1. Introduction

Barium oxide has the highest base strength among alkaline earth metal oxides because Ba has the lowest electronegativity in this group. The base strength increases in the order MgO < CaO < SrO < BaO. Barium oxide catalysts are applicable to many base-catalyzed reactions such as aldol condensation, alkene isomerization, benzaldehyde reduction, transesterification, and the Tishchenko reaction. However, few studies have examined the preparation and application of BaO as a base catalyst, partly because of the difficulties in the preparation of BaO.

In general, alkaline earth metal oxides are obtained by thermal decomposition of the corresponding hydroxide or carbonate at elevated temperatures. For example, Mg(OH)₂ is converted into MgO by thermal decomposition around 650 K and MgCO₃ is converted around 820 K. However, thermal decomposition of BaCO₃ to BaO requires very high temperatures, higher than 1249 K, because of the high thermal stability of BaCO₃.

Barium hydroxide is obtained as a solid containing water of crystallization, Ba(OH)₂·8H₂O. Some of the water molecules can be removed from the crystal bulk by heating at 373 K. However, Ba(OH)₂·8H₂O is decomposed to BaO at 823 K and Ba(OH)₂ at 1273 K. Consequently, the conventional preparation method of thermal decomposition of BaCO₃ and Ba(OH)₂ cannot obtain an appropriate sample of BaO for use as a solid base catalyst. To overcome the problem, Ba(OH)₂·8H₂O can be decomposed into BaO and water by heating at 373 K, the water molecules can be removed from the crystalline structure of BaO,

Solid base BaO–Al₂O₃ catalyst was synthesized using the solid-liquid interface reaction of Ba(OH)₂·8H₂O in the solid phase with Al(OCH(CH₃)₂)₃ dissolved in ethyl acetate. Water of crystallization in the barium hydroxide, Ba(OH)₂·8H₂O was consumed by hydrolysis of Al(OCH(CH₃)₂)₃ into Al₂O₃ and isopropanols. BaO–Al₂O₃ catalyst synthesized by solid-liquid interface reaction of Ba(OH)₂·8H₂O with equal mols of Al(OCH(CH₃)₂)₃ and heat-treated at 673 K showed the highest activity among the prepared catalysts for the retro-aldol reaction of diacetone alcohol. Active BaO–Al₂O₃ catalysts with various contents of BaO were obtained by heating at appropriate temperatures just below those of Ba₅Al₂O₈ and BaAl₂O₄ crystallization. X-ray diffraction analysis detected no BaO phase in this solid base catalyst. Barium oxide highly dispersed in amorphous Al₂O₃ was prepared by the solid-liquid interface reaction. The interface reaction of metal hydroxide in the solid phase with alkoxide in the liquid phase is useful to form well-dispersed mixed metal oxides.

Keywords
Barium oxide, Solid base, Solid-liquid interface, Retro-aldol reaction
water molecules located around the metal hydroxide molecules are consumed by hydrolysis of metal alkoxide. The metal hydroxide molecules separated from the metal hydroxide crystal cannot be dissolved in a nonpolar organic solvent, form a precipitate. Another metal hydroxide formed by hydrolysis of the metal alkoxide is also obtained as a precipitate. Therefore, well-mixed precipitates of hydroxides would be formed.

By separating metal hydroxide molecules from the solid surface, a layer containing metal hydroxide is released from the surface and a new hydrated metal hydroxide surface appears, and further hydrolysis of the metal alkoxide by water molecules in the crystal will continue to take place. The solid-liquid interface reaction of hydrated metal oxide and metal alkoxide would provide a well-mixed hydroxide precipitate containing both metal hydroxides.

We previously reported that an appropriate metal alkoxide dissolved in ethyl acetate reacted with hydroxide groups in a double hydroxide layer of Mg(OH)2 and Ca(OH)2. We succeeded in covering the surface of MgO and CaO with a monolayer or bilayer of Al2O3, SiO2, or TiO2. The hydroxyl groups in the alkali earth metal oxide and metal hydroxide formed from the alkoxide by hydrolysis were also decomposed by reaction with excess metal alkoxide. As a result of these reactions, a M·O·M’ (M = Mg, Ca; M’ = Al, Si, Ti) bridging bond was formed. These results lead us to believe that the solid-liquid interface reaction of Ba(OH)2·nH2O with Al(OCH(CH3)2)3 would result in a well-mixed hydroxide precipitate.

