transform IR spectrophotometer. Samples were compressed into KBr discs.

## 3. Results and Discussion

### 3.1 Retroaldol Reaction

The retroaldol reaction was performed with the prepared catalysts (MgO modified with ZnO) under atmospheric conditions. The base catalytic activity of the catalysts was compared. MgO, ZnO, and ZnO supported on MgO were also considered for the reaction. The starting materials used and the reaction rate constants are summarized in Table 1. The decomposition of diacetone alcohol to form acetone is a reverse aldol reaction catalyzed by acids and bases. In the case of a reaction catalyzed by acid, the dehydration of diacetone alcohol yields mesityl oxide. We observed that a little amount of mesityl oxide was formed on the prepared catalysts in the present case. This indicated that the ZnO/MgO catalysts exhibited base catalytic activity. The acid sites generated following the modification of MgO with ZnO were not considered.

**Table 1** Retroaldol reaction with MgO catalysts modified with ZnO.

Entry	Starting Materials	Solvent	Activity/mol g <sup>-1</sup> h <sup>-1</sup>	Elution*
1	Zn(acac) <sub>2</sub> , MgO	AcOEt	0.73	-
2	Zn(acac) <sub>2</sub> , MgO	THF	0.72	-
3	Zn(acac) <sub>2</sub> , MgO	Toluene	0.73	-
4	Zn(acac) <sub>2</sub> , MgO	Dioxane	0.69	-
5	Zn(acac) <sub>2</sub> , MgO	Acetone	0.55	-
6	Zn(acac) <sub>2</sub> , MgO	Ethanol	0.57	+
7	Zn(acac) <sub>2</sub> , Mg(OH) <sub>2</sub>	AcOEt	0.65	-

8	Zn(acac) <sub>2</sub> , Mg(OH) <sub>2</sub>	THF	0.47	-
9	Zn(acac) <sub>2</sub> , Mg(OH) <sub>2</sub>	Toluene	0.37	-
10	Zn(acac) <sub>2</sub> , Mg(OH) <sub>2</sub>	Dioxane	0.33	-
11	Zn(acac) <sub>2</sub> , Mg(OH) <sub>2</sub>	Acetone	0.35	-
12	Zn(acac) <sub>2</sub> , Mg(OH) <sub>2</sub>	Ethanol	0.35	+
13	MgO	non	0.50	+
14	Zn(NO <sub>3</sub> ) <sub>2</sub> , MgO	Water	0.01	-
15	ZnO	non	0.006	-

\*Metal ion elution for diacetone alcohol after reaction (checked by adding Eriochrome Black T).

All catalysts used in the study exhibited catalytic activity. However, low activities were recorded for the ZnO catalyst prepared by adding NH<sub>3</sub> to the solution of Zn(NO<sub>3</sub>)<sub>2</sub> (Entry 15) and the ZnO/MgO catalyst (prepared following a conventional impregnation method in an aqueous solution (Entry 14)). The results indicated that pure ZnO was not an active component. It did not exhibit high activity for the retroaldol reaction. MgO and ZnO are expected to be well mixed in the ZnO/MgO sample (prepared following the impregnation method), as MgO is partially soluble in water. As Mg<sup>2+</sup> gets partially dissolved in water, Zn<sup>2+</sup> and Mg<sup>2+</sup> are impregnated simultaneously. The significantly low activity of this catalyst indicates that good mixing of MgO and ZnO results in a decrease in base catalytic activity.

Among all the ZnO/MgO catalysts, the ZnO/MgO catalyst prepared by the modification of MgO exhibited high activity for this reaction. The catalyst prepared by modifying MgO using AcOEt as the solvent in the preparation of ZnO/MgO (Entry 1) exhibited maximum activity. The activity was 46% higher than that of pure MgO (Entry 13). The results obtained using nonpolar solvents (AcOEt, THF, and toluene: Entries 1–3) were better than the results obtained using polar solvents (acetone and ethanol: Entries 5 and 6).

