1. Introduction

Alkaline earth metal oxides such as MgO are well known to show activities as solid base catalysts. The preparation, active site structure, and application of MgO to numerous base-catalyzed organic reactions have been extensively investigated\textsuperscript{1)\textendash}4). Strontium oxide (SrO) has a higher base strength among the alkaline earth metal oxides, because strontium (Sr) has lower electronegativity within the group of alkaline earth metals. The base strength increases in the order MgO \textless CaO \textless SrO \textless BaO\textsuperscript{5),6)}. Therefore, SrO is expected to achieve higher catalytic activity in various organic reactions.

Highly dispersed SrO in amorphous Al\textsubscript{2}O\textsubscript{3}, SrO\textsubscript{2}Al\textsubscript{2}O\textsubscript{3}, was synthesized by solid-liquid interface reaction of Sr(OH)\textsubscript{2}\cdot8H\textsubscript{2}O in the solid phase with Al(OCH(CH\textsubscript{3})\textsubscript{2})\textsubscript{3} dissolved in 2-propanol. The water of crystallization in Sr(OH)\textsubscript{2}\cdot8H\textsubscript{2}O was consumed for the hydrolysis of Al(OCH(CH\textsubscript{3})\textsubscript{2})\textsubscript{3}. SrO\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} catalyst synthesized by solid-liquid interface reaction of equimolar amounts of Sr(OH)\textsubscript{2}\cdot8H\textsubscript{2}O and Al(OCH(CH\textsubscript{3})\textsubscript{2})\textsubscript{3}, then heat treated at 673 K, exhibited the highest activity among the prepared catalysts for the base-catalyzed retro-aldol reaction of diacetone alcohol. Catalytic activity of SrO\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} catalyst calcined at 673 K was twice that of SrO\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} catalyst prepared by physical mixing of Sr(OH)\textsubscript{2}\cdot8H\textsubscript{2}O with Al\textsubscript{2}O\textsubscript{3}. Active SrO\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} catalyst was obtained by heating at a temperature just below that of Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6} crystallization. Formation of SrO by heat treatment at 673 K was confirmed using X-ray absorption near edge structure analysis. The SrO particle size was too small for detection by powder X-ray diffraction. We found that interface reaction of a metal hydroxide in the solid phase with an alkoxide in the liquid phase is useful for the preparation of well-dispersed mixed metal oxides under mild conditions.

Keywords

Strontium oxide, Solid base, Solid-liquid interface, Retro-aldol reaction

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Synthesis of SrO\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} Solid Base Catalysts from Strontium Hydroxide and Aluminum Alkoxide by a Solid-liquid Interface Reaction

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ward H₂O is converted into the corresponding metal hydroxide and alcohol by hydrolysis. The water of crystallization contained in the metal hydroxide would be consumed by this hydrolysis reaction in a nonaqueous solvent. Water molecules are necessary to maintain the crystalline structure of the metal hydroxide. Therefore, the crystalline structure will be disrupted as water molecules are removed from the lattice. Metal hydroxide molecules are likely to be displaced from a solid surface if the surrounding water molecules are consumed by hydrolysis of the metal alkoxide. Such displaced metal hydroxide molecules are insoluble in an organic solvent so can be expected to precipitate. Therefore, newly formed metal hydroxide solids will be obtained as precipitates as results of both displacement and hydrolysis.

Displacement of metal hydroxide molecules from the solid surface will expose a new hydrated metal hydroxide surface, and so further hydrolysis of the metal alkoxide by the water molecules in the crystal structure will continue. Both hydroxide precipitates are formed simultaneously by the reaction on the hydroxide surface, and no solvation by 2-propanol is expected. Therefore, the solid-liquid interface reaction would provide hydroxide precipitates well mixed on the molecular level.

Water of crystallization contained in Sr(OH)₂·8H₂O can be eliminated by heating at 373 K. Therefore, the water molecules formed by dehydration of Sr(OH)₂ to form SrO would also be consumed by hydrolysis of the metal alkoxide. Consequently, dehydration of Sr(OH)₂ should be promoted by mixing with a metal alkoxide.

