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Description	

Fine-Crystallized LDHs Prepared with SiO₂ Sphere as Highly Active Solid Base Catalyst

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Abstract

Fine-crystallized layered double hydroxides were prepared by co-precipitation method with coexistence of SiO₂ sphere (SiO₂@LDH), and these base catalysis and structural properties were investigated. As-prepared SiO₂@LDHs exhibited higher base catalysis for the Knoevenagel condensation than conventional LDHs prepared by co-precipitation method in absence of co-existence of SiO₂ sphere. Such increase in activity for base catalysis was also observed in various types of SiO₂@LDHs with different metal compositions (M²⁺: Mg²⁺ or Ni²⁺, M³⁺: Al³⁺ or Ga³⁺, M²⁺/M³⁺: 1 or 3). X-ray diffraction (XRD) measurement suggested that addition of SiO₂ induced the decrease in LDH crystallite size. The results of transmission electron microscopy – energy dispersive X-ray spectroscopy (TEM-EDS) and ²⁹Si cross polarization magic angle spinning nuclear magnetic resonance (²⁹Si CP-MAS NMR) on SiO₂@Mg-Al LDH suggested that the crystal of Mg-Al LDH is immobilized on SiO₂ surface through the Si-O-Al and Si-O-Mg covalent bonds. According to these results, we concluded that the co-precipitation method in the presence of colloidal spherical SiO₂ seeds, especially possessing 40 nm diameter, composed the highly-dispersed points of LDH crystal growth on SiO₂ surface, and which lead the generation of fine-crystallized highly active LDH nanocrystals.

Introduction

Layered double hydroxide (LDH) is one of well-known layered clay minerals which is composed of brucite-like two-dimensional sheets and interlayer anions. A chemical formal of LDH is generally denoted as $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{n-}_{x/n} \cdot mH_2O$, where $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}$ corresponds to two-dimensional sheets consisting of octahedral M²⁺ and M³⁺ complex hydroxide layer. This hydroxide layer possesses positive charge derived from partially substituted M³⁺ ion. Interlayer anions Aⁿ⁻, such as carbonate and hydroxide, and molecular water are inserted to interlayer of complex metal hydroxide layer resulting to compensate for the charge between sheets.¹⁻³ LDHs have been utilized

as various functional materials because of these unique characters. As examples, LDHs can be used to anions removal, drug delivery system, and preparation of nano-scale organic/inorganic hybrid materials such as bio-composite and biosensor because LDHs possess anion-exchange ability: LDHs can intercalate inorganic anions,^{1, 4-5} organic anions and organic molecules.⁶⁻⁸

Additionally, the LDH materials have been widely applied as unique hydrophilic solid base catalyst for variety types of organic reactions by many researchers in the world.⁹⁻²⁸ The identical anions which are adsorbed onto LDH surface, such as OH⁻ and HCO₃⁻, are known to act as base sites. As a solid base catalyst, LDH materials have some unique characteristics described as follows; (i) the base properties are varied in accordance with the composition of metal hydroxide and type of interlayer anions, and (ii) LDHs can be transformed to Lewis acidic and basic bifunctional metal composite oxide by calcination. An enormous number of studies have been devoted to investigate these utility for various organic reactions such as aldol condensation,^{14, 16, 23, 25} Knoevenagel condensation,^{9, 12, 15, 24} epoxidation,^{10-11, 20} transesterification,^{13, 17, 26} and so on. Recently, LDHs have been also utilized to advanced environmental-friendly reactions such as biomass derived saccharides conversion^{18-19, 21-22, 24, 27-28} and photocatalytic conversion of CO₂ in an aqueous solution.²⁹⁻³¹ However, generally the anions in the interlayer space cannot participate in these chemical reactions because the high charge density of the LDHs layers and the high content of anionic species and water molecules result in strong interlayer electrostatic interactions between the sheets.^{3, 32} Therefore, not only the continuous studies for applications of highly active LDH-based solid catalysts but also the improvement of preparation method to upgrade the LDH derived-solid base catalyst have been envisaged.

To overcome this issue and to upgrade the LDH derived-solid base catalyst, two strategies have been proposed; one is the delamination of LDH nanosheets, and the other is the fine-crystallization of LDH crystallite. In 2000, Adachi *et al.* reported the method of delamination of LDHs using various anionic surfactants which will lead to a novel

generation of LDH based materials in which total surface of the layered compound can be rendered accessible for chemical reactivity.³² After that, several reports on delamination of LDHs³³⁻³⁸ and method to prepare nano-hybrid materials composed of LDH nanosheets³⁹⁻⁴³ has been presented. These methods are effective to utilize the flat plane of LDH nanosheets. Actually, various LDH nanosheets-based materials, which possess the laminated structure with other layered materials or metal nanoparticles, have been evaluated on their characteristics and utility as photo- and electro- catalysts.^{39-40, 42} However, in order to improve the base catalysis of LDH itself, the delamination method seems to be insufficient, because the highly reactive sites of catalysts including LDHs are generally considered to be the edges and corners of the crystallites owing to the presence of low coordination state of atoms. As Roeffaers *et al.* reported, in the case of Li-Al LDH, transesterification occurs mainly at the {0001} plane where the basal surface of the LDH crystal, while, ester hydrolysis requires the OH⁻ ions at the {10 $\bar{1}$ 0} faces where the entrance of the galleries.⁴⁴ According to these previous reports, we believe that the both avoidance of *ab*-face stacking and fine-crystallization are required to maximize the base catalysis of LDH.

Immobilization of active species onto the support is one of the general methods to improve the catalytic property by avoidance of aggregation and excess growth of active species. Although the LDHs has often been used as a carrier to immobilize active species, we anticipated that the fine-crystallized LDHs can be prepared if the active LDHs can be immobilized onto the adequate carrier. To date, several nano-LDH materials which possess core-shell, yolk-shell or hollow-shell structure had been demonstrated.⁴⁵⁻⁵⁰ A typical structure generally denoted as SiO₂@LDH is one of a hierarchical core-shell LDH material which promises strategy to avoid the *ab*-face stacking aggregation.⁵⁰ Two type procedures to prepare hierarchical SiO₂@LDH materials have been reported. Shen *et al.* demonstrated that core-shell, yolk-shell and hollow-shell SiO₂@LDH and SiO₂-coated Fe₃O₄ magnetite core-shell Fe₃O₄@SiO₂@LDH material can be obtained by layer-by-layer deposition process followed by *in situ* coating of AlOOH on SiO₂ (~340

nm) or Fe₃O₄@SiO₂ (~310 nm) core surface and successive growth of LDH crystals.⁴⁵⁻⁴⁶ Using similar layer-by-layer method, Wang *et al.* prepared SiO₂@LDH nanoparticles over more small SiO₂ nanoparticles (~50 nm).⁴⁹ Another procedure is a simple method by using an *in situ* co-precipitation to directly deposit LDH precursors on the SiO₂ surface without any binder, reported by Chen *et al.*^{47, 50} Advantages of Chen's reports are (i) the preparation method is very simple and easily handled and (ii) the size of SiO₂ spheres and the composition of LDH as well as the thickness of LDH layer can be controlled.