2. Experimental

2.1. Catalyst Preparation
Barium hydroxide octahydrate (Ba(OH)2·8H2O; Wako Pure Chemical Industries, Ltd.) was placed in a desiccator, and dried in a vacuum at room temperature for 3 h to eliminate some of the water molecules in the crystal. Treatment of dried Ba(OH)2·nH2O with Al(OCH(CH3)2)3 was performed as follows. The desired amount of Al(OCH(CH3)2)3 (Wako Pure Chemical Industries, Ltd.) was dissolved in an appropriate amount of ethyl acetate in a round-bottom flask and Ba(OH)2·nH2O was added to the solution. After stirring for 2.5 h at room temperature, the ethyl acetate was removed by evaporation in a rotary evaporator to obtain BaO·Al2O3 precursor as a precipitate. The obtained precipitate was dried at 373 K for 12 h and heat-treated at 573-1073 K for 1 h for activation of the catalysts. Heat-treated catalysts were kept in a sealed ampoule until use. All treatments for catalyst preparation were performed under atmospheric conditions. The Ba2+ concentrations of the examined samples were 75, 60, 50, 40, and 33 mol% of Ba2+ based on the total mol of Ba2+ and Al3+. The prepared samples are denoted as BaX, where X is the mol% of Ba2+ in the sample. The mol ratios of Ba2+:Al3+ were 3 : 1, 3 : 2, 1 : 1, 2 : 3, and 1 : 2 for 75, 60, 50, 40, and 33 mol% samples, respectively. In addition to the mixed samples, Ba(OH)2 samples obtained by drying of Ba(OH)2·8H2O at 473 K and 573 K in air were also prepared for comparison of catalytic activity.

2.2. Catalyst Characterization
Thermogravimetry and differential thermal analysis (TG-DTA; TG 8120; Rigaku Corp., Japan) were performed on the prepared samples under nitrogen before heat-treatment to observe the thermal decomposition profiles. For the thermal analysis of pure barium hydroxide, an equal weight of silica was mixed to avoid damage to the sample pan in TG-DTA apparatus by melting hydroxide. Powder X-ray diffraction (XRD) spectra of heat-treated samples were measured using Cu-Kα radiation. The size of the crystal particles was determined using Scherrer’s equation applied to (202) diffraction peak of BaAl2O4. Specific surface area was calculated by the BET method using N2 adsorption.

2.3. Retro-aldol Reaction of Diacetone Alcohol
The base-catalyzed decomposition reaction of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) to form acetone, the retro-aldol reaction, was performed in a batch-reaction system (Scheme 1). The reaction was carried out at 299 K for 3 h using 90 mg of catalyst and 100 mmol of diacetone alcohol in a round-bottom flask. The catalyst was taken from the sealed ampoule just before use, and put immediately into the round-bottom flask containing the substrate. The diacetone alcohol was used as received. Part of the reaction mixture was taken every 30 min from the flask and analyzed by gas liquid chromatography (GLC) using a column (1 m · 3 mm i.d.) packed with SE-30.

3. Results

3.1. Determination of Molecules of Water of Crystallization
Barium hydroxide contains water of crystallization. The octahydrate and monohydrate of Ba(OH)2 are stable species. XRD analysis showed the sample dried in vacuum for 3 h contained peaks assigned to BaCO3 (PDF #: 11-697) but no peak assigned to hydroxides. Therefore, the number of water molecules in the crystalline sample could not be determined from the result of XRD analysis. Therefore, TG-DTA was performed to determine the number of water molecules. The TG and DTA profiles of Ba(OH)2·8H2O mixed with silica are shown in Fig. 1. The large endothermic change below 390 K was due to the desorption of 7H2O molecules. The remaining H2O molecule was eliminated by heating from 390 to 415 K. A sharp endothermic peak at 650 K in the DTA profile indicated the melting of Ba(OH)2. This endothermic event was not accom-
panied by weight change. After melting of the solid, a weight decrease indicating Ba(OH)$_2$ decomposition into BaO and H$_2$O was observed in the temperature range from 650 to 690 K.

The TG-DTA investigation of Ba(OH)$_2$·8H$_2$O showed that 7H$_2$O molecules were eliminated at temperatures lower than 390 K, and the remaining H$_2$O molecule was eliminated completely at 415 K. Dehydrated hydroxide melted at 650 K and decomposition occurred at a temperature just higher than that of the melting, and was complete at 690 K. Therefore, the measurement of weight decrease from room temperature to 650 K should be performed to determine the number of water of crystallization molecules in the dried sample.

