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Synthesis of a water tolerant solid base of CaO covered with Al_2O_3

Hiromi Matsuhashi*, Tetsuro Fujita

Department of Science, Hokkaido University of Education, Hakodate 040–8567, Japan

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ABSTRACT

Solid base catalysts composed of CaO covered with 5–20 mol% of Al_2O_3 were prepared by decomposition of $Al(OCH(CH_3)_2)_3$ over an $Ca(OH)_2$ surface in an ethyl acetate solution, followed by thermal decomposition in air at 773–1023 K. The catalysts containing Al^{3+} and treated at 773–973 K showed sufficient activity for a retro-aldol reaction to convert diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) into acetone at 299 K. The dissolution of the active component of CaO into a polar solvent was strongly inhibited by a covering of a small amount of Al_2O_3. The prepared catalysts showed excellent tolerance to H_2O contained in the substrate. The catalyst reusability was also examined.

1. Introduction

Alkaline earth metal oxides are well-known solid bases, and MgO in particular is a representative solid base catalyst [1–3]. Many papers have been published concerning the structure of base sites and the applications of many base-catalyzed reactions. The base sites on an MgO surface are poisoned by H_2O and CO_2 in the atmosphere [1,3]. Therefore, the decomposition of hydroxide or carbonate species, which are precursors of MgO, and the subsequent activation must be carried out under either high-vacuum conditions or in a high-purity inert atmosphere. The hydroxides and carbonates of alkaline earth metals have much greater thermal stability. Therefore, a high-temperature treatment above 773 K is required to remove these species from the active sites of the surface O^{2-} groups.

Deactivation caused by H_2O or CO_2 accompanies a change in the bulk structure from oxide to hydroxide or carbonate species, respectively. Elimination of these molecules at higher temperature is accompanied by an exchange of oxygen atoms between the surface and the molecules [4–7]. In addition, alkaline earth metal oxides dissolve in several polar solvents, such as H_2O. There are many cases where oxide catalysts act as homogeneous catalysts. Many studies have attempted to improve the base-catalytic activity of MgO by mixing it with, or supporting it on, aluminum oxide [8–13]. However, these studies did not pay attention to the dissolution of the catalyst in a polar solvent.

We covered the surface of an MgO base catalyst with SiO_2, Al_2O_3, TiO_2, and ZrO_2 to overcome the two disadvantages of poisoning by H_2O and CO_2 and dissolution in a polar solvent [14]. Among the base catalysts tested, MgO covered with >7 mol% Al^{3+} showed tolerance to H_2O and a sufficient reusability for the acetone–aldol reaction. The base strength of Al_2O_3/MgO containing 10 mol% of Al^{3+} ions is >26.5 in H_- scale. Data from Al *K*-edge XANES spectra indicate that octahedral Al^{3+} ions, which are present in the surface region, play a role as the principal active structure [15]. Base sites are expected to be constructed from O^{2-} ions bonded to octahedral Al^{3+} ions attached to the MgO surface and/or substituted for Mg^{2+} ions near the MgO surface.

The base strength of CaO is higher than that of MgO [3]. A solid base catalyst composed of CaO would have the same disadvantages as MgO. The solubility of CaO in water is higher than that of MgO. Thus, the preparation method used for Al_2O_3/MgO was applied to the synthesis of the Al_2O_3/CaO base catalyst. The prepared catalyst showed a higher activity toward the retro-aldol reaction of diacetone alcohol into acetone than Al_2O_3/MgO did. A high tolerance to water and reusability were observed, similar to Al_2O_3/MgO.

2. Experimental

2.1. Catalyst preparation

The calcium hydroxide used in this study was prepared as follows. Commercial $Ca(OH)_2$ (Wako Pure Chemical Industries, Japan) was placed in a beaker and boiled for 1 h in distilled water to obtain $Ca(OH)_2$ having similar properties to $Mg(OH)_2$ [14–16]. The $Ca(OH)_2$ obtained was dried at 373 K and comminuted to a powder with a particle size of a 32–50 mesh.

Catalysts covered with Al_2O_3 were prepared as follows. $Al(OCH(CH_3)_2)_3$ (Wako Pure Chemical Industries, Japan) was dissolved in ethyl acetate, and then $Ca(OH)_2$ was added to the solution, which was then stirred for 1 h. The solvent was then removed by evaporation and the sample was dried again at 373 K

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* Corresponding author. Tel.: +81 138 44 4325.
E-mail address: matsuhas@hak.hokkyodai.ac.jp (H. Matsuhashi).