The LDH nanosheets derived materials, SiO₂@LDH nanoparticles and alkylcarboxylate-intercalated layered hydroxyl double salts, have been evaluated on their characteristics and utility as photo- and electro- catalysts,^{39-40, 42} high active base catalyst for the Knoevenagel condensation⁵¹ and epoxidation,⁵² magnetic separation of proteins,⁴⁵ pseudocapacitance,⁴⁶ flame retardancy of epoxy resins⁴⁸ and adjuvant.⁴⁹ However, there are no reports on investigation of the improvement of base catalysis of LDH itself by fine-crystallization followed by *in situ* growth method of SiO₂@LDH nanoparticles.

The main subject of this research is the improvement of base catalysis of widely-used LDH material with unique strategy. Herein, we establish the small-crystallized LDH catalyst on SiO₂ nanoparticles and compare its base catalysis for the Knoevenagel condensation of benzaldehyde with conventional LDHs. A crystallite property, morphology and correlation between SiO₂ sphere and LDH were investigated by XRD, TEM-EDS and ²⁹Si CP-MAS NMR analytical methods. It is revealed that the coexistence of small SiO₂ sphere surfaces generate the starting points of LDH growth *via* Si-O-M covalent bond formation, leading to the fine-crystal LDH forming and enhancement of base catalysis for the Knoevenagel condensation.

Experimental

Materials and synthesis of catalysts

Tetraethyl orthosilicate (TEOS), triethanolamine (TEA) and benzaldehyde were purchased from Sigma-Aldrich Inc. Sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH) and toluene were supplied by Kanto Chem. Co. Ltd. Cetyltrimethylammonium bromide (CTAB), aqueous solution of ammonium (25%), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminium nitrate enneahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), gallium nitrate *n*-hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$) and benzoic acid were obtained from Wako Pure Chemical Ind., Ltd. Co. Urea and ethyl cyanoacetate were purchased from Junsei Chemical Co., Ltd. and Tokyo Chemical Ind., Co., Ltd., respectively. The commercial Mg-Al(3)LDH (denoted as LDH(com.)) was obtained from Tomita Pharmaceutical Co., Ltd.

Spherical SiO_2 (40nm) was prepared according to the previous reports.^{49, 53} 96 mmol of TEA and 2 mL of TEOS were combined in a 200 mL of eggplant flask. The two-phase mixture was heated in an oil bath at 363 K for 20 min without stirring. When the mixture was taken out from the oil bath, 26.0 mL of an aqueous solution (2.8 wt%) of CTAB pre-heated at 333 K was immediately added as structure directing agent in a condensation process, and then continuously stirred for 24 h at room temperature. Thereafter, the resulting mixture was added in 50 mL of ethanol to obtain colloidal aqueous suspension. The obtained precipitate was centrifuged for 5 min at 4000 rpm. After decantation, the sediment was re-dispersed through vigorous stirring in 50 mL of an ethanolic solution of ammonium nitrate (20 g L^{-1}) and then refluxed for 1 h. This procedure was repeated three times. Then, the same operation was also performed with a solution of concentrated hydrochloric acid in ethanol (5 g L^{-1}) to replace the ammonium ions. The final sediment was washed with ethanol, and then dried *in vacuo*. The obtained spherical SiO_2 powder was calcined at 823 K under 1 L min^{-1} of air flow for 6 h.

Spherical SiO₂(250nm) was prepared using a modified literature method.⁵⁰ 13.5 mmol of TEOS was added to a mixed solution of 6.45 mL of ammonia (25 wt%), 23.55 mL of water and 50 mL of ethanol. The white suspension was stirred for 17 h at room temperature, and then centrifuged for 1 min at 4000 rpm. The obtained sediment was washed with ethanol, and then dried *in vacuo*. The resulting spherical SiO₂ powder was calcined at 823 K under 1 L min⁻¹ of air flow for 6 h.

The SiO₂(X)@M²⁺-M³⁺(Y)LDH catalysts (X: desired size of spherical SiO₂; 40 nm or 250 nm, Y: M²⁺/M³⁺ mol ratio; 1 or 3) were prepared *via* an *in situ* co-precipitation method according to a previous report.⁵⁰ Spherical SiO₂ particles with the desired size were dispersed in 20 mL of water using ultrasound treatment. After 30 min, the 0.96 mmol of Na₂CO₃ was added to the solution and a further 5 min of sonication was carried out. 19.2 mL of metal nitrates aqueous solution ([M²⁺] + [M³⁺] = 0.075 M) was slowly dropped into the above spherical SiO₂ dispersed solution under stirring at room temperature. The pH was maintained at 10.0 by an aqueous NaOH solution (1 M) during titration. The obtained suspension was stirred further 1 h. The resulting paste was filtered, washed with 1 L of water and ethanol, and then dried at 383 K overnight. The Si/(M²⁺+M³⁺) atomic ratios were basically adjusted to 0.50.

The M²⁺-M³⁺(3)LDH(CP) was synthesized by co-precipitation method. An aqueous solution of M²⁺(NO₃)₂·mH₂O and M³⁺(NO₃)₃·nH₂O (M²⁺/M³⁺ = 3, [M²⁺] + [M³⁺] = 0.075 M, 19.2 mL) was slowly dropped into an aqueous Na₂CO₃ solution (0.048 M, 20 mL) with stirring at room temperature. The pH was kept to 10.0 by an aqueous NaOH solution (1 M) during titration. The obtained mixture was stirred further 1 h. The resulting paste was filtered, washed with 1 L of water and ethanol, and then dried at 383 K overnight. These LDHs are denoted as M²⁺-M³⁺(Y)LDH or LDH(CP).

The Mg-Al(3)LDH(U-CP) was prepared by urea co-precipitation method. 5.625 mmol of Mg(NO₃)₂·6H₂O, 1.875 mmol of Al(NO₃)₃·9H₂O and 17.5 mmol of urea were dissolved in 500 mL of water, and then stirred at 373 K for 48 h. After cooling for 2 h, the obtained sediment was filtered, washed with 1.5 L of water and then dried at 333 K

overnight. This LDH is denoted as LDH(U-CP).

Reaction

Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate was performed in a 20 mL of Shlenk tube under an N₂ flow (30 mL min⁻¹). The reaction was typically performed using 1.0 mmol of benzaldehyde, 1.2 mmol of ethyl cyanoacetate, 10 mg of catalysts and 3 mL of toluene at 313 K. The obtained products were analysed using GC-FID (SHIMADZU GC-2014) equipped with a polar column (Agilent, DB-FFAP).

Characterizations

X-ray diffraction patterns (XRD) were collected on a SmartLab (Rigaku) using Cu K α X-ray source (40 kV, 30 mA). The LDH (003) and (110) crystallite sizes were calculated by the Scherrer equation; $D_{hkl} = K\lambda/(\beta\cos\theta)$ (K : Scherrer number (0.9), λ : incident ray wavelength (0.1542 nm), β : peak width at half height (rad), θ : Bragg angle). ²⁹Si cross polarization magic angle spinning nuclear magnetic resonance (²⁹Si CP-MAS NMR) measurements were performed on a AVANCE III 500 MHz (Bruker) in a 4 mm ZrO₂ rotor. The spinning rate was 8 kHz. The ²⁹Si chemical shifts are referenced to hexamethyl cyclotrisiloxane (taken to be at $\delta = -9.6875$ ppm). Scanning electron microscope (SEM) images were collected on a S-4500 (Hitachi). The sample powder was fixed onto a carbon tape and pretreated with a PtPd ion-sputter (Hitachi, E-1030) to reduce charge up issue. Transmission electron microscopy (TEM) images were taken using a H-7100 (Hitachi) at 100 kV. TEM-energy dispersive X-ray spectroscopy (TEM-EDS) elemental mapping was obtained by a JEM-ARM200F (JEOL) at 200 kV. N₂ adsorption measurements were carried out to determine the BET (Brunauer-Emmett-Teller) specific surface area for spherical SiO₂. The measurements were conducted at 77 K on a BELSORP-max (BEL Japan, Inc.). Inductively coupled plasma - atomic emission spectrometry (ICP-AES) was operated on the iCAP6300Duo (Thermo Fisher Sci.) to estimate the amount of precipitated M(OH)_x and SiO₂ in SiO₂@LDHs.