The weight decrease in the temperature range from room temperature to 600 K corresponded to 0.9H$_2$O in the sample dried in a vacuum (Fig. 1). Therefore, the starting material for the treatment with alkoxide was determined to be Ba(OH)$_2$·H$_2$O. The obtained Ba(OH)$_2$·H$_2$O releases two H$_2$O molecules when converted into BaO, by desorption of the water of crystallization and hydroxide decomposition. The weight decrease observed up to 600 K from room temperature was almost equal to that of hydroxide decomposition from 650 to 690 K. The total weight decrease (18.5%) was close to the theoretical (20.8%).

3. 2. Retro-aldol Reaction

Results of the retro-aldol reaction of diacetone alcohol to form acetone are shown in Fig. 2. GLC analysis detected a very small amount of mesityl oxide formed by dehydration of diacetone alcohol. The catalytic activity for the aldol reaction is strongly dependent on the basicity. The finding of acetone formation with higher selectivity indicates that the prepared catalysts were solid bases; and participation of acid sites in this reaction was negligible. Acid sites catalyze dehydration to form mesityl oxide. Ba(OH)$_2$ samples heated at 473 K and 573 K showed much lower activities com-
pared with the BaO·Al2O3 catalysts prepared in this study. The catalytic activity of Ba(OH)2 and BaO was greatly improved by combining with Al2O3.

The effects of the molar ratio of Ba(OH)2·H2O to Al(OCH(CH3)2)3 during preparation and the heat-treatment temperature on retro-aldol reaction activity are also shown in Fig. 2. All BaO·Al2O3 catalysts, except Ba33, showed almost identical activity if heat-treated at 573 K, despite the different ratio of BaO. The activity of Ba75 rapidly decreased with higher heat-treatment temperature. Lower Ba2+ content in the samples was associated with reduced effect of heat-treatment temperature on the decrease in activity. Catalysts with lower Ba2+ content showed catalytic activity with higher temperature activation. Conversion of diacetyl alcohol into acetone after 3 h was highest using catalyst with equal moles of Al(OCH(CH3)2)3 to Ba(OH)2·H2O during preparation, and heat-treatment at 673 K for 1 h. This temperature was in the range of Ba(OH)2 decomposition into BaO (650-690 K) as shown in Fig. 1.

The reaction rate of Ba50 heat-treated at 673 K calculated by applying the first order reaction equation was 0.91 mol g−1 h−1, lower than that of CaO prepared from Ca(OH)2 (1.16 mol g−1 h−1)23, and higher than that of MgO (0.48 mol g−1 h−1) prepared from Mg(OH)2 by a conventional method24. Base catalysts prepared by treatment with alkoxides showed much higher activity. The reaction rate of CaO treated with TiO2 was 3.16 mol g−1 h−1 23).

Interestingly, the change in catalytic activity of the Ba33 sample with heat-treatment temperature differed greatly from the other catalysts. Ba33 catalyst was almost inactive at lower treatment temperatures, and showed the highest activity after heat-treatment at 973 K. Other BaO·Al2O3 catalysts were inactive prepared at this higher temperature.

Effect of heat-treatment temperature on the surface area of Ba50 sample is shown in Fig. 3. The surface area decreased monotonously from 573 to 773 K, but was constant at 773 K or higher. This change was different from that of catalytic activity. Therefore, the surface area of prepared BaO·Al2O3 catalysts was not a main factor in determining the catalytic activity.

3.3. XRD Analysis

XRD profiles of heat-treated BaO·Al2O3 catalysts are shown in Fig. 4. The XRD profiles of catalysts with relatively higher activity are shown with a solid line, and catalysts with lower or no activity are shown with a gray line. Observed XRD peak sets were assigned to BaCO3 and BaAl2O4 (PDF #: 17-306). A few samples showed peaks assigned to Ba3Al2O6 (PDF #: 28-120). The peak sets of the expected chemical species, BaO, Ba(OH)2, Al2O3, and Al(OH)3, were not observed in this study.

The strongest peak positions are 2θ = 25° and 28° for BaCO3 and Ba3Al2O6, respectively, as indicated with dotted lines in Fig. 4. A peak at 2θ = 31° for Ba5Al2O6 is also shown for Ba75 and Ba60 samples. The main component of samples heat-treated at 573 K was BaCO3. The XRD profile was the same as that of Ba(OH)2·H2O obtained by drying of Ba(OH)2·8H2O in vacuum. Barium carbonate was present in the starting material as an impurity. The BaO·Al2O3 samples dried at 373 K showed only a peak set of BaCO3 in XRD analysis, as for the samples heat-treated at 573 K. In addition, a small portion of Ba(OH)2 or BaO was converted into carbonate during preparation. We discuss the carbonate formation in the next section.