We previously reported the synthesis of BaO·Al₂O₃ solid base catalyst under mild conditions using the solid-liquid interface reaction of Ba(OH)₂·H₂O in the solid phase with Al(OC(CH₃)₂)₃ dissolved in ethyl acetate. The prepared catalyst consisted of catalytically active BaO highly dispersed in amorphous Al₂O₃.

The present investigation applied a catalyst-preparation technique using a solid-liquid interface reaction to the following system: Sr(OH)₂, with and without water of crystallization, and Al(OCH(CH₃)₂)₃. This research aimed to show that the interface reaction of a metal hydroxide in the solid phase with an alkoxide in the liquid phase, carried out under mild conditions, is useful for the formation of catalytically active and well-dispersed mixed metal oxides.

2. Experimental

2.1. Catalyst Preparation

All catalysts were prepared under atmospheric conditions. Strontium hydroxide, with and without water of crystallization, was used in the solid-liquid interface reaction to prepare the catalyst precursors. Strontium hydroxide octahydrate (Sr(OH)₂·8H₂O; FUJIFILM Wako Pure Chemical Corp.) was used as received, or heated in an oven at 373 K for 12 h to eliminate the water of crystallization to form Sr(OH)₂. Treatment of Sr(OH)₂·8H₂O or Sr(OH)₂ with Al(OCH(CH₃)₂)₃ was performed as follows. The required amount of Sr(OH)₂·8H₂O or Sr(OH)₂ was kneaded in a mortar together with an equimolar amount of Al(OCH(CH₃)₂). An appropriate volume of 2-propanol was added to the mixture in the mortar and kneaded for a further 10 min. The 2-propanol suspension was then transferred to an Erlenmeyer flask and stirred at 333–343 K for 12 h. The precipitate was separated by filtration, to yield the SrO·Al₂O₃ precursor. The solid product (after filtration) was dried at 373 K for 2 h and then heat treated for activation at 573–1073 K for 1 h. Heat-treated catalysts were kept in sealed ampoules until use.

The mole ratio of Al/Sr was 1 in the sample prepared from anhydrous Sr(OH)₂. The mole ratios of Al/Sr were 1, 2, and 3 in samples prepared from Sr(OH)₂·8H₂O. In addition, pure Sr(OH)₂ catalyst heat treated at 673 K was also used for comparison.

The physically mixed sample was prepared as follows. The required quantities of Sr(OH)₂·8H₂O and γ-Al₂O₃ (JRC-ALO-6, Catalysis Society of Japan) were mixed by kneading in a mortar together with a small volume of ethanol for 15 min, in a glove box. The mixture was allowed to stand at room temperature until all solvent had evaporated. The obtained solid was heated in a muffle furnace at 673–873 K for 1 h. The mole ratio of Al/Sr was fixed at 1.17.

The SrO·Al₂O₃ samples prepared from Sr(OH)₂, Sr(OH)₂·8H₂O (Al/Sr = 1), Sr(OH)₂·8H₂O (Al/Sr = 2), Sr(OH)₂·8H₂O (Al/Sr = 3) are named SAA, SAH₁, SAH₂, and SAH₃, respectively, and the physical mixing sample is named SAP.

2.2. Retro-aldol Reaction of Diacetone Alcohol

All reactions were carried out under atmospheric conditions. The base-catalyzed decomposition reaction of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone, FUJIFILM Wako Pure Chemical Corp., DAA) to form acetone (the retro-aldol reaction) was performed in a batch reaction system at 299 K for 3 h (Scheme 1). First, the catalyst 50 mg was removed from its sealed ampoule, then immediately placed in a round-bottom flask together with the substrate 50 mmol DAA (used as received). Samples of the reaction mixture were removed from the reaction flask at intervals of 30 min and analyzed by gas-liquid chromatography (GLC).

2.3. Catalyst Characterization

Thermogravimetry and differential thermal analysis (TG-DTA) was performed on the prepared samples under nitrogen before heat treatment to observe the thermal decomposition profiles. An equal weight of silica was mixed with the pure Sr(OH)₂ to avoid damaging the sample pan of the TG-DTA apparatus by
melting hydroxide. Powder X-ray diffraction (XRD) spectra of the heat-treated samples were measured using Cu-Kα radiation.