Results and discussion

Synthesis and base catalysis evaluation of $\text{SiO}_2(40\text{nm})@M^{2+}\text{-}M^{3+}\text{LDHs}$

Preliminarily, we prepared $\text{SiO}_2(40\text{nm})@LDHs$ with various combinations and composition ratios of metal hydroxide (Mg-Al, Ni-Al and Mg-Ga type LDH with M^{2+}/M^{3+} ratio of 1 or 3) in order to investigate the correlation between these base catalytic activities and structural properties. The particle diameter of spherical $\text{SiO}_2(40\text{nm})$ was confirmed by TEM observation as about 40 nm (Fig. 1(A)). SEM images suggested that SiO_2 spheres were uniformly distributed as shown in Fig. 1(B)). N_2 adsorption-desorption isotherm of spherical $\text{SiO}_2(40\text{nm})$ showed type IV isotherm (Fig. S1), and its specific surface area calculated by BET-theory was $1081\text{ m}^2\text{ g}^{-1}$.

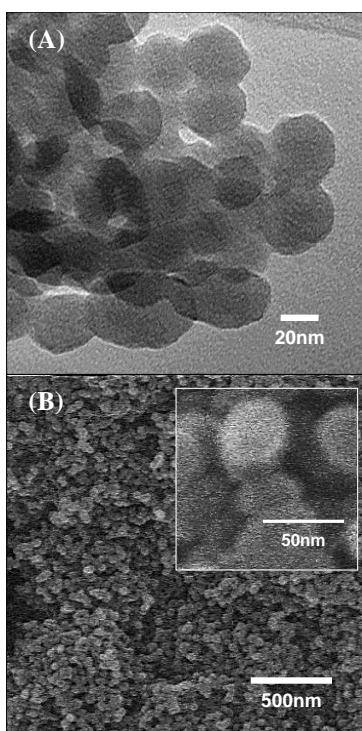


Figure 1 (A) TEM image and (B) SEM images of spherical $\text{SiO}_2(40\text{ nm})$.

Next, we synthesized various $\text{SiO}_2(40\text{nm})@M^{2+}\text{-}M^{3+}$ LDHs with M^{2+}/M^{3+} ratio of 3 by a co-precipitation with coexistence of obtained $\text{SiO}_2(40\text{nm})$ sphere. The actual ratios of $\text{Si}/(M^{2+}+M^{3+})$ and M^{2+}/M^{3+} in obtained materials were summarized in Table S1. The possibility of the residual sodium cation in the $M^{2+}\text{-}M^{3+}(3)$ type LDHs were negligible in all $M^{2+}\text{-}M^{3+}(3)$ type LDHs, evidenced by XPS (Fig. S2).

Fig. 2 shows time courses of benzaldehyde conversion in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate over various $M^{2+}\text{-}M^{3+}(3)$ LDHs and $\text{SiO}_2(40\text{nm})@M^{2+}\text{-}M^{3+}(3)$ LDHs. It was clearly shown that $\text{SiO}_2(40\text{nm})@M^{2+}\text{-}M^{3+}(3)$ LDHs efficiently mediated the Knoevenagel condensation than $M^{2+}\text{-}M^{3+}(3)$ LDHs in all type LDHs. The reaction rates for the Knoevenagel condensation were calculated using reaction constant k which were estimated from the rate equation of pseudo first-order reaction, and summarized in Table 1. In the case of Mg-Al type LDH, the reaction rate for Mg-Al(3)LDH was $77 \text{ mmol g}^{-1} \text{ h}^{-1}$ whereas that of $\text{SiO}_2(40\text{nm})@Mg\text{-Al}(3)$ LDH was increased to $117 \text{ mmol g}^{-1} \text{ h}^{-1}$. The increases of reaction rate by coexistence of spherical $\text{SiO}_2(40\text{nm})$ were more prominent in the case of Ni-Al and Mg-Ga type LDHs, and these values were respectively improved from 26 to $61 \text{ mmol g}^{-1} \text{ h}^{-1}$ and from 23 to $59 \text{ mmol g}^{-1} \text{ h}^{-1}$. It is noted that the blank test and bare $\text{SiO}_2(40\text{nm})$ sphere gave no product for the Knoevenagel condensation. Thus, these results clearly indicate that co-existence of SiO_2 acts as a promoter for the base catalysis on LDHs.

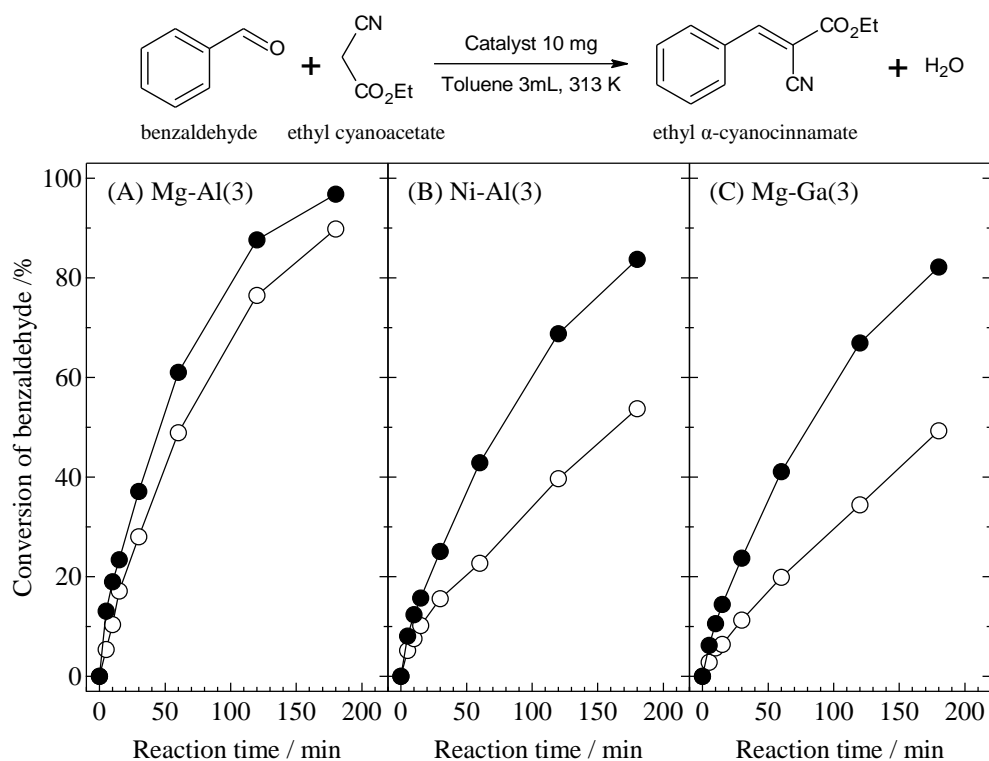


Figure 2 Activities of (○) $\text{M}^{2+}\text{-M}^{3+}(3)\text{LDH}$ and (●) $\text{SiO}_2(40\text{nm})@\text{M}^{2+}\text{-M}^{3+}(3)\text{LDH}$ with various metal compositions for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. *Reaction conditions:* benzaldehyde (1.0 mmol), ethyl cyanoacetate (1.2 mmol), catalyst (10 mg), toluene (3 mL), 313 K, N_2 flow (30 mL min^{-1}).