Catalysts with appropriate Ba2+ content, in the range of 75 to 40 %, showed adequate catalytic activity (Fig. 2). Ba33, the most active catalyst with heat-treatment at 973 K, also showed the XRD profile of BaCO3. As shown above, the BaCO3 phase was observed in both active and inactive catalysts. These findings indicate that BaCO3 was not an active species for the retro-aldol reaction.

The intensity of the XRD peaks of the BaCO3 set was increased by further heat-treatment at higher temperatures. The observed phase was BaCO3 and small peaks assigned to BaAl2O4 also appeared. Catalysts with the XRD profile of BaAl2O4 showed lower or no catalytic activity for the reaction, as well as BaCO3. Therefore, BaAl2O4 was not an active species. XRD analysis could not identify the active species.

The size of the BaAl2O4 crystal particles was determined using Scherrer’s equation applied to the (202) diffraction peak at 28.4°. Particle size increased with higher heat-treatment temperature as shown in Fig. 5, with the temperature of 973 K or below. Particle sizes of samples heat-treated at 1073 K were smaller than those heat-treated at 973 K or below. This decrease in particle size was considered to result from the simultaneous formation of BaAl2O4 from BaO and Al2O3, and
transformation to BaCO$_3$. The BaAl$_2$O$_4$ was expected to form BaCO$_3$ before the particle size increased.

3.4. TG Analysis

TG analysis of dried samples was performed after removing the solvent in a rotary evaporator to investigate the heat-treatment as shown in Fig. 6. Large weight decrease from 300 to 400 K was observed in all samples. The weight loss in this temperature range increased with higher content of Al(OCH(CH$_3$)$_2$)$_3$ used for the preparation of catalyst precursors. The Ba33 sample showed the largest decrease in weight. Weight decrease in this temperature range could be ascribed to the desorption of isopropanol formed by hydrolysis of Al(OCH(CH$_3$)$_2$)$_3$ in the solid phase reaction.

Weight increase was observed around 560 K in all samples except Ba75. This weight change was accompanied by an exothermal reaction in a narrow temperature range. A representative DTA result of the Ba50 sample is shown in Fig. 6. Combustion of an organic compound remaining on the surface and forma-
tion of BaCO$_3$ were anticipated. Both combustion and BaCO$_3$ formation are exothermic reactions. Conversion of BaO or Ba(OH)$_2$ into BaCO$_3$ is a weight-increasing reaction. However, BaCO$_3$ formation was not confirmed in the XRD profile shown in Fig. 4. Therefore, BaCO$_3$ formed in this temperature range was amorphous and crystallized in a higher temperature range.

The Ba75 sample showed a small weight decrease around 650 K, which might be caused by thermal decomposition of Ba(OH)$_2$. The Ba75 sample contained the largest amount of Ba(OH)$_2$, and the amount of Al(OCH(CH$_3$)$_2$)$_3$ was insufficient to convert Ba(OH)$_2$ to the mixed oxide with Al. Excess of Ba(OH)$_2$ resulted in a weight decrease profile in TG analysis.

4. Discussion

The starting material for the solid-liquid interface reaction with alkoxide was determined to be Ba(OH)$_2$·H$_2$O from the result of TG-DTA. Barium carbonate was included in the starting material as an impurity. However, XRD analysis did not observe Ba(OH)$_2$·H$_2$O in the samples. Particles of Ba(OH)$_2$·8H$_2$O were presumably crushed in the drying process in vacuum as a result of losing crystal water. Ba(OH)$_2$·8H$_2$O would be converted into very small particles of Ba(OH)$_2$·H$_2$O that did not give a diffraction peak in XRD. In addition, the crystal structure of Ba(OH)$_2$·H$_2$O would also be destroyed by the solid-liquid interface reaction. Consequently, Ba(OH)$_2$ was not observed in the XRD analysis.

Similarly, no XRD peak of chemical species including Al was detected in the samples treated at lower temperatures. These observations suggest that large amounts of Ba and Al compounds were present in the amorphous state in catalytically active samples. Higher heat-treatment temperature promoted the crystallization of amorphous species into BaAl$_2$O$_4$.