X-ray absorption near edge structure (XANES) experiments were performed at the UVSOR Synchrotron Facility, Institute for Molecular Science, Okazaki, Japan. The BL2A beamline with KTP (KTiOPO4) (011) double-crystal monochromator was used for measurements at the Sr L-edge in the total electron yield (TEY) mode. The penetration depth of each L-edge spectrum (at ca. 1.94 keV) in TEY mode is possibly several hundred angstroms into the bulk because both LMM Auger electrons and low energy secondary electrons constitute a significant fraction. Thus, the L-edge spectra reflect the structures of the samples in the “near-surface region.” SrO (Aldrich), Sr(OH)2 (FUJIFILM Wako Pure Chemical Corp.), SrAl2O4 (Kojundo Chemical Laboratory Co., Ltd.), and SrF2 (Alfa Aesar) were employed as reference samples. Normalization of each XANES spectrum was conducted using REX2000 (Rigaku Corp.) software. Curve deconvolution of the normalized XANES profiles was performed using the Voigt function, given by a combination of the Lorentz function and the Gaussian function.

3. Results and Discussion

3.1. Retro-aldol Reaction

Results of the retro-aldol reaction of DAA to form acetone are shown in Fig. 1. The substrate contained a very small quantity of mesityl oxide as an impurity. The amount of mesityl oxide remained constant during the reaction. The prepared catalysts showed no activity for the dehydration of DAA. Dehydration of DAA takes place on acid sites or acid-base pair sites on a catalyst surface32). The absence of mesityl oxide formation indicated that the prepared catalysts were solid bases. Acid sites were not present as active sites in this reaction.

The catalytic activity in the aldol reaction is strongly dependent on the basicity6,33). The aldol reaction is initiated by abstraction of a proton from a methyl group of acetone. The retro-aldol reaction also commences with proton abstraction from an OH group. Therefore, the base strength is as important in the retro-aldol reaction as in the aldol reaction.

Active sites on conventional solid bases, such as MgO, are severely poisoned by H2O and CO2 in the atmosphere. The strong base sites, active in 1-butene isomerization under vacuum conditions23,34), appeared to be poisoned under the experimental conditions used in our study. Isomerization of 1-butene is initiated by elimination of a proton in the alkene, which has a higher pK<sub>a</sub> value estimated at about 35. In contrast, the first step in the decomposition of DAA is elimination of a proton from the OH group in DAA. The pK<sub>a</sub> of an alcohol proton is not high. Base sites with moderate strength can eliminate protons from an OH group. Many organic reactions catalyzed by a base do not require very strong base sites, which are necessary for alkene isomerization31). Therefore, higher catalytic activity is caused by a large number of active sites on the surface.

In the SAH catalyst series (described in section 2.1.), the highest activity was obtained by calcination at 673 K, for all contents of Sr. The calcination temperatures that gave the highest activity for the SAA and SAP catalysts were 773 K and 723 K, respectively. The base catalytic activity decreased with higher calcination temperature for all catalysts. The reaction rate calculated by applying the first order reaction equation was 0.89 mol g<sup>–1</sup> h<sup>–1</sup> for SAH1 treated at 673 K, almost equal to 0.91 mol g<sup>–1</sup> h<sup>–1</sup> of BaO-Al2O3 prepared from Ba(OH)<sub>2</sub>-H2O and Al(OCH(CH3)2)3 using solid-liquid interface reaction30), and higher than 0.48 mol g<sup>–1</sup> h<sup>–1</sup> of MgO prepared from Mg(OH)<sub>2</sub> by a conventional method22). The turnover frequency normalized by the number of atoms of alkaline earth elements contained was 138, 186, and 19 h<sup>–1</sup>, for SAH1, BaO-Al2O3, and MgO, respectively.

The calcination temperatures giving the highest activity were lower than the temperatures of Sr(OH)2 melting in the SAH series and SAP, but was close to the melting temperature for the SAA catalyst. The SAH1
catalyst calcined at 673 K had the highest activity. SAH2 and SAH3 had lower activities than SAH1. The catalytic activity was corresponded to the Sr content in each catalyst. The changes in decomposition activity with treatment temperature in SAH2 and SAH3 were very similar to that of SAH1. The highest activity was obtained by treatment at 673 K, and gradually decreased with higher treatment temperature in a wide range. The active species were the same in all SAH catalysts. The Sr(OH)2 catalysts exhibited the lowest activity of all catalysts tested.