Table 1 Correlation between base activity and base property of $\text{M}^{2+}\text{-M}^{3+}(3)\text{LDHs}$ and $\text{SiO}_2(40\text{nm})@\text{M}^{2+}\text{-M}^{3+}(3)\text{LDHs}$.

Catalyst		Reaction rate ^a / mmol g ⁻¹ h ⁻¹	Base amount ^b / mmol g ⁻¹	$\text{M}(\text{OH})_x$ amount ^c / mmol g ⁻¹	Base/ $\text{M}(\text{OH})_x$ ^d / %
Mg-Al(3)	LDH	76.9	0.45	12.16	3.7
	$\text{SiO}_2@\text{LDH}$	116.7	0.48	8.27	5.8
Ni-Al(3)	LDH	25.5	0.30	9.35	3.2
	$\text{SiO}_2@\text{LDH}$	60.6	0.44	7.12	6.2
Mg-Ga(3)	LDH	23.1	0.12	10.62	1.1
	$\text{SiO}_2@\text{LDH}$	58.8	0.37	7.52	4.9

^aReaction rate for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

^bBase amount calculated from poisoning test by benzoic acid titration.

^cTotal metal M^{2+} and M^{3+} hydroxide amount calculated by ICP-AES.

^dBase amount per total metal hydroxide amount.

Fig. 3 showed XRD patterns of various $M^{2+}-M^{3+}(3)$ LDHs and $SiO_2(40nm)@M^{2+}-M^{3+}(3)$ LDHs. Clear reductions in the crystalline by coexistence of spherical $SiO_2(40nm)$ were observed in all type LDHs. Crystal properties obtained from XRD patterns are summarized in Table 2. The both crystallite sizes of stacking direction and plane direction, respectively denoted as $D(003)$ and $D(110)$ in $SiO_2(40nm)@M^{2+}-M^{3+}(3)$ LDHs, were clearly smaller than those of $M^{2+}-M^{3+}(3)$ LDHs, indicating coexistence of spherical $SiO_2(40nm)$ inhibited the crystal growth of LDH in not only stacking direction but also plane direction. Since there were no significant change in the lattice parameter a and c between $M^{2+}-M^{3+}(3)$ LDHs and $SiO_2(40nm)@M^{2+}-M^{3+}(3)$ LDHs, the coexistence of spherical $SiO_2(40nm)$ did not affect LDH unit structures. These results suggested that (i) coexistence of spherical $SiO_2(40nm)$ inhibits the crystal growth of LDH, (ii) the obtained $SiO_2(40nm)@M^{2+}-M^{3+}(3)$ LDHs

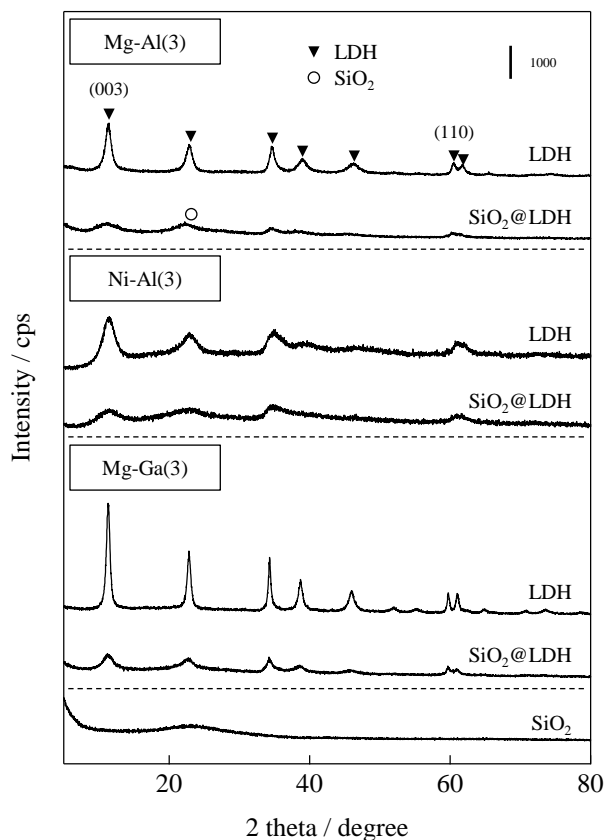


Figure 3 XRD patterns of $M^{2+}-M^{3+}(3)$ LDHs and $SiO_2(40nm)@M^{2+}-M^{3+}(3)$ LDHs.

possess higher activity for the basic Knoevenagel condensation than conventional M^{2+} - M^{3+} (3)LDHs, and (iii) those effects are similarly evolved in the cases of Mg-Al, Ni-Al and Mg-Ga type LDHs.

Table 2 Crystal properties of M^{2+} - M^{3+} (3)LDHs and $SiO_2(40nm)@M^{2+}$ - M^{3+} (3)LDHs.

Catalyst		Lattice parameter c / nm	Crystallite size (003) ^a / nm	Lattice parameter a / nm	Crystallite size (110) ^a / nm
Mg-Al(3)	LDH	2.33	7.6	0.31	13.4
	$SiO_2@LDH$	2.43	2.8	0.31	8.3
Ni-Al(3)	LDH	2.31	4.0	0.30	8.1
	$SiO_2@LDH$	2.35	2.4	0.30	4.1
Mg-Ga(3)	LDH	2.34	13.0	0.31	24.8
	$SiO_2@LDH$	2.34	4.7	0.31	14.0

^aThe crystallite sizes of LDHs were calculated by Scherrer equation; $D_{hkl} = K\lambda/\beta\cos\theta$ (K : Scherrer number (0.9), λ : incident ray wavelength (0.1542 nm), β : peak width at half height (rad)).