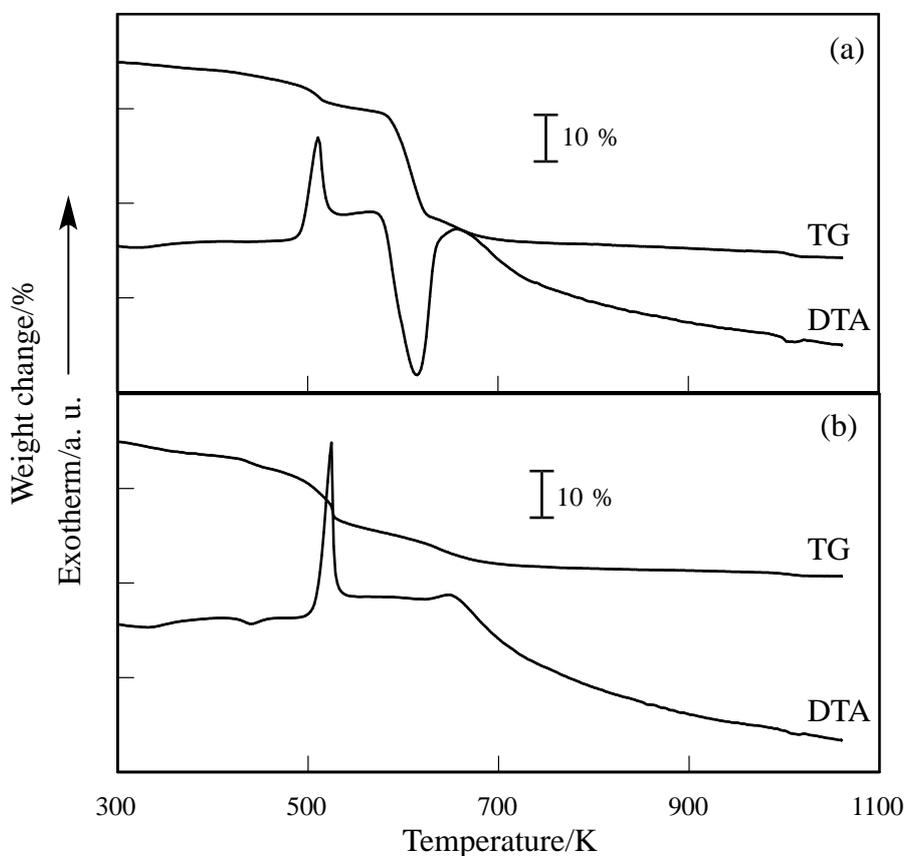
The activities of the ZnO/MgO catalysts prepared from Mg(OH)<sub>2</sub> (Entries 7–12) were lower than the activities of the catalysts prepared using MgO. The solvent effect was similar to that observed in the case of the MgO. AcOEt was found to be the most effective solvent (Entry 7). The activity of the catalysts prepared using other solvents (Entries 8–12) was lower than the activity of pure MgO.

A scrambling of cations takes place during the conversion process of hydroxide to oxide because the process of conversion is accompanied by the movement of cations. The level of mixing of MgO and ZnO seems to be higher in samples prepared from Mg(OH)<sub>2</sub> than the level of mixing observed in samples prepared using MgO. As a result of cation scrambling, greater mixing of ZnO with MgO on the MgO surface was achieved. Consequently, the ZnO/MgO catalysts prepared from Mg(OH)<sub>2</sub> exhibited lower activity for retroaldol reactions than the ZnO/MgO catalysts prepared by modifying MgO.

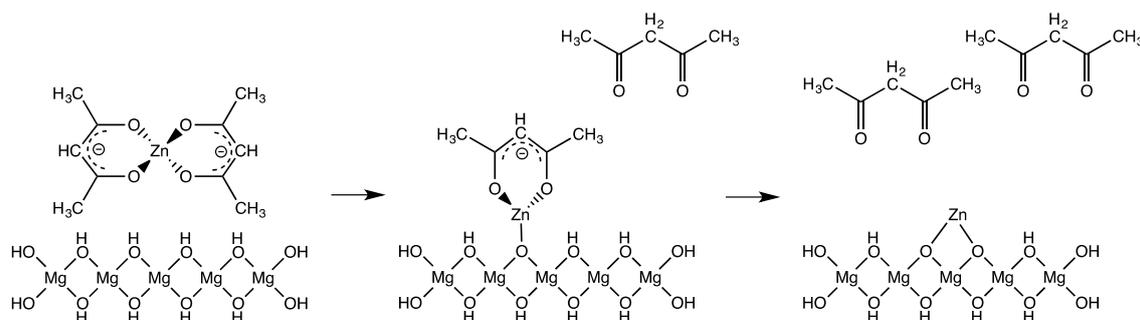
The elution of metal cations was checked by adding Eriochrome Black T after 3 h of reaction. The result is presented in Table 1. A color change in the liquid phase, caused by metal cation elution, was evident in samples of unmodified MgO (Entry 13) and ZnO/MgO prepared using ethanol as the solvent (Entries 6 and 12). ZnO did not dissolve in diacetone alcohol (Entry 15). The elution prevention effect was also observed in the ZnO/MgO system prepared following the conventional impregnation method (Entry 14). This effect of ZnO was evident in all samples tested in this study (exception: ZnO/MgO prepared using ethanol). The process of surface modification of MgO using ZnO helped in the generation of a system that could prevent dissolution in a polar solvent.