### 3.2. TG-DTA Analysis

TG-DTA was performed to elucidate the decomposition profiles of the prepared catalyst precursors as shown in Fig. 2. The profile of Sr(OH)2·8H2O mixed with silica demonstrated an endothermic reaction, with large weight decrease, continuing from the commencement of measurements to 420 K. This large weight decrease was due to the loss of water of crystallization. Sr(OH)2·8H2O lost all its water molecules in this temperature range and was converted to anhydrous Sr(OH)2. Endothermic peaks appeared at 759 K, without weight decrease, due to the melting of Sr(OH)2, and at 815 K, with weight decrease associated with conversion to SrO24).

In contrast, the TG-DTA profiles of uncalcined SAH1 and SAA samples showed no clear endothermic reactions caused by loss of water of crystallization. The SAA sample contained no water of crystallization as anhydrous hydroxide was used for catalyst preparation. The SAH1 sample lost water of crystallization by consumption in the solid-liquid interface reaction. Hydration of Al(OCH(CH3)2)3 forming 2-propanol and aluminum hydroxide was very likely to have consumed the water of crystallization in Sr(OH)2·8H2O. The TG-DTA profile of SAH1 showed a rounded endothermic peak at around 530 K and gradual weight decrease over a wide temperature range, up to around 740 K. The Sr(OH)2 decomposition temperature was strongly lowered in the samples obtained by interface reaction.

Lower decomposition temperature was also observed for SAA. Hydroxide decomposition was observed as a broad endothermic peak in a slightly lower temperature range than for Sr(OH)2 mixed with silica. The peak of the endothermic reaction was 750 K. In this case, no clear peak due to Sr(OH)2 melting was observed because of overlapping with the peak of hydroxide decomposition.

The TG-DTA profile of SAP was very similar to that of Sr(OH)2·8H2O mixed with silica. However, the endothermic peak due to Sr(OH)2 melting was unclear. Endothermic peaks associated with weight decrease were observed at 524, 758, and 790 K. The first peak occurred at almost the same temperature as observed in SAH1 (530 K) and the last peak was close to that of the Sr(OH)2 decomposition temperature (815 K). Sr(OH)2 melting might take place simultaneously with hydroxide decomposition. The remaining endothermic peak (758 K) was observed at similar temperature to that in SAA (750 K). Therefore, the the TG-DTA profile of SAP looked like the "mixed" profiles of SAH and SAA. Possibly the former can be attributed to reaction of a well-mixed sample and the latter to that of a less well-mixed sample. Additionally, the endothermic peak at 790 K indicates that part of the Sr(OH)2 in SAP was isolated from Al2O3. This isolated Sr(OH)2 or SrO was formed by decomposition of isolated Sr(OH)2 and would show lower activity due to the smaller surface area.

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**Fig. 2** TG-DTA Profiles of SrO·Al2O3 Precursors and Sr(OH)2·8H2O
3.3. XRD

XRD was used to investigate the chemical transformation of SrO-Al₂O₃ precursors by heat treatment as shown in Figs. 3 and 4, which illustrate the XRD profiles of SAH1 and SAA, respectively, calcined at various temperatures. SAH1 precursors dried at 373 K showed XRD peaks of Sr₃Al₂(OH)₁₂ and Sr(OH)₂·H₂O before calcination. The presence of Sr₃Al₂(OH)₁₂ indicates that a well-mixed hydroxide was prepared using the solid-liquid interface reaction of Sr(OH)₂·8H₂O with Al(OCH(CH₃)₂)₃. The diffraction peaks of Sr₃Al₂(OH)₁₂ disappeared after calcination at 573 K. Small peaks assigned to Sr(OH)₂ appeared instead. The XRD profile of SAH1 calcined at 673 K was similar to that of SAH1 calcined at 573 K. Strontium aluminates, assigned to Sr₃Al₂O₈, Sr₄Al₂O₇, Sr₃Al₂O₆, and Sr₁₂Al₁₄O₃₃, appeared after further calcination at higher temperatures, together with lower catalytic activity. Therefore, strontium aluminates were not active species in the retro-aldol reaction.