To evaluate versatility, we prepared M^{2+} - M^{3+} (1)LDHs and $SiO_2(40nm)@M^{2+}$ - M^{3+} (1)LDHs, and then applied these catalysts to the Knoevenagel condensation. Because base activities of $M^{2+}/M^{3+} = 1$ type LDHs were much lower than $M^{2+}/M^{3+} = 3$, the Knoevenagel condensation was carried out using substrates with half scale. As shown in Fig. S3, $SiO_2(40nm)@M^{2+}$ - M^{3+} (1)LDHs showed higher activity than conventional M^{2+} - M^{3+} (1)LDHs in all combinations of metal hydroxides. The reaction rates were increased by coexistence of spherical $SiO_2(40nm)$, from 7.6 to 20 $mmol\ g^{-1}\ h^{-1}$, from 9.6 to 29 $mmol\ g^{-1}\ h^{-1}$ and from 15 to 20 $mmol\ g^{-1}\ h^{-1}$ in the case of Mg-Al, Ni-Al and Mg-Ga type LDHs, respectively. Reductions in the crystalline by coexistence of spherical $SiO_2(40nm)$ were also observed from XRD patterns as shown in Fig. S4. As same as M^{2+} - M^{3+} (3) type LDHs, the lattice parameter c are almost identical between M^{2+} - M^{3+} (1)LDHs and $SiO_2(40nm)@M^{2+}$ - M^{3+} (1)LDHs whereas LDH (003) plane

crystallite sizes were reduced from 3.6 nm to 3.0 nm and from 9.7 nm to 3.4 nm in Mg-Al(1) and Mg-Ga(1) type LDHs, respectively. The reduction of crystallite size in plane direction is also observed in Mg-Al (1) and Mg-Ga(1) type LDHs whereas lattice parameter a does not change. The lattice parameter c and (003) plane crystallite size of $\text{SiO}_2(40\text{nm})@\text{Ni-Al}(1)\text{LDH}$ were hardly estimated because of the low intensity of diffraction peak. The lattice parameter a and (110) crystallite size of $\text{Ni-Al}(1)\text{LDH}$ and $\text{SiO}_2(40\text{nm})@\text{Ni-Al}(1)\text{LDH}$ were also hardly estimated. These results indicated that the suppression of the crystal growth and increase of base activity were also observed in $\text{M}^{2+}/\text{M}^{3+} = 1$ type LDHs.

Correlation between catalytic activity and base property

Next, we investigated the correlation between base activity and basicity of $\text{M}^{2+}/\text{M}^{3+} = 3$ type LDHs. Base amounts were estimated by the Knoevenagel condensation in the presence of benzoic acid agent: *i.e.* because the benzoic acid interfered the basic sites of LDH for the Knoevenagel condensation, the correlation between the amounts of benzoic acid and product of ethyl α -cyanocinnamate showed a linear relationship leading to the base amount. Table 1 summarizes reaction rate for the Knoevenagel condensation and base amount of LDHs. Total divalent and trivalent metal hydroxide amount ($\text{M}(\text{OH})_x$ amount) obtained from ICP-AES and base amount per total metal hydroxide amount ($\text{Base}/\text{M}(\text{OH})_x$) are also listed in Table 1. Compared with conventional $\text{M}^{2+}-\text{M}^{3+}(3)\text{LDHs}$, $\text{M}(\text{OH})_x$ values were *ca.* 24~32% reduced in $\text{SiO}_2(40\text{nm})@\text{M}^{2+}-\text{M}^{3+}(3)\text{LDHs}$ because of the coexistence of spherical $\text{SiO}_2(40\text{nm})$. On the other hand, the $\text{Base}/\text{M}(\text{OH})_x$ ratios were 1.6~4.5 times increased by coexistence of spherical $\text{SiO}_2(40\text{nm})$. This suggests that coexistence of spherical $\text{SiO}_2(40\text{nm})$ plays crucial role to increase the number of hydroxide layers acting as surface base sites, and it would be contributed to the enhancement in the base catalysis for the Knoevenagel condensation in the cases of $\text{SiO}_2(40\text{nm})@\text{M}^{2+}-\text{M}^{3+}(3)\text{LDHs}$.⁶¹

The morphology and interaction between SiO_2 and LDH in $\text{SiO}_2(40\text{nm})@\text{Mg-Al}(3)\text{LDH}$ were investigated by TEM and ²⁹Si CP-MAS NMR

experiment. Fig. 4 showed TEM images of Mg-Al(3)LDH and SiO₂(40nm)@Mg-Al(3)LDH. The platen crystal size of SiO₂(40nm)@Mg-Al(3)LDH was smaller than that of Mg-Al(3)LDH. Besides, since SiO₂ spheres that should coexist in SiO₂(40nm)@Mg-Al(3)LDH was hardly observed in Fig. 4(B), we applied EDS elemental mapping to SiO₂(40nm)@Mg-Al(3)LDH as shown in Fig. 5. It was confirmed that Mg and Al was uniformly dispersed in wide range whereas Si was prejudiced and covered with Mg and Al to form SiO₂ core — LDH shell like structure (Fig. 5 (A)-(E)). Same trend was observed in high magnification visual fields (Fig. 5 (F)-(J)). Moreover, the shape of SiO₂ was not spherical but shapeless. These results suggested that spherical structure of SiO₂ was crumbled in the course of catalyst preparation, and was transferred to the shapeless structure. Because it is well known that SiO₂ is dissolved in basic condition, SiO₂(40nm) spheres possessing small high specific surface area would be partially dissolved and reprecipitated in the course of LDH crystal growth method. In fact, when we treated spherical SiO₂(40nm) in basic condition (pH = 10) for 1 h at room temperature, it formed shapeless structure (Fig. S5).⁶²

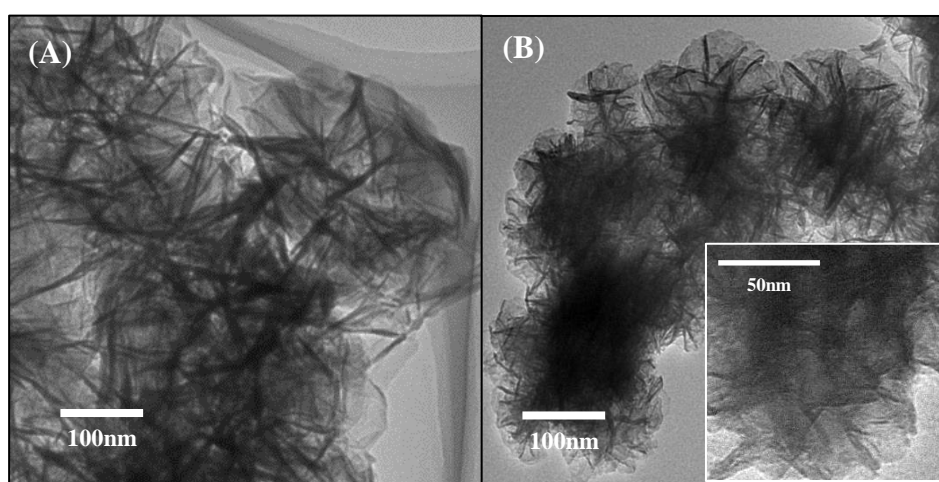


Figure 4 TEM images of (A) Mg-Al(3)LDH and (B) SiO₂(40nm)@Mg-Al(3)LDH.