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for 12 h. The sample treated with alkoxide was calcined in air at 773–1073 K for 3 h. The ratio of Al^{3+} ions to Ca^{2+} ions, calculated as $Al^{3+}/(Al^{3+}+Ca^{2+}) \times 100$, was in the range 5–20 mol%. The samples were denoted as Al_2O_3/CaO-*n*, where n = the Al^{3+} ion content in mol%. The calcined catalysts were kept in a glass ampoule until use.

2.2. *Retro-aldol reaction of diacetone alcohol*

The base-catalyzed decomposition reaction of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) into acetone, the retro-aldol reaction, was performed in a batch reaction system. The reaction was carried out at 299 K for 3 h using 0.2 g of catalyst and 100 mmol of diacetone alcohol. The diacetone alcohol was used as received. The main product was acetone, and a very small amount of mesityl oxide formed by dehydration was detected. The products were analyzed by GLC. The retro-aldol reaction of diacetone alcohol was also carried out with 5 wt% of H_2O to confirm the tolerance against H_2O. The catalyst used for the reaction with water was washed with acetone, and then applied to another reaction.

2.3. *Catalyst characterization*

Thermogravimetry–differential thermal analysis (TG–DTA, Rigaku TG 8120, Japan) was performed on the sample before calcination to determine the decomposition temperature of $Ca(OH)_2$ and to detect the remaining organic compounds. Powder X-ray diffraction spectra of unmodified and modified samples were measured using Cu Kα radiation.

The base strength was measured from the change in color method using Hammett indicators, and was carried out using a literature procedure [15]. The catalyst that had been thermally activated and stored in a glass ampoule was placed in dried cyclohexane containing 0.2% of the indicator.

2.4. *Detection of dissolved Ca^{2+}*

Dissolution of Ca^{2+} in diacetone alcohol was confirmed by use of the chelating agent Eriochrome Black T. After reaction for 3 h, part of the liquid phase was withdrawn with a pipette and a few drops of Eriochrome Black T solution (Wako Pure Chemical Industries, Japan) was added to the separated diacetone alcohol solution. The color of the solution changed from blue to orange when Ca^{2+} was dissolved in diacetone alcohol.

3. Results and discussion

3.1. *Differential thermal analysis*

TG–DTA was performed on samples before calcination to determine the decomposition temperature of $Ca(OH)_2$ and to detect any remaining organic compounds. The results of the DTA measurements are shown in Fig. 1. The decomposition temperature of $Ca(OH)_2$ into CaO was observed around 710 K in an unmodified $Ca(OH)_2$ sample. The endothermic peak and weight loss observed at around 940 K was attributed to the decomposition of calcium carbonate. There was no exothermic peak observed from the combustion of an organic species. This indicates that the conversion of $Al(OCH(CH_3)_2)_3$ into oxide or hydroxide was complete before the heat treatment used to decompose $Ca(OH)_2$ and its activation.

Calcium hydroxide has the brucite structure, the surface consisting of a basic hydroxide layer. Aluminum isopropoxide is a strong Lewis acid. Neutralization of $Al(OCH(CH_3)_2)_3$ with OH^- would take place on the surface. The exchange of $(CH_3)_2CHO^-$ with OH^- and condensation of the aluminum compound with surface OH groups to form Ca–O–Al bonds are also expected.

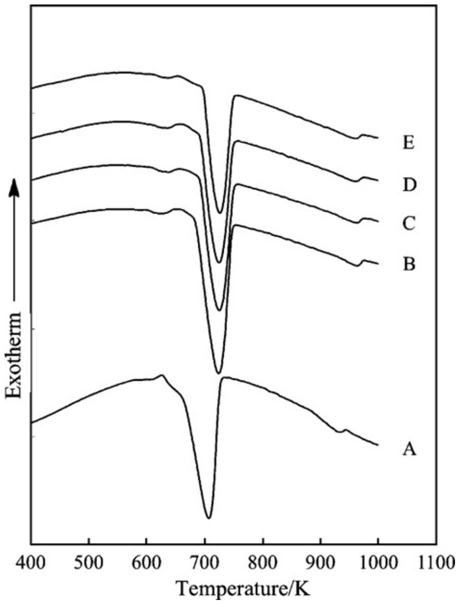

Fig. 1. DTA profiles of the prepared catalysts before calcination. (A) $Ca(OH)_2$, (B) Al_2O_3/CaO-5, (C) Al_2O_3/CaO-10, (D) Al_2O_3/CaO-15, and (E) Al_2O_3/CaO-20.