Peaks assigned to Sr(OH)₂ with low intensity was observed in the active SAA catalyst calcined at 673 K. The peak intensity of Sr(OH)₂ was much smaller than that of Sr₃Al₂(OH)₁₂, as observed in the sample heated at 373 K. The peak intensity of Sr₃Al₂O₈, formed by dehydration of Sr₃Al₂(OH)₁₂, was much smaller than expected (based on the Sr₃Al₂(OH)₁₂ peak intensity) in the sample calcined at 773 K. XRD detected much of the Sr²⁺ and Al³⁺ (from Sr₃Al₂(OH)₁₂) in SAH1 calcined at 673 K but not in SAA calcined at 773 K.

Simple hydroxides Sr(OH)₂·H₂O and Sr(OH)₂ were observed in SAA. No compound containing Al was observed in SAA dried at 373 K. The solid-liquid interface reaction proceeded better using hydrated substrate than anhydrous substrate. The most active SAA catalyst calcined at 773 K showed small XRD peaks of Sr₃Al₂O₈ with strong peaks of SrCO₃, which are both inactive species, as mentioned earlier. The catalytically active component, expected to be SrO, was not detected using XRD analysis.

SAP sample calcined at 723 K also showed little trace of Sr(OH)₂ peaks. As stated above, strontium aluminates such as Sr₃Al₂O₈, and SrCO₃ were not catalytically active phases in the reaction. However, catalysts without Sr(OH)₂ phase exhibited sufficient activity, as seen in our experimental results. Sr(OH)₂ demonstrated much lower activity, as shown in Fig. 1. XRD analysis detected only catalytically inactive com-
ponents of mixed hydroxide, strontium aluminates, and SrCO$_3$. These results showed that XRD could not detect the active compound. Therefore, the catalytically active species is likely to be present in the amorphous phase or small particles.

3.4. Sr L$_3$-edge XANES Spectra

XANES spectra were obtained to confirm the formation of SrO in SAH1 calcined at 573-1073 K. Sr$^{2+}$ occupies the octahedral site in the rock salt-type structure of SrO. Sr$^{2+}$ is coordinated by seven OH$^-$ ions in the lattice of Sr(OH)$_2$. Sr$^{2+}$ has a coordination number of about 5 in strontium aluminates. Sr$^{2+}$ in a SrAl$_2$O$_4$ crystal is surrounded by five O$_2^-$ ions, but the interatomic distances to the five O$_2^-$ ions are not the same. Furthermore, another four O$_2^-$ ions are located slightly farther away. Therefore, the exact coordination number of Sr$^{2+}$ is difficult to determine in the lattice of strontium aluminates. Sr$^{2+}$ in SrAl$_2$O$_4$ is coordinated by nine O$_2^-$ ions at different distances. SrF$_2$ has the same crystal structure as CaF$_2$. Sr$^{2+}$ is located in the center of a cubic site in SrF$_2$ and is surrounded by eight F$^-$ anions. SrO, Sr(OH)$_2$, SrAl$_2$O$_4$, and SrF$_2$ all have strong ionic bond character. SrAl$_2$O$_4$ and SrF$_2$ have no catalytic activity.

XANES profiles of standard samples are shown in Fig. 5. Maximum energy and full width at half maximum of the divided peaks in XANES profiles are summarized in Table 1. Curve deconvolution is frequently applied to white line analysis in XANES. Each normalized XANES profile was divided into three peaks. A state of 4d orbital separation causes the two peaks in the lower energy region. The transition to the continuous state is assigned to the peak in the higher energy region.

The original XANES profile of SrF$_2$ had a peak at 1944.6 eV and a shoulder in the lower energy region. The profile mainly consisted of a divided large peak at 1944.66 eV and a peak at a lower energy of 1942.87 eV, as shown in Table 1.

The XANES profile of SrO is characterized by a large broad peak in the higher energy region at 1945.71 eV. However, the peak position at 1944.0 eV in the measured original profile was strongly influenced by the center peak at 1944.07 eV, and the left peak at 1942.65 eV. The peak of the SrO profile occurred at a slightly lower energy than that of SrF$_2$ (1944.6 eV).

The profile of Sr$^{2+}$ in Sr(OH)$_2$ consisted mainly of the center peak at 1944.01 eV, which was almost the same as that of SrO (1944.07 eV). The Sr(OH)$_2$ profile also contained two other small peaks.