### 3.2 TG-DTA

Figure 1 presents the typical TG-DTA profiles of  $\text{Mg}(\text{OH})_2$  and  $\text{MgO}$  (treated with  $\text{Zn}(\text{acac})_2$ ; dissolved in THF). TG-DTA analysis was performed with samples treated with  $\text{Zn}(\text{acac})_2$  and dried at 373 K. A small decrease in the weight of the sample was detected at approximately 373 K. This could be attributed to the process of water desorption. This was observed for both the treated samples, and the results revealed that the samples were dried well during the process of preparation. In the profiles recorded for both the samples, a sharp exothermic peak was observed at 525 K. A significant decrease in weight was observed in this case, and this was attributed to the combustion of the residual organic species on the samples post drying. This intensity of the exothermic peak corresponding to the  $\text{MgO}$  sample was higher than the intensity of the exothermic peak corresponding to the  $\text{Mg}(\text{OH})_2$  sample. This indicated that the extent of decomposition of  $\text{Zn}(\text{acac})_2$  was more in the case of  $\text{Mg}(\text{OH})_2$  when THF was used as the solvent. It is likely that the hydroxyl groups on  $\text{Mg}(\text{OH})_2$  participated in the decomposition of  $\text{Zn}(\text{acac})_2$ . Conversion to free acetylacetonate would take place under these conditions, resulting in surface bonding. This results in the formation of  $\text{Mg-O-Zn}$ , as shown in Scheme 1. However, the presence of the large exothermic peak in the DTA profile indicated that the decomposition of  $\text{Zn}(\text{acac})_2$  was incomplete.



**Figure 1** TG-DTA profiles of  $\text{Mg}(\text{OH})_2$  and  $\text{MgO}$  treated with  $\text{Zn}(\text{acac})_2$  in THF. (a)  $\text{Mg}(\text{OH})_2$  and (b)  $\text{MgO}$ .



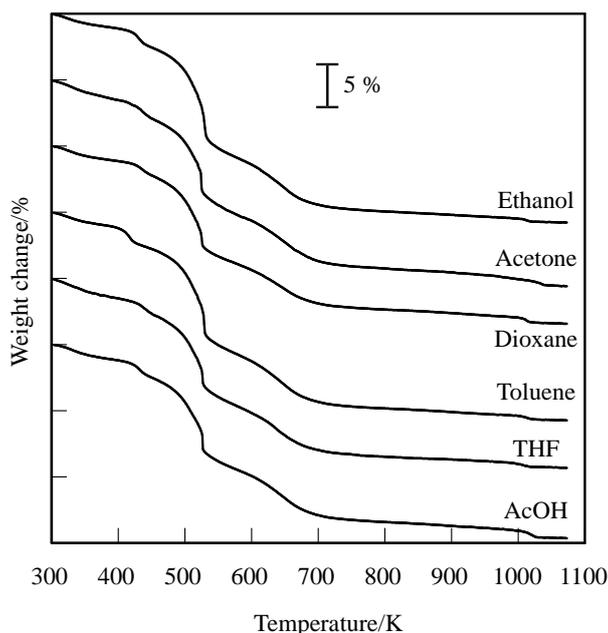
**Scheme 1** Possible reaction path for the reaction between  $\text{Zn}(\text{acac})_2$  and  $\text{Mg}(\text{OH})_2$ .

A large decrease in weight was observed at 650 K in the case of the treated  $\text{Mg}(\text{OH})_2$  sample. The decrease in weight could be attributed to the thermal decomposition of  $\text{Mg}(\text{OH})_2$  to  $\text{MgO}$ . This endothermic process was not observed in a  $\text{MgO}$ -treated sample. The decomposition of hydroxide was observed at approximately 650 K in pure  $\text{Mg}(\text{OH})_2$  [11]. The temperature at which the decrease in weight was observed for  $\text{Zn}(\text{acac})_2$ -treated  $\text{Mg}(\text{OH})_2$  was almost the same as the temperature at which a decrease in weight was observed for pure  $\text{Mg}(\text{OH})_2$ . The hydroxide decomposition temperature was low for the aluminum isopropoxide-treated  $\text{Mg}(\text{OH})_2$  sample [7]. The change in the decomposition temperature indicated a strong interaction between the hydroxide groups and the aluminum species. A constant hydroxide decomposition temperature indicated that the interaction between  $\text{Mg}(\text{OH})_2$  and Zn complex was significantly weak. It was hypothesized that a large portion of the  $\text{ZnO}$  present in the obtained catalysts would be present on the surface of  $\text{MgO}$ . It is believed that weak interactions are operative.