The endothermic hydroxide decomposition was moved slightly toward higher temperatures on modification with 5 mol% of Al_2O_3. The decomposition of $Ca(OH)_2$ was inhibited by the aluminum oxide and/or hydroxide formed on the $Ca(OH)_2$ surface. This means that there is a strong interaction between the $Ca(OH)_2$ and Al compounds.

3.2. *XRD analysis*

The XRD profiles of Al_2O_3/CaO-10 calcined at 773 K and Al_2O_3/CaO-20 calcined at 973 K are shown in Fig. 2. The set of strong diffraction peaks were assigned to CaO. Small peaks from $CaCO_3$ were also observed in the XRD profile of Al_2O_3/CaO-10. This result corresponds to that obtained from the TG–DTA measurements. The endothermic peak at higher temperature was ascribed to decomposition of the carbonate. Diffraction peaks attributable to a compound containing both Ca and Al, such as $Ca(AlO_2)_2$, were not observed. It is suspected that Al exists on the surface of the CaO as an Al_2O_3 monolayer. We showed that a high fraction of the Al^{3+} ions are in octahedral sites in the case of an Al_2O_3/MgO sample [15].

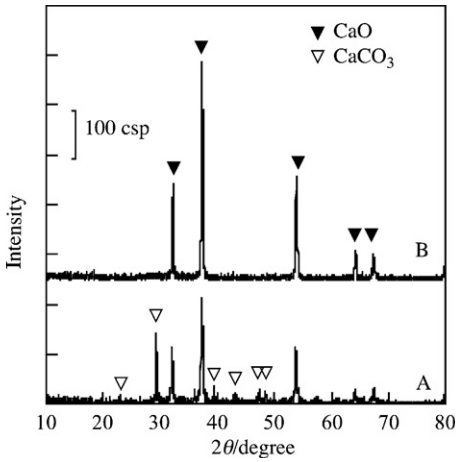

Fig. 2. XRD profiles of: (A) Al_2O_3/CaO-10 calcined at 773 K and (B) Al_2O_3/CaO-20 calcined at 973 K.

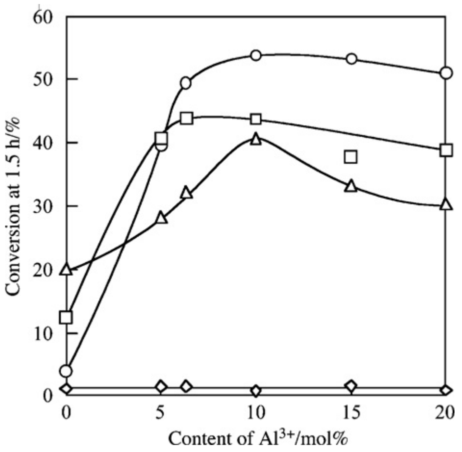

Fig. 3. The change in activity for the retro-aldol reaction of diacetone alcohol versus Al^{3+} ion content in Al_2O_3/CaO activated at various temperatures. ○: 773 K, □: 873 K, △: 973 K, ◇: 1073 K.

The Mg^{2+} ions must be substituted by Al^{3+} ions, or the structure of the aluminum oxide would be strongly affected by the MgO with a rock salt structure. A similar situation is expected to occur in the Al_2O_3/CaO samples.

3.3. Retro-aldol reaction of diacetone alcohol

The retro-aldol reaction of diacetone alcohol into acetone was performed to determine the effect of the Al content and calcination temperature on the base-catalyzed decomposition activity of the prepared catalysts. The aldol reaction is catalyzed by acid, base, and acid–base pair sites. The base catalyst showed a higher efficiency than the acid catalyst did for the aldol reaction. Diacetone alcohol is converted into mesityl oxide by dehydration on acid sites or acid–base pair sites [17]. In our experiments, the product obtained from the retro-aldol reaction of diacetone alcohol was acetone, with a negligible amount of dehydrated product of mesityl oxide.