The XANES profile of SrAl$_2$O$_4$ consisted mainly of a peak at 1943.89 eV as in the case of Sr(OH)$_2$. The divided peak at the lowest energy, 1942.65 eV, was relatively large in the profile of SrAl$_2$O$_4$. In addition, a small broad peak was found at 1946.86 eV in the higher energy region. The peak of the XANES profile at

![Fig. 5 XANES Profiles of Standard Samples](image)

| Sample   | Calcination temp. [K] | Peak 1 | Peak 2 | Peak 3 |
|----------|-----------------------|--------|--------|--------|
| SrF$_2$  | -                     | Max. energy [eV] 1942.87 | FWHM [eV] 2.57 | Max. energy [eV] 1944.66 | FWHM [eV] 2.37 | Max. energy [eV] 1945.68 | FWHM [eV] 3.37 |
| SrO      | -                     | Max. energy [eV] 1942.65 | FWHM [eV] 2.58 | Max. energy [eV] 1944.07 | FWHM [eV] 2.29 | Max. energy [eV] 1945.71 | FWHM [eV] 5.87 |
| Sr(OH)$_2$ | -                  | Max. energy [eV] 1942.73 | FWHM [eV] 1.97 | Max. energy [eV] 1944.01 | FWHM [eV] 2.47 | Max. energy [eV] 1945.43 | FWHM [eV] 3.38 |
| SrAl$_2$O$_4$ | 573             | Max. energy [eV] 1942.65 | FWHM [eV] 2.02 | Max. energy [eV] 1943.89 | FWHM [eV] 2.51 | Max. energy [eV] 1946.86 | FWHM [eV] 6.41 |
| SAH1     | 673                  | Max. energy [eV] 1942.93 | FWHM [eV] 2.28 | Max. energy [eV] 1944.11 | FWHM [eV] 2.87 | Max. energy [eV] 1947.09 | FWHM [eV] 5.96 |
| SAH1     | 773                  | Max. energy [eV] 1943.25 | FWHM [eV] 2.06 | Max. energy [eV] 1944.48 | FWHM [eV] 1.98 | Max. energy [eV] 1945.58 | FWHM [eV] 5.93 |
| SAH1     | 873                  | Max. energy [eV] 1943.13 | FWHM [eV] 2.70 | Max. energy [eV] 1944.37 | FWHM [eV] 2.86 | Max. energy [eV] 1946.81 | FWHM [eV] 3.13 |
| SAH1     | 973                  | Max. energy [eV] 1942.90 | FWHM [eV] 2.64 | Max. energy [eV] 1944.14 | FWHM [eV] 2.01 | Max. energy [eV] 1945.70 | FWHM [eV] 5.36 |
| SAH1     | 1073                 | Max. energy [eV] 1942.61 | FWHM [eV] 2.37 | Max. energy [eV] 1943.90 | FWHM [eV] 2.32 | Max. energy [eV] 1945.64 | FWHM [eV] 4.62 |
1943.5 eV was the lowest among the reference samples considered in this study. The resulting observed profile had a greater width.

The results of the XANES measurement of reference samples indicated that the energy of the peak position in a XANES profile was slightly dependent on the coordination number of Sr$^{2+}$ in the crystal lattice. However, formation of SrO was difficult to confirm from peak positions in the XANES profiles.

The Auger line has greater energy width in ionic character compounds containing Sr$^{2+}$ [37]. In the divided XANES profile, a large divided peak in a higher energy position and/or lower energy position results in a peak of wider width. As described above, compounds with high ionic character are inactive as base catalysts and have wider XANES profiles.

The XANES profiles of SAH1 calcined at 573-1073 K are also illustrated in Fig. 6, and the data of divided peaks in these profiles are summarized in Table 1. The peak of SAH1 calcined at 573 K appeared at 1943.9 eV, almost the same as that for Sr$^{2+}$ in the octahedral site (SrO, 1944.0 eV) and seven coordinated sites in Sr(OH)$_2$ (1943.9 eV). The large divided peak in the center position (1944.01 eV) was observed in the XANES profile of Sr(OH)$_2$. These results, which showed relatively small peaks at higher and lower energy positions, could indicate that Sr(OH)$_2$ was present in this sample.