Comparing the data on the effect of activation temperature (Fig. 2) and XRD profiles (Fig. 4), the formation of BaAl$_2$O$_4$ reduced catalytic activity. Catalysts treated at higher temperatures showed lower activity for the retro-aldol reaction, and simultaneous development of the BaAl$_2$O$_4$ crystal phase. Therefore, both Ba and Al compounds, which were the sources of BaAl$_2$O$_4$, were present in the amorphous state in the catalytically active samples. The formation of barium aluminates was confirmed in the samples heat-treated at 673 K. Barium aluminate formation at lower temperature would indicate that well-mixed binary oxides or hydroxides of BaO·Al$_2$O$_3$, Ba(OH)$_2$·Al$_2$O$_3$, or Ba(OH)$_2$·Al(OH)$_3$ in the amorphous state were formed by the solid-liquid interface reaction used in this study. Moreover, the weight decrease resulting from water desorption around 400 K was not observed in the TG profiles in Fig. 6. Therefore, the water of crystallization in the hydroxide sample was eliminated in the solid-liquid interface reaction as follows.

\[
\text{Ba(OH)}_2 \cdot \text{H}_2\text{O} + \text{Al(OCH(CH}_3)_2)_3} \\
\rightarrow \text{Ba(OH)}_2 + \text{Al(OH)}(\text{OCH(CH}_3)_2)_2 + (\text{CH}_3)_2\text{CHOH}
\]

TG profiles of samples treated with Al(OCH(CH$_3$)$_2)_3$ showed large weight decreases from 300 to 400 K attributed to the desorption of isopropanol formed by hydrolysis of Al(OCH(CH$_3$)$_2)_3$ in the solid phase reaction. Hydrolysis of Al(OH)(OCH(CH$_3$)$_2)_2$ and Al(OH)$_2$OCH(CH$_3$)$_2$ seems to be included. Water
molecules used for the hydrolysis of Al(OCH(CH$_3$)$_2$)$_3$ is evolved from mixed hydroxides by heating. Possible reactions are as follows.

$$\text{Ba(OH)}_2 \rightarrow \text{BaO} + \text{H}_2\text{O}$$
$$2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$$

Formed water molecules are consumed immediately by hydrolysis of Al(OCH(CH$_3$)$_2$)$_3$, Al(OH)(OCH(CH$_3$)$_2$)$_2$, and Al(OH)$_2$OCH(CH$_3$)$_2$ to form amorphous alumina and isopropanol.

$$2\text{Al(OH)}(\text{OCH(CH$_3$)$_2$})_2 + 3\text{H}_2\text{O}$$
$$\rightarrow \text{Al}_2\text{O}_3 + 6(\text{CH}_3)_2\text{CHOH}$$

If the amount of Al(OCH(CH$_3$)$_2$)$_3$ is small, some of the H$_2$O formed by dehydration of the mixed hydroxide will be desorbed without hydrolysis of Al(OCH(CH$_3$)$_2$)$_3$. The resulting weight decrease would be small in TG analysis.

None of the prepared samples showed the endothermal DTA profile of Ba(OH)$_2$ melting. In addition, no weight decrease accompanying Ba(OH)$_2$ decomposition to BaO was observed between 400 K and 700 K in the Ba33, Ba40, Ba50, or Ba60 samples. Therefore, the formation of barium aluminates occurred without hydroxide decomposition. Therefore, the barium aluminates originated from BaO and Al$_2$O$_3$.

The water molecules evolved from the mixed hydroxide were consumed immediately by hydrolysis of Al(OH)(OCH(CH$_3$)$_2$)$_2$ and related compounds. Weight decrease due to (CH$_3$)$_2$CHOH formation was completed at 400 K. The resultant material was well-mixed binary oxides in the amorphous state. Reactions forming the mixed oxide from hydroxides and alkoxide were also complete below 400 K.

$$3\text{Ba(OH)}_2 + 2\text{Al(OCH(CH$_3$)$_2$})_2$$
$$\rightarrow 3\text{BaO} + \text{Al}_2\text{O}_3 + 6(\text{CH}_3)_2\text{CHOH}$$

$$\text{Al(OH)}_3 + \text{Al(OCH(CH$_3$)$_2$})_2$$
$$\rightarrow \text{Al}_2\text{O}_3 + 3(\text{CH}_3)_2\text{CHOH}$$