Fig. 3 shows the change in the diacetone alcohol conversion activity versus the content of Al^{3+} ions in Al_2O_3/CaO activated at various temperatures. The conversions at 1.5 h are indicated. The pure CaO catalysts showed a lower activity than the CaO covered with Al_2O_3 for all heat-treatment temperatures. The solid CaO was transformed into a suspension in the diacetone alcohol during the reaction. Part of the CaO was dissolved in the diacetone alcohol, and this could have acted as a homogeneous catalyst. Dissolved Ca^{2+} in diacetone alcohol was detected by the formation of an orange chelate compound with Eriochrome Black T. The solubility of CaO was strongly inhibited by covering it with a small amount of Al_2O_3. The Al_2O_3/CaO-5 sample gave a clear solution. The color change of Eriochrome Black T was not observed with this sample.

Covering CaO with Al_2O_3 had a much stronger effect on the retro-aldol reaction of diacetone alcohol. The most active catalyst was obtained by covering the CaO with 10 mol% of Al^{3+} ions and heat treatment at 773 K (Fig. 3). The catalytic activity gradually decreased with increasing heat-treatment temperature. Catalysts treated at 973 K exhibited an activity that was about half that observed for catalysts treated at 773 K. A high heat-treatment temperature led to serious damage to the catalysts. The activity of the catalyst almost disappeared after heat treatment at 1073 K. The reduction of catalytic activity with increasing heat-treatment temperature was expected to be due to the increase in Al_2O_3 layers. We reported that MgO covered with Al_2O_3 showed relatively higher activity for the aldol reaction when the number of layers of Al_2O_3 was in the range 1.0–1.4 [15]. This indicates that a monolayer covering by Al_2O_3 is suitable to obtain the active catalyst. The surface area of CaO would be decreased by heat treatment at higher temperature. It is expected that the layers of Al_2O_3 on the surface are increased with decrease of CaO surface area.

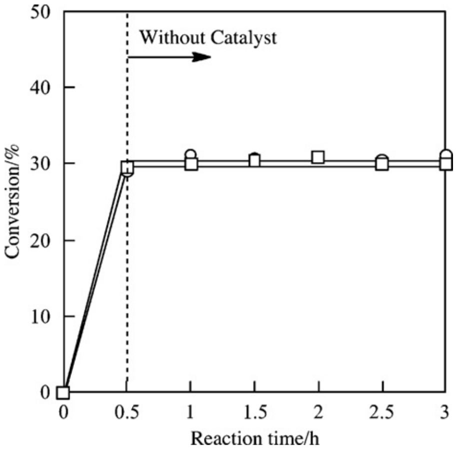

Fig. 4. The conversion of diacetone alcohol without a catalyst. ○: Al_2O_3/CaO-5, □: Al_2O_3/CaO-10.

The liquid phase was separated by decantation after being reacted for a period of 0.5 h, and was kept under the same reaction conditions without a catalyst to check for leaching of any active components. As shown in Fig. 4, the conversion of diacetone alcohol did not change after catalyst separation in the catalysts tested. This result indicates that the retro-aldol reaction of diacetone alcohol only took place on the surface of the catalyst.

The activity of Al_2O_3/CaO-10 for the above reaction was compared with that of Al_2O_3/MgO-10, which was the most active base catalyst for MgO covered with Al_2O_3. The activity of the covered CaO catalysts was higher than that of Al_2O_3/MgO-10, and the activity of Al_2O_3/CaO-10 was almost twice that of Al_2O_3/MgO-10, as shown in Fig. 5. This is a reflection of the stronger basicity of CaO than MgO. The effect of covering by Al_2O_3 on the surface basicity was small. The surface basicity of the covered catalyst is related to that of the base alkaline earth metal oxide. The base strength of Al_2O_3/CaO containing 10 mol% of Al^{3+} ions was >26.5 in H_- scale.