The most active SAH1 catalyst calcined at 673 K showed a peak at higher energy than SAH1 calcined at 573 K. The composition of the divided peak was similar to that of SrO, as shown in Fig. 5. The large divided peak at the higher energy position (1945.71 eV) was characteristic of the SrO profile. The large peak at higher energy position (1945.58 eV) was also observed in SAH1 calcined at 673 K, which confirmed formation of SrO in the SAH1 calcined at 673 K. SrO would be highly dispersed in the Al$_2$O$_3$ matrix. The particle size of the active species of SrO in this sample might be too small to be detected by XRD analysis.

Further calcination at higher temperatures (773, 873, and 973 K) showed peaks moving toward the lower energy region due to the large divided peaks at lower energy positions below 1943 eV. Much of the Sr$^{2+}$ is expected to have strong ionic character in these samples. The peak profile of SAH1 calcined at 1073 K was the same as that of SrAl$_2$O$_4$. The peak top was observed at 1943.8 eV in SAH1 calcined at 1073 K, almost the same as that of SrAl$_2$O$_4$ (1943.5 eV). The presence of divided peaks was also very similar to that of SrAl$_2$O$_4$. This finding agreed with the observation of strontium aluminate formation, as confirmed by XRD analysis. Sr$^{2+}$ occurred as both SrO and strontium aluminates in SAH1 calcined at 773 K and higher.

The results of our XANES measurements indicated that SrO with crystal size too small to be detected by XRD analysis was the active species in the retro-aldol reaction of diacetone alcohol. Such SrO with small crystal size provided a large amount of active sites on the surface of SAH samples.

4. Conclusions

High activity solid base catalyst consisting of SrO dispersed in amorphous Al$_2$O$_3$ was synthesized by applying the solid-liquid interface reaction of Sr(OH)$_2\cdot$ 8H$_2$O with Al(OCH(CH$_3$)$_2$)$_3$, in 2-propanol, followed by calcination at 673 K. The highest base catalytic ac-
tivity for DAA decomposition was obtained with calcination temperature of 673 K. This temperature was lower than that used in conventional solid base preparation. Sr(OH)$_2$·8H$_2$O treated with an equal number of moles of Al(OCH(CH$_3$)$_2$)$_3$ (SAH1) exhibited the highest catalytic activity. The base catalytic activities of SrO–Al$_2$O$_3$ prepared by the solid-liquid interface reaction of anhydrous Sr(OH)$_2$ with Al(OCH(CH$_3$)$_2$)$_3$ (SAA) and by kneading of Sr(OH)$_2$·8H$_2$O with Al$_2$O$_3$ (SAP) were less than half that of SAH1. The calcination temperature that resulted in the highest activity (673 K) was much lower than the decomposition temperatures of Sr(OH)$_2$ and SrCO$_3$.

TG-DTA revealed that water of crystallization in Sr(OH)$_2$·8H$_2$O was consumed by hydration of Al(OCH(CH$_3$)$_2$)$_3$. The obtained catalyst precursor was a well-mixed binary hydroxide. Formation of active species of SrO was confirmed by curve deconvolution analysis of the XANES spectra. We conclude that the solid-liquid interface reaction is useful for the preparation of well-mixed binary hydroxides.

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要  旨

水酸化ストロンチウムとアルミニウムアルコキシドとの固-液界面の反応によるSrO-Al2O3固体塩基触媒の合成

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固相のSr(OH)2·8H2Oと2-プロパノールに溶解したAl(OCH(CH3)2)3の固-液界面の反応によって、高濃度に分散したSrO-Al2O3を合成した。Al(OCH(CH3)2)3は、固-液界面の反応中にSr(OH)2·8H2Oの結晶水によって加水分解されたSr(OH)2·8H2Oと同数のAl(OCH(CH3)2)3によって合成し、673 Kで熱処理したSrO-Al2O3は、塩基触媒反応であるジアセトンアルコールのレトロアルドール反応に、Sr(OH)2·8H2OとAl2O3の物理混合で調製した触媒の2倍の活性を示した。最高活性を示す温度は、SrAl2O4の結晶化の温度よりもわずかに低かった。活性種であるSrOはXRDでは検出できず、XANESによって確認した。本研究で使用した固-液界面反応により、簡単な条件でSrOが高濃度にAl2O3に分散した複合金属酸化物を調製できることが明らかとなった。