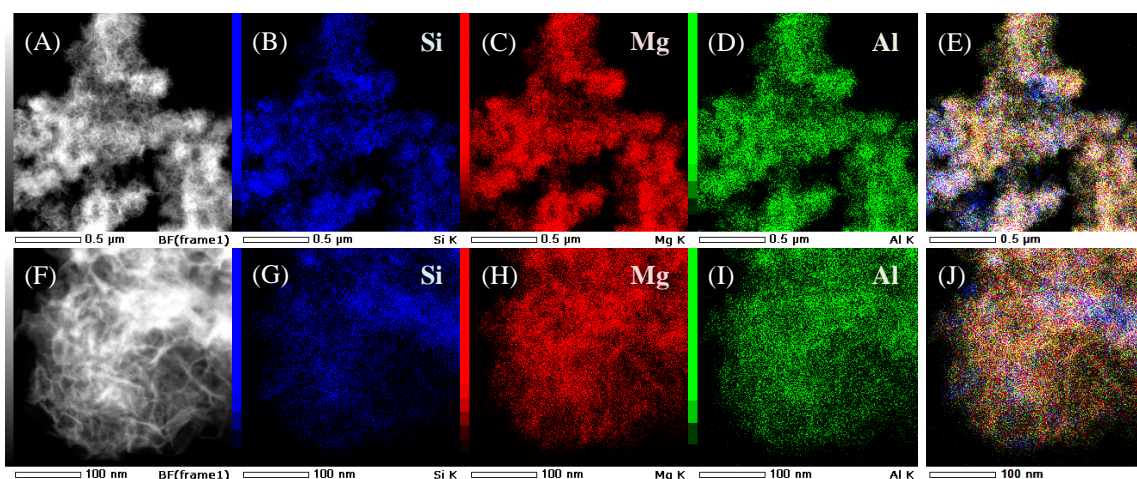


Figure 5 (A, F) Dark-field TEM images. Also shown are (B-E), (G-J) EDS mapping results of $\text{SiO}_2@\text{Mg-Al}(3)\text{LDH}$. (A-E): Low magnification visual field, and (F-J): high magnification visual field.

Fig. 6 shows the ^{29}Si CP-MAS NMR spectra of spherical SiO_2 and $\text{SiO}_2(40\text{nm})@\text{Mg-Al}(3)\text{LDH}$. Q^n designated the Si-centered tetrahedral structural species where Q refers to silicon atom and n denotes the number of bridging oxygens. The ^{29}Si CP-MAS NMR of spherical $\text{SiO}_2(40\text{nm})$ showed three peaks at -91, -100, and -109 ppm which respectively correspond to Q^2 , Q^3 , and Q^4 .⁵⁴⁻⁵⁶ On the other hand, $\text{SiO}_2(40\text{nm})@\text{Mg-Al}(3)\text{LDH}$ showed a broad resonance between -70 to -115 ppm, which can be deconvoluted into four peaks centered at -78, -85, -92, and -101 ppm. The peak at -78 ppm can be assigned to Q^0 and/or Q^1 species⁵⁵ generated because of dissolution and reprecipitation of SiO_2 sphere. Reportedly, Si-centered tetrahedral structure which possess Si-O-Al and Si-O-Mg bond gave some resonances between -73 to -105 ppm^{50, 57-59} and -70 to -93 ppm,^{56, 60} respectively, as described in Table S2. According to previous reports, the two signals appearing at -85 and -92 ppm were assigned respectively to Si-centered compound which has Si-O-Mg and/or Si-O-Al bonds as well as overlapping with Q^2 . This strongly indicates that LDH sheets and SiO_2 do not interact only by electrostatic force but also the formation of Si-O-Al and Si-O-Mg covalent bonds. According to these results, the mechanism of generation of nano-crystallized

Mg-Al LDH on SiO₂ spheres is predicted as follows: (i) a part of SiO₂ tetrahedral dissolves and reprecipitates (e.g. $2Q^n \leftrightarrow Q^{n+1} + Q^{n-1}$) in a basic mother solution, (ii) titrated Mg²⁺ and Al³⁺ ions in basic mother solution adsorb on unsaturated Si-O sites of SiO₂ surface, cause dispersion of starting points of LDH crystal growth, (iii) LDH nanosheets grow up from each dispersed points on SiO₂ to lead generation of small crystallite size LDH.

Evaluation of base catalysis on Mg-Al(3)LDHs with various crystalline

To evaluate the correlation between crystalline of LDH and base catalysis on LDH or SiO₂@LDH, Mg-Al(3)LDH catalysts were prepared by various methods to assess these structural properties and catalytic activities for the Knoevenagel condensation. LDH(U-CP) and SiO₂(250nm)@LDH, synthesized respectively by an urea

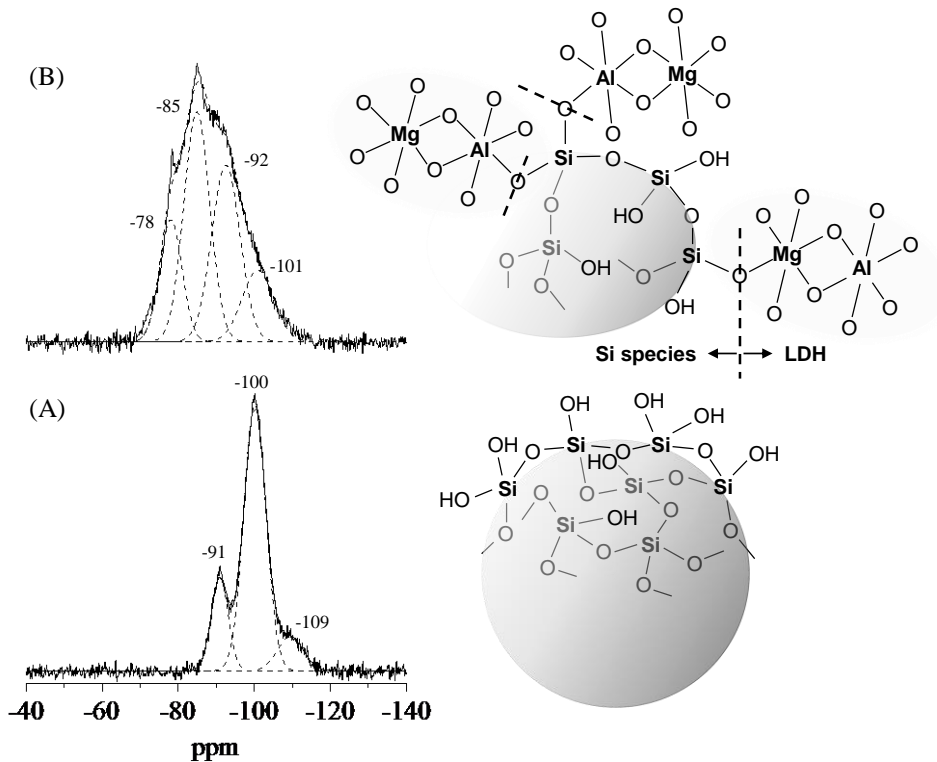


Figure 6 ²⁹Si CP-MAS NMR spectra of (A) spherical SiO₂(40nm) and (B) SiO₂(40nm)@Mg-Al(3)LDH.

co-precipitation method and an *in situ* co-precipitation method with coexisting of SiO₂(250nm) spheres, were prepared in addition to LDH(CP) and SiO₂(40nm)@LDH. LDH(com.) purchased from Tomita Pharmaceutical Co., Ltd. was also evaluated its crystalline and base catalysis as a comparison.

Fig. 7 shows TEM images of five different Mg-Al(3)LDHs. LDH(U-CP) has well crystalline hexagonal structure. Orientations of most of LDH crystals in LDH(U-CP) and LDH(com.) are face up whereas these of SiO₂@LDHs and LDH(CP) are random, indicating the *ab*-face crystal sizes of LDH(U-CP) and LDH(com.) are bigger than LDH(CP). Moreover, the observed crystal size of SiO₂(40nm)@LDH was clearly smaller than that of SiO₂(250nm)@LDH, LDH(CP), and LDH(U-CP). SiO₂(250nm)@LDH possess a defined core-shell structure as well as result reported by Chen,⁵⁰ and its LDH crystal size was similar to that of LDH(CP).