The reusability of Al_2O_3/CaO-10 was then examined. After the first reaction, the liquid phase was separated by decantation, and the catalyst was washed with diacetone alcohol. Then, the next reaction was performed using the same procedures as for the first reaction. The results are shown in Fig. 6. A small decrease in the catalytic activity was observed with increasing number of reuse

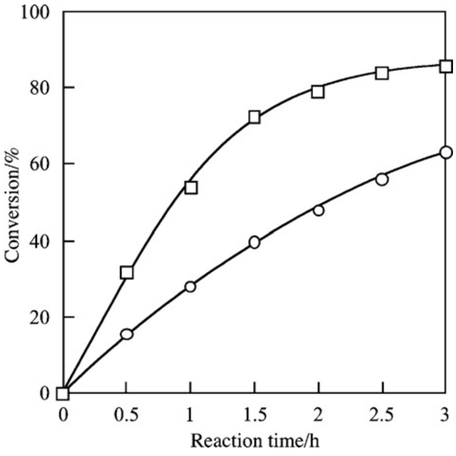

Fig. 5. A comparison of the activity of covered CaO catalyst (Al_2O_3/CaO-10 (□)) with that of Al_2O_3/MgO-10 (○).

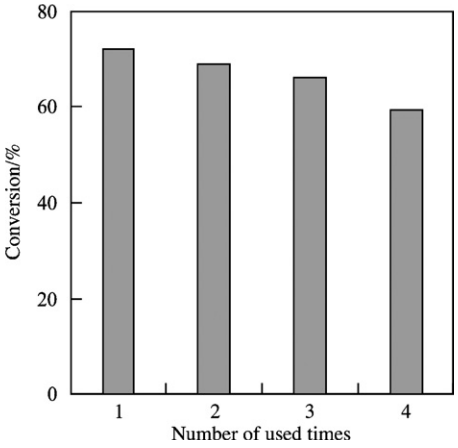

Fig. 6. Reuse of Al_2O_3/CaO-10 for the retro-aldol reaction of diacetone alcohol.

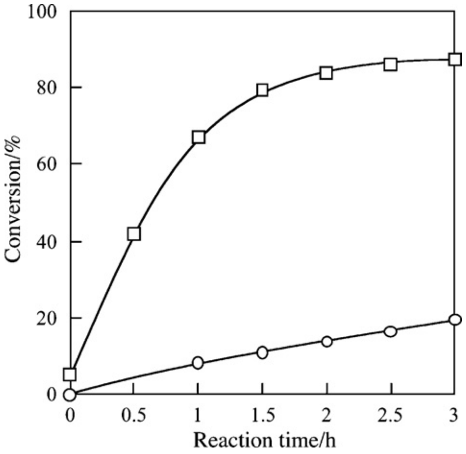

Fig. 7. Effect of water addition on the activity of Al_2O_3/CaO-10 for the retro-aldol reaction. ○: 5 wt% water addition to diacetone alcohol, □: after washing with acetone.

times. The decrease in activity was in the acceptable range. Thus, it was concluded that the reusability of CaO covered with Al_2O_3 was acceptable.

The tolerance of Al_2O_3/CaO-10 toward H_2O was examined by adding H_2O to the diacetone alcohol. The results are shown in Fig. 7. The first reaction was performed with diacetone alcohol containing 5 wt% H_2O. After reacting for a period of 3 h, the liquid phase was separated by decanting, and the catalyst was washed with acetone. The second reaction was carried out with diacetone alcohol under the same reaction conditions as the first reaction. The activity of Al_2O_3/CaO-10 toward the reaction was reduced by the addition of H_2O, as shown in Fig. 7. This is understood in terms of the stronger adsorption of H_2O molecules than of diacetone alcohol molecules because of the strong polarization of H_2O. The activity of the catalysts was recovered completely by washing them with acetone. The degree of conversion in the second reaction on Al_2O_3/CaO-10 was almost the same as that using a fresh catalyst. Thus, it was confirmed that CaO covered with Al_2O_3 has sufficient stability against H_2O.

4. Conclusions

Solid base catalysts of CaO covered with 5–20 mol% of Al_2O_3 were prepared by the decomposition of $Al(OCH(CH_3)_2)_3$ over a $Ca(OH)_2$ surface in an ethyl acetate solution, followed by thermal decomposition in air at 773–1023 K. Catalysts containing 5–20 mol% of Al^{3+} ions treated at 773–973 K showed sufficient activity for the retro-aldol reaction of diacetone alcohol at 299 K. The most active catalyst was obtained for a covering with 10 mol% of Al^{3+} ions and heat treated at 773 K. The dissolution of the active component of CaO into a polar solvent was strongly inhibited by the covering containing a small amount of Al_2O_3. The prepared catalysts showed excellent tolerance towards H_2O and reusability.

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