Changes in the chemical species during preparation were as follows. Barium hydroxide monohydrate was converted to anhydrous hydroxide in the solid-liquid interface reaction. Hydroxides of Ba and Al were also formed, then decomposed to water molecules and corresponding oxides in the first stage of heat-treatment. Water molecules were consumed immediately by hydrolysis of Al(OCH(CH$_3$)$_2$)$_3$ observed as a large weight decrease in the lower temperature range of the TG profiles. Excess Al(OCH(CH$_3$)$_2$)$_3$ was combusted at elevated temperature around 550 K observed as an exothermal reaction in a narrow temperature range. The resultant well-mixed oxides was converted to barium aluminates by heat-treatment at higher temperatures.

Samples treated at higher temperatures showed XRD peak sets of BaCO$_3$ and BaAl$_2$O$_4$, as shown in Fig. 4. No peaks of the expected chemical species of BaO, Ba(OH)$_2$, Al(OH)$_3$, and Al$_2$O$_3$, the sources of BaCO$_3$ and barium aluminates, were observed in the XRD spectra of the prepared active catalysts. However, formation of BaAl$_2$O$_4$ by heat-treatment at higher temperatures without decrease in BaCO$_3$ indicated that the sources of the barium aluminates were mixed oxides of BaO-Al$_2$O$_3$ in the amorphous state. Formation of BaAl$_2$O$_4$ was assumed to involve conversion of BaO into small particles dispersed on Al$_2$O$_3$ and/or on the surface of barium aluminates. Barium oxide is the active component of the solid base catalyst. We conclude that the catalytically active species of BaO was present as small crystallites that were not detected as a diffraction peak in XRD, and was well dispersed on the surface of the amorphous Al$_2$O$_3$ and/or barium aluminates.

5. Conclusions

Solid base BaO catalyst was synthesized by dehydration of Ba(OH)$_2$ + H$_2$O in the solid phase using hydrolysis of Al(OCH(CH$_3$)$_2$)$_3$ dissolved in ethyl acetate. The BaO catalyst synthesized by equal mols of Al(OCH(CH$_3$)$_2$)$_3$ and heat-treatment at 673 K showed the highest activity among the prepared catalysts for base-catalyzed retro-aldol reaction of diacetone alcohol to acetone.

XRD analysis detected no definite active species. The active species was concluded to be small particles of BaO well dispersed on an amorphous Al$_2$O$_3$ and/or barium aluminate matrix. TG analysis observed no clear weight decrease by Ba(OH)$_2$ dehydration in the prepared samples. The formation of barium aluminates without weight decrease indicates that Ba(OH)$_2$ was converted into BaO at lower temperature than barium aluminate formation. The temperature of Ba(OH)$_2$ dehydration in the Al$_2$O$_3$ matrix was much lower than that at which simple Ba(OH)$_2$ dehydration occurs. Amorphous BaO and Al$_2$O$_3$ were converted into catalytically inactive barium aluminates by further thermal treatment.

We conclude that the solid-liquid interface reaction of metal hydroxide in the solid phase with metal alkoxide in the liquid phase is useful to prepare well-dispersed mixed metal oxides.

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要 旨
水酸化バリウムとアルミニウムアルコキシドとの固-液界面の反応を利用した 二元系酸化物 BaO-Al2O3 固体塩基触媒の合成

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酢酸エチルに溶解した Al(OCH(CH3)2)3 と、固相の Ba(OH)2・H2O との固-液界面反応を用いて、BaO-Al2O3 固体塩基触媒を合成した。Al(OCH(CH3)2)3 は、Ba(OH)2・H2O の結晶水分子で加水分解され、アルミナとイソプロパノールに変化した。Ba(OH)2・H2O と等モルの Al(OCH(CH3)2)3 を用いて合成した試料を 673 K で熱処理した触媒が、ジアセトンアルコールの逆アルドール反応に最も高い活性を示した。BaO 含有量を 33 ～ 75 mol% の範囲で変化させたところ、含有量によって適切な活性化温度があることが明らかとなった。それの含有量で活性化温度は、XRD で Ba5Al2O8 および BaAl2O4 の相が見られる温度よりも低い温度が適切であった。活性化触媒では XRD で BaO 相が見られないが、無定形の Al2O3 に高濃度に分散した BaO が活性種であると思われる。本研究の結果、固相の金属水酸化物と液相のアルコキシドの界面反応は、高濃度に分散した複合金属酸化物を調製するのに有用であることが確認された。

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