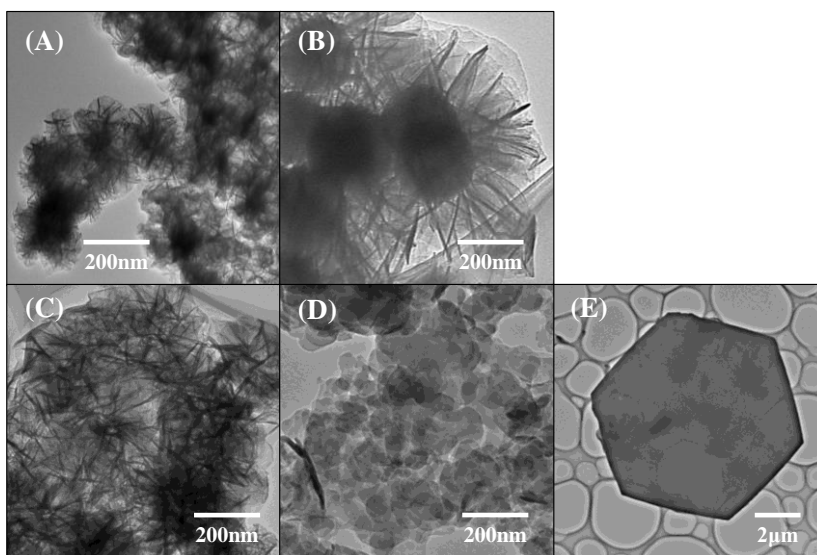


Figure 7 TEM image of various Mg-Al(3) type LDHs. (A)SiO₂(40nm)@LDH, (B) SiO₂(250nm)@LDH, (C) LDH(CP), (D) LDH(com.) and (E) LDH(U-CP).

Fig. 8 shows XRD patterns of various Mg-Al(3)LDHs. Lattice parameters and LDH (003) or (110) crystallite sizes are listed in Table 3. Similar diffraction patterns and lattice parameters were observed in all samples, indicating those LDHs composed of same LDH unit.

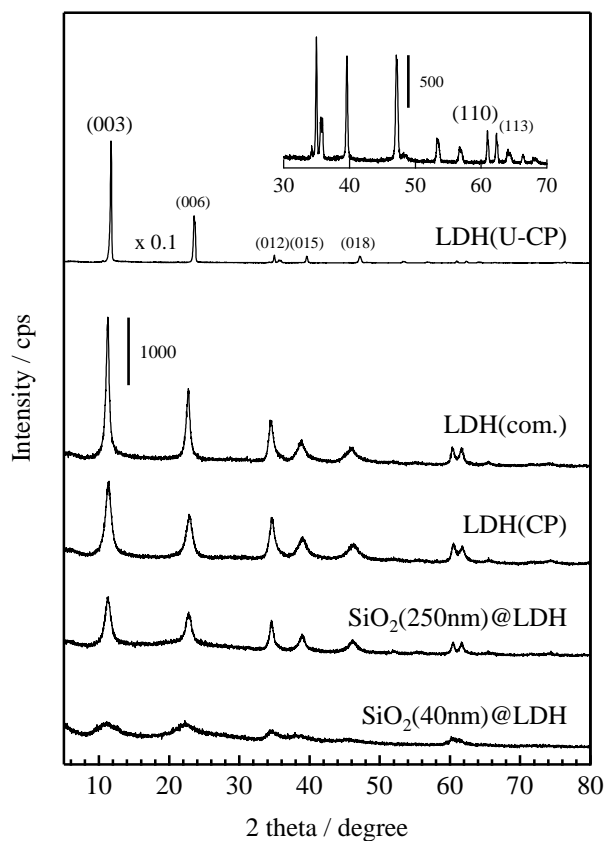


Figure 8 XRD patterns of various Mg-Al(3) type LDHs.

Table 3 Crystal properties of various Mg-Al(3)LDHs.

Type of Mg-Al(3)LDH	Lattice parameter c / nm	Crystallite size (003) ^a / nm	Lattice parameter a / nm	Crystallite size (110) ^a / nm
SiO ₂ (40nm)@LDH	2.43	2.8	0.31	8.3
SiO ₂ (250nm)@LDH	2.35	7.9	0.31	20.0
LDH(CP)	2.33	7.6	0.31	13.4
LDH(com.)	2.36	14.8	0.31	18.4
LDH(U-CP)	2.26	37.8	0.30	49.6

^aThe crystallite sizes of LDHs were calculated by Scherrer equation; $D_{hkl} = K\lambda/\beta\cos\theta$ (K : Scherrer number (0.9), λ : incident ray wavelength (0.1542 nm), β : peak width at half height (rad)).

The crystallite sizes of LDH(U-CP) and LDH(com.) were bigger than SiO₂@LDHs and LDH(CP), as expected by TEM images. Interestingly, crystallite size of SiO₂(40nm)@LDH was smaller than LDH(CP) whereas that of SiO₂(250nm)@LDH was little bigger than LDH(CP), indicating coexistence of spherical SiO₂(250nm) is not suitable for fine-crystallization of LDH. Fig 9(A) shows ²⁹Si CP-MAS NMR spectra of SiO₂(250nm) sphere. Although the broad peak between -80 to -120 ppm could be deconvoluted into three peaks centered at -92, -101, and -110 ppm as well as SiO₂(40nm) sphere, ratios of these peaks in SiO₂(40nm) sphere and SiO₂(250nm) sphere were different as shown in Table S3; the ratio for Q⁴, assigned to bridging saturation silicon, in SiO₂(250nm) sphere (25%) was higher than SiO₂(40nm) sphere (11%) whereas ratios for unsaturated silicon Q³ and Q² in SiO₂(250nm) sphere was lower than SiO₂(40nm) sphere. Moreover, S_{BET} of SiO₂(250nm) sphere (50 m² g⁻¹) was much lower than SiO₂(40nm) sphere (1081 m² g⁻¹). These indicate that the surface of SiO₂(40nm) sphere possess more adsorption sites for Mg²⁺ and Al³⁺ ions than

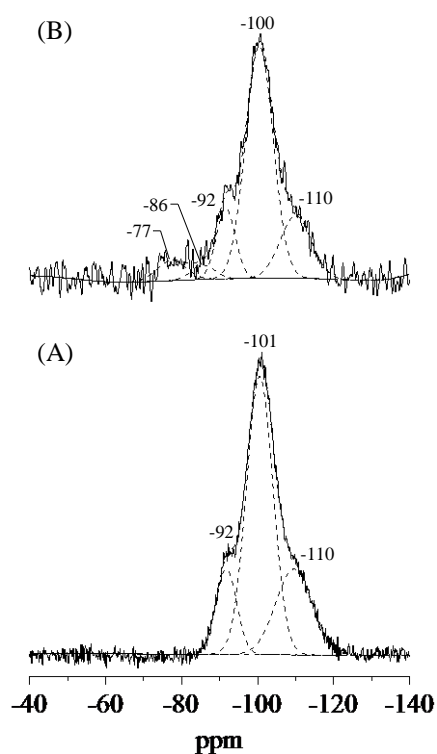


Figure 9 ²⁹Si CP-MAS NMR spectra of (A) spherical SiO₂(250nm) and (B) SiO₂(250nm)@Mg-Al(3)LDH.