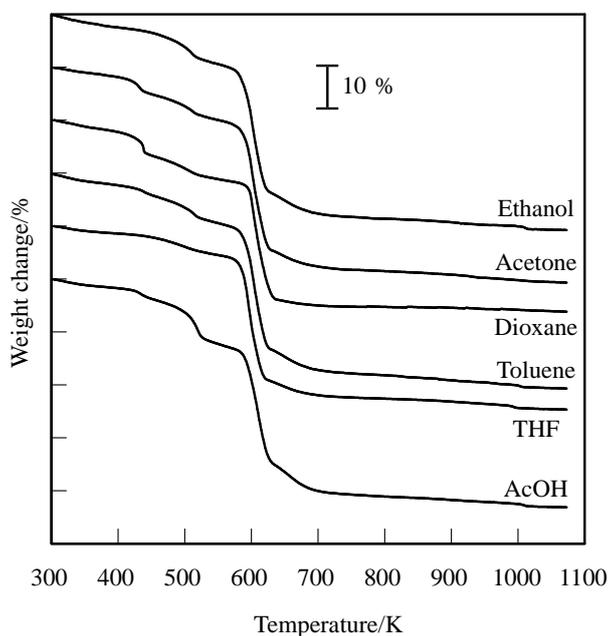
A continuous decrease in weight without an exothermal or endothermal reaction was observed in the temperature range of 530–560 K in the TG profile recorded for a  $\text{MgO}$  sample. A continuous weight decrease in this temperature range was observed for Mg carbonates [11]. Hence, it was suspected that  $\text{MgO}$  transformed to  $\text{MgCO}_3$  in the case of the  $\text{MgO}$  samples treated with  $\text{Zn}(\text{acac})_2$ . A portion of the  $\text{CO}_2$  formed during the combustion of organic species remaining on the  $\text{MgO}$  surface at 520 K was expected to be consumed for the formation of  $\text{MgCO}_3$ .

A small decrease in weight was observed following the weight decrease following hydroxide decomposition. The trend in the decrease in weight in the high-temperature region was similar to the trend observed during carbonate decomposition. The TG profile recorded for the treated  $\text{MgO}$  sample was analyzed to arrive at the results. A small part of  $\text{Mg}(\text{OH})_2$  was converted to  $\text{MgCO}_3$  following the combustion of organic species.

Figure 2 and Figure 3 present the TG profiles corresponding to  $\text{MgO}$  and  $\text{Mg}(\text{OH})_2$  treated with  $\text{Zn}(\text{acac})_2$  dissolved in other solvents. As shown in Figure 2, the TG profiles recorded for the treated  $\text{MgO}$  samples were very similar. The step decrease in weight was ascribed to the combustion of organic species, and the continuous decrease in weight was attributed to conversion of  $\text{MgCO}_3$  to  $\text{MgO}$  in the high-temperature range. These observations were made for all the  $\text{MgO}$  samples.



**Figure 2** TG profiles recorded for MgO samples treated with Zn(acac)<sub>2</sub> dissolved in various solvents.



**Figure 3** TG profiles recorded for Mg(OH)<sub>2</sub> samples treated with Zn(acac)<sub>2</sub> dissolved in various solvents.

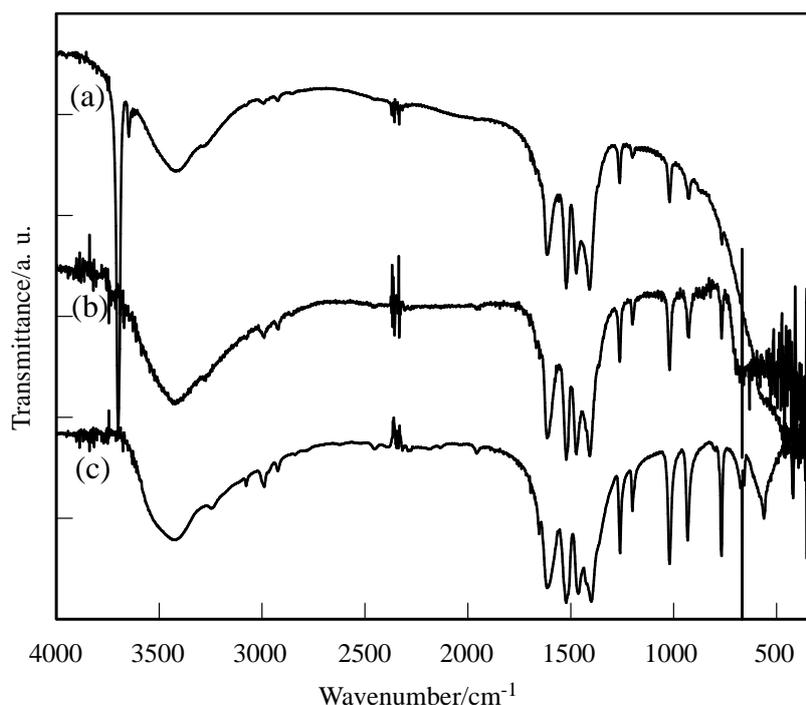
A solvent effect was observed in the TG profiles recorded for treated Mg(OH)<sub>2</sub> samples (Figure 3). A decrease in weight due to the combustion of organic species was observed in the lower temperature range. The large decrease in weight was caused by hydroxide decomposition. The weight also decreased due to the decomposition of carbonates. These observations were made for all the samples. The decrease in weight attributable to the process of carbonate decomposition was observed in the temperature range of 630–690 K. The maximum decrease in weight was observed

for the sample when AcOEt was used as the solvent as shown in Figure 3. The extent of decrease in weight observed in this case was significantly smaller than the extent of decrease in weight observed when dioxane was used as the solvent.

The results obtained using the TG-DTA technique revealed that a large portion of the  $\text{Zn}(\text{acac})_2$  content was deposited on the surface of MgO as a complex. A portion of  $\text{Zn}(\text{acac})_2$  was converted to acetylacetone and Zn species during the process of deposition on  $\text{Mg}(\text{OH})_2$ . A portion of  $\text{CO}_2$  produced during the combustion of organic species was used consumed for the formation of  $\text{MgCO}_3$ .

### 3.3 IR Analysis

Figure 4 presents the IR spectral profiles of  $\text{Mg}(\text{OH})_2$  and MgO samples treated with  $\text{Zn}(\text{acac})_2$  in ethanol. The samples were dried at 373 K. The spectra were recorded prior to heat treatment at 773 K. The spectrum of pure  $\text{Zn}(\text{acac})_2$  has been presented. The C–H stretching vibration was observed as small bands at approximately  $2900\text{ cm}^{-1}$ . A strong band at  $3700\text{ cm}^{-1}$  was observed in the profile recorded for the  $\text{Mg}(\text{OH})_2$  sample, and it was assigned to O–H stretching. IR bands appearing in the region below  $2000\text{ cm}^{-1}$  in the profiles of all the samples were similar in nature. This indicated that a large part of the Zn complex was not decomposed during the deposition process (as described in the previous section). The intensity of the peak corresponding to the  $\text{Mg}(\text{OH})_2$  sample was lower than the intensity of the peak corresponding to the MgO sample. A small amount of  $\text{Zn}(\text{acac})_2$  decomposed on the surface of  $\text{Mg}(\text{OH})_2$  during the treatment procedure in the liquid phase. The lower peak intensity of  $\text{Zn}(\text{acac})_2$  in the  $\text{Mg}(\text{OH})_2$  sample was coincident with the smaller exothermic peak intensity of this sample, as indicated by the DTA profiles.

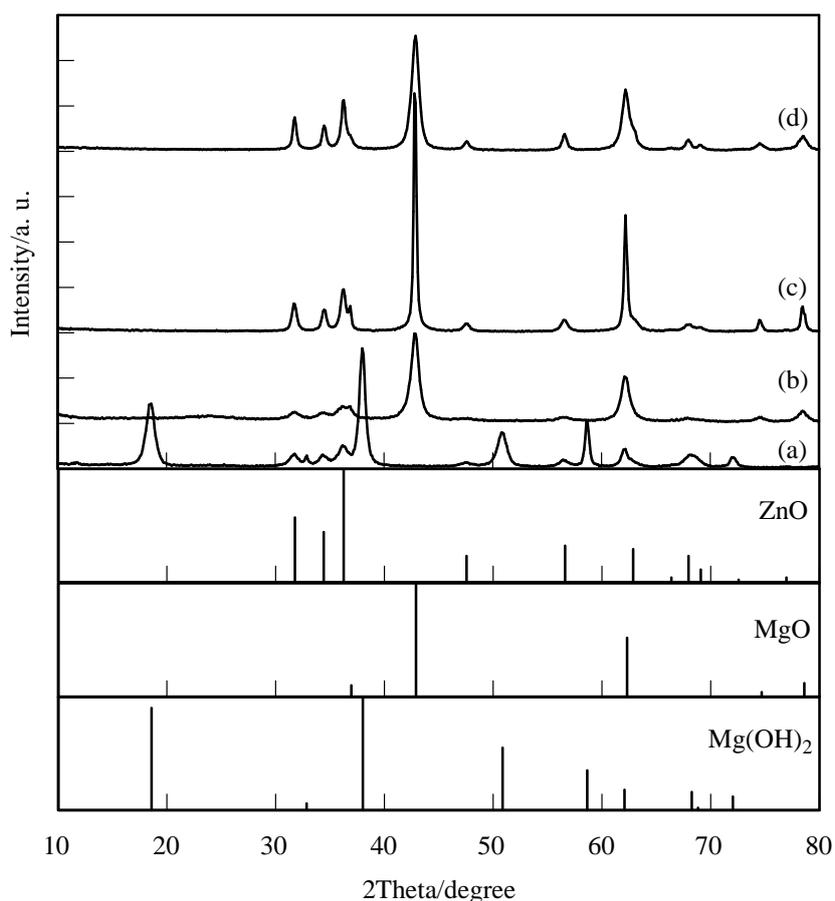


**Figure 4** IR spectral profiles recorded for  $\text{Mg}(\text{OH})_2$  and MgO samples treated with  $\text{Zn}(\text{acac})_2$  dissolved in ethanol. (a)  $\text{Mg}(\text{OH})_2$  treated with  $\text{Zn}(\text{acac})_2$ , (b) MgO treated with  $\text{Zn}(\text{acac})_2$ , and (c)  $\text{Zn}(\text{acac})_2$ .

All surface ligands of  $\text{Zn}(\text{acac})_2$  were decomposed during the heat treatment process at elevated temperatures during the process of catalyst activation. This was different from the case of aluminum tetraisopropoxide treatment, which has been reported previously [7]. In this case, aluminum isopropoxide decomposed completely during the deposition process in a liquid phase. The residual  $\text{Zn}(\text{acac})_2$  units on the dried samples impart stability to  $\text{Zn}(\text{acac})_2$ .

### 3.4 XRD Analysis

XRD patterns recorded for dried and heat-treated samples prepared using ethanol as the solvent for  $\text{Zn}(\text{acac})_2$  are shown in Figure 5. The observed peak sets were assigned to  $\text{Mg}(\text{OH})_2$  (Powder Diffraction File No. 7–239),  $\text{MgO}$  (4–829), and  $\text{ZnO}$  (36–1451). Peaks corresponding to  $\text{Zn}(\text{acac})_2$  were not observed in the profiles of any of the samples. The results obtained using the TG and IR spectroscopy techniques revealed the presence of  $\text{Zn}(\text{acac})_2$  in the dried sample. Analysis of the XRD patterns indicated that  $\text{Zn}(\text{acac})_2$  was highly dispersed on the surface of  $\text{MgO}$  and  $\text{Mg}(\text{OH})_2$ .



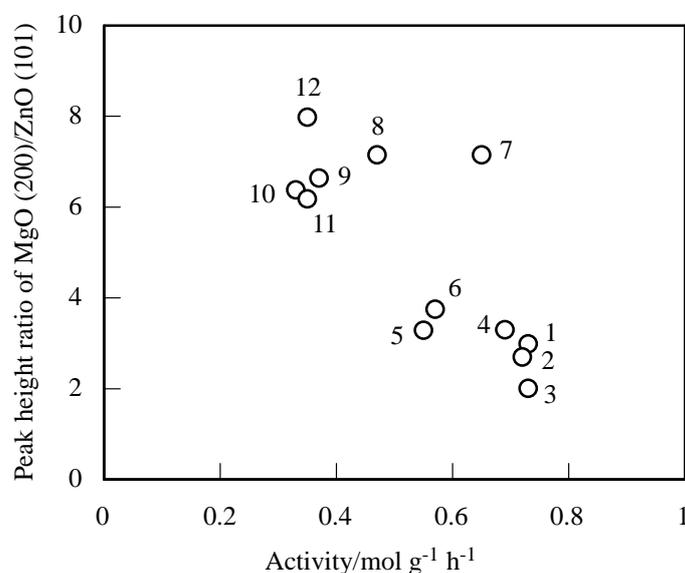
**Figure 5** XRD patterns recorded for dried and heat-treated  $\text{Mg}(\text{OH})_2$  and  $\text{MgO}$  samples treated with  $\text{Zn}(\text{acac})_2$ . (a)  $\text{Mg}(\text{OH})_2$  treated with  $\text{Zn}(\text{acac})_2$ , (b)  $\text{MgO}$  treated with  $\text{Zn}(\text{acac})_2$ , (c)  $\text{Mg}(\text{OH})_2$  treated with  $\text{Zn}(\text{acac})_2$  and heated at 773 K, and (d)  $\text{MgO}$  treated with  $\text{Zn}(\text{acac})_2$  and heated at 773 K.

Peak sets corresponding to  $\text{Mg}(\text{OH})_2$  and  $\text{ZnO}$  were observed in the profiles recorded for the  $\text{Mg}(\text{OH})_2$  sample treated with  $\text{Zn}(\text{acac})_2$  and dried at 373 K in air. The peaks assigned to  $\text{ZnO}$  were

also observed in the patterns recorded for the MgO sample. It was determined that a portion of  $\text{Zn}(\text{acac})_2$  was converted to ZnO prior to heat-treatment at 773 K. As mentioned in Section 3.3 (IR analysis), the presence of residual  $\text{Zn}(\text{acac})_2$  was detected in  $\text{Mg}(\text{OH})_2$  and MgO samples treated with  $\text{Zn}(\text{acac})_2$ . Results from DTA analysis revealed the existence of organic species on the surface of the catalysts. Analysis of XRD results revealed that a part of  $\text{Zn}(\text{acac})_2$  was converted to ZnO.

Profiles recorded for heat-treated samples revealed the presence of peaks corresponding to MgO and ZnO. The intensities of the diffraction peaks corresponding to MgO and ZnO were stronger than those of samples that were not subjected to heat-treatment conditions. In particular, the strongest diffraction peaks were recorded for the MgO sample prepared from  $\text{Mg}(\text{OH})_2$ . ZnO or  $\text{Zn}(\text{acac})_2$  can potentially exert a promotion effect on the growth of MgO crystals.

It was observed that peaks corresponding to ZnO appeared in the XRD patterns of all the samples, but the peaks corresponding to  $\text{Zn}(\text{acac})_2$  were not detected in the XRD patterns recorded for the samples. Similar observations were made for other samples prepared using different solvents. Large crystals give strong and narrow diffraction peaks. The peak height ratio of MgO/ZnO was an index of the crystallization degree of ZnO. The XRD peaks at  $d = 2.11$  ( $2\theta = 42.9^\circ$ ) (MgO ((200) facet)) and  $d = 2.48$  ( $2\theta = 38.0^\circ$ ) (ZnO ((101) facet)) were selected as the index of ZnO crystallization degree. The relation between catalytic activities and peak height ratio values is illustrated in Figure 6.



**Figure 6** Relationship between catalytic activity of ZnO/MgO and the XRD peak height ratio of MgO (200)/ZnO (101). (The numbers indicated in the figure are the same as the entry numbers shown in Table 1)

A high peak height ratio index indicates that highly crystallized MgO is modified with a large number of small ZnO particles. As shown in Figure 4, high peak intensities were observed for ZnO for catalysts that exhibited high activity. Low index values (<4) were recorded for these active catalysts (Entries 1–6). High peak height ratio indices (>6) were recorded for the ZnO/MgO catalysts prepared using  $\text{Mg}(\text{OH})_2$  (Entries 7–12). As is evident from Table 1, ZnO was not an active component. Good mixing of MgO with ZnO would result in a decrease in the catalytic activity.

The base sites on the surface of the alkaline earth metal oxides (such as MgO) are coordinative unsaturated surface O ions or a cluster of oxygen ions on the (111) micro surface [1–3]. The high

electron pair donating property of coordinative unsaturated  $O^{2-}$  on MgO is attributed to the low electronegativity of Mg. The electronegativity of Zn is higher than that of Mg. If some of the  $Mg^{2+}$  units coordinated to the active sites of the  $O^{2-}$  ions are replaced with  $Zn^{2+}$ , the base strength of the active sites will decrease.

The active sites for the retroaldol reaction of diacetone alcohol are situated on the uncovered MgO surface. Catalysts with a low index value were characterized by the presence of small MgO particles. These were modified with large particles or a thick layer of ZnO. As a result, a large part of the active MgO surface area gets exposed.

The catalytic activities of samples prepared using MgO and  $Mg(OH)_2$  (in AcOEt) were higher than the activities achieved with unmodified MgO. Analysis of the TG data revealed that a portion of the MgO units was converted to  $MgCO_3$  under conditions of  $CO_2$  evolution. This was achieved when the organic species remaining on the solid surface were combusted. A large amount of  $MgCO_3$  was formed in the case of the sample prepared using  $Mg(OH)_2$  and AcOEt, as shown in Figure 3. It has been previously reported that during the decomposition of the starting material, which had a high decomposition temperature, a larger number of evolving gas molecules were formed. The process proceeded provided a solid base with high activity under atmospheric conditions was used [11]. The characteristics of  $Mg(OH)_2$  and  $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$  were compared, and it was observed that the latter was a better starting material for MgO. The results indicated that the activity of MgO prepared from oxalate was higher than the activity of MgO prepared from hydroxide. MgO and  $Mg(OH)_2$  are converted into  $MgCO_3$  due to the production of  $CO_2$  during the burning of acetylacetone and related compounds during heat-treatment for activation. Finally, we obtained MgO that exhibited high activity. The high activity could be attributed to the thermal decomposition of  $MgCO_3$ .

#### 4. Conclusions

Solid base catalysts consisting of MgO modified with 10 mol% ZnO were prepared by depositing  $Zn(acac)_2$  (dissolved in polar and nonpolar organic solvents) on the surface of MgO and  $Mg(OH)_2$ . The process was followed by a 3-h long thermal decomposition process conducted in air at 773 K. Better results were achieved with nonpolar solvents such as AcOEt, THF, and toluene. The activity of the catalysts prepared by the deposition of  $Zn(acac)_2$  on  $Mg(OH)_2$  was lower than that of unmodified MgO. Surface modification of MgO by ZnO helped prevent dissolution in polar solvents.

TG-DTA results revealed that a large portion of the  $Zn(acac)_2$  system was deposited on the surface of MgO as an unchanged complex, while a small portion of  $Zn(acac)_2$  was converted to acetylacetone and ZnO during the deposition on  $Mg(OH)_2$ . The remaining  $Zn(acac)_2$  species were highly dispersed and remained unchanged. Strong peaks corresponding to ZnO were observed in the XRD patterns recorded for samples with high catalytic activity. The index values of the crystallization degree of ZnO and the peak height ratio (<4) of MgO/ZnO were recorded for these active catalysts. In highly active catalysts, ZnO was deposited in the form of large particles on the surface of MgO.

#### Acknowledgment

The author acknowledges Mr. Shin-nosuke Miura for his work related to this study.

## Author Contributions

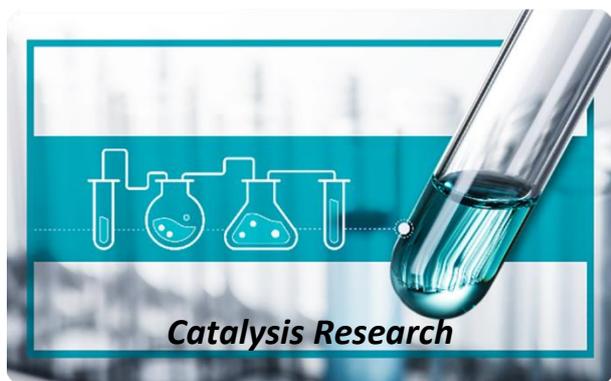
The author did all the research work of this study.

## Competing interests

The author declares that no competing interests exist.

## References

1. Corma A, Iborra S. Optimization of alkaline earth metal oxide and hydroxide catalysts for base-catalyzed reactions. *Adv Catal.* 2006; 49: 239-302.
2. Hattori H. Solid base catalysts: Generation of basic sites and application to organic synthesis. *Appl Catal A.* 2001; 222: 247-259.
3. Hattori H. Solid base catalysts: Generation, characterization, and catalytic behavior of basic sites. *J Jpn Petrol Inst.* 2004; 47: 67-81.
4. Busca G. Bases and basic materials in chemical and environmental processes. Liquid versus solid basicity. *Chem Rev.* 2010; 110: 2217-2249.
5. Zabeti M, Daud WMAW, Aroua MK. Activity of solid catalysts for biodiesel production: A review. *Fuel Process Technol.* 2009; 90: 770-777.
6. Matsushashi H. Synthesis of novel solid base of MgO covered with metal oxides. *Top Catal.* 2009; 52: 828-833.
7. Matsushashi H, Nagashima K, Naijo N, Aritani H. Surface base sites of MgO covered with Al<sub>2</sub>O<sub>3</sub>: XANES analysis of Al and Mg K-edges. *Top Catal.* 2010; 53: 659-663.
8. Eischens RP, Pliskin WA, Low MJD. The infrared spectrum of hydrogen chemisorbed on zinc oxide. *J Catal.* 1962; 1: 180-191.
9. Dent AL, Kokes RJ. Hydrogenation of ethylene by zinc oxide. I. Role of slow hydrogen chemisorption. *J Phys Chem.* 1969; 73: 3772-3780.
10. Kitagawa M, Misu S, Ichikawa J, Matsushashi H. Preparation of active MgO by short-time thermal decomposition of Mg(OH)<sub>2</sub>. *Res Chem Intermed.* 2015; 41: 9463-9473.
11. Kitagawa M, Ishida N, Yoshino E, Matsushashi H. Comparison of the base catalytic activity of MgO prepared by thermal decomposition of hydroxide, basic carbonate, and oxalate under atmospheric conditions. *Res Chem Intermed.* 2020; 46: 3703-3715.
12. Davis GL, Burrows GH. Equilibrium and free energy relationships in the system acetone-diacetone alcohol. *J Am Chem Soc.* 1936; 58: 311-312.



Enjoy *Catalysis Research* by:

1. [Submitting a manuscript](#)
2. [Joining in volunteer reviewer bank](#)
3. [Joining Editorial Board](#)
4. [Guest editing a special issue](#)

For more details, please visit:

<http://www.lidsen.com/journals/cr>