SiO₂(250nm) sphere. In fact, the ratio for ²⁹Si CP-MAS NMR peak in SiO₂(250nm)@LDH (Fig. 9(B)), the degree of interactions between the SiO₂ and the LDH crystal, was only ≤ 16% whereas that of SiO₂(40nm)@LDH was ≤ 68%. These results strongly suggest that the size and surface area of spherical SiO₂ are the crucial factors to generate a small crystallite size LDH because a small spherical SiO₂ which possess high surface area can be expected to be in contact with Mg²⁺ and Al³⁺ ions, leading to enhance the dispersion of starting points of LDH crystal growth.

Catalytic activities for the Knoevenagel condensation are shown in Fig. 10 as time course of benzaldehyde conversion (Fig. 10(A)) and reaction rate (Fig. 10(B)), respectively. A high crystalline LDH(U-CP) hardly showed catalytic activity. Although LDH(com.) enhanced the Knoevenagel condensation, reaction rate was only 14 mmol g⁻¹ h⁻¹. Remarkably, SiO₂(40nm)@LDH showed the highest activity with reaction rate of 117 mmol g⁻¹ h⁻¹ as

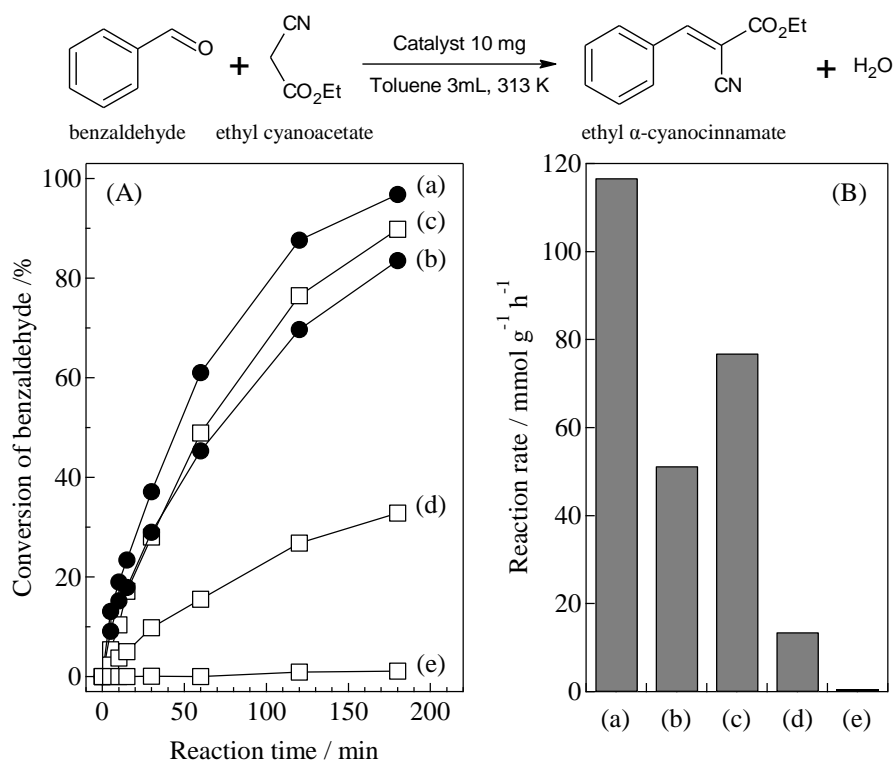


Figure 10 Activities of various Mg-Al(3) type LDHs (a) SiO₂(40nm)@LDH, (b) SiO₂(250nm)@LDH, (c) LDH(CP), (d) LDH(com.) and (e) LDH(U-CP) for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate as (A) time cause and (B) reaction rate. *Reaction conditions:* benzaldehyde (1.0 mmol), ethyl cyanoacetate (1.2 mmol), catalyst (10 mg), toluene (3 mL), 313 K, N₂ flow (30 mL min⁻¹).

previously described. Although SiO₂(250nm)@LDH resulted reaction rate of 60 mmol g⁻¹ h⁻¹, its activity was little lower than LDH(CP) (77 mmol g⁻¹ h⁻¹). This strongly suggests that catalytic activity is affected by not only morphologies of LDH catalysts (*ex.* SiO₂ core – LDH shell structure) but also LDH crystallite size. On the basis of ICP-AES results, we calculated the amount of LDH structure (wt%) in the various Mg-Al(3)LDHs as shown in Table S4. The reaction rate per each LDH structure was also plotted with both LDH(003) and LDH(110) crystallite sizes in Fig.S7. These data clearly showed that the catalytic activity of obtained LDH is drastically changed by the crystallite sizes, and this tendency became significant especially below crystallite sizes of 20 nm; the catalytic activity of LDH increased with decreasing of crystallite sizes. These results support that the fine-crystallization of LDH crystallite is a crucial factor to increase the base catalysis of LDH materials.

Base amounts and apparent TOF of each base sites (TOF_{base}) in various Mg-Al(3)LDHs are listed in Table 4. Base amount of SiO₂(250nm)@LDH estimated to 0.29 mmol g⁻¹ is little lower than LDH(CP) whereas apparent TOF_{base} of both SiO₂(250nm)@LDH and LDH(CP) are similar. Because crystallite of SiO₂(250nm)@LDH is similar to that of LDH(CP), it is suggested that coexistence of SiO₂(250nm) results to just immobilize LDH crystal onto SiO₂ surface without avoiding the *ab*-face stacking, so that reaction rate was smaller than LDH(CP) whereas TOF_{base} was not changed. On the other hand, SiO₂(40nm)@LDH showed higher base amount and apparent TOF_{base} than LDH(CP), indicating effects of coexistence of SiO₂(40nm) is not only

Table 4 Correlation between base activity and base property of various Mg-Al(3)LDHs.

Type of Mg-Al(3)LDH	Reaction rate ^a / mmol g ⁻¹ h ⁻¹	Base amount ^b / mmol g ⁻¹	TOF _{base} / h ⁻¹
(a) SiO ₂ (40nm)@LDH	116.7	0.48	243
(b) SiO ₂ (250nm)@LDH	59.5	0.29	205
(c) LDH(CP)	76.9	0.45	171
(d) LDH(com.)	13.6	0.13	105
(e) LDH(U-CP)	0.5	n.d.	n.d.

^aReaction rate for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

^bBase amount calculated from poisoning test by benzoicacid titlation.

increase total base amount of LDH where the exchanged OH^- ions at the entrance of the galleries but also increase ratio of higher active site on LDH surface by fine-crystallization.

Conclusions

Highly active $\text{SiO}_2(40\text{nm})@LDH$ catalysts were synthesized by co-precipitation method with coexistence of small SiO_2 sphere whose particle size of *ca.* 40 nm. The results of XRD suggested that the crystallite sizes of $\text{SiO}_2(40\text{nm})@LDHs$ were smaller than conventional LDHs prepared by co-precipitation method without coexistence of SiO_2 sphere. All $\text{SiO}_2(40\text{nm})@LDHs$ showed higher catalytic activity for the Knoevenagel condensations of benzaldehyde with ethyl cyanoacetate than conventional LDHs regardless of metal compositions and ratios. Detailed characterizations on $\text{SiO}_2(40\text{nm})@Mg-Al(3)LDH$ using TEM-EDS and ^{29}Si CP-MAS NMR clearly revealed that $\text{SiO}_2(40\text{nm})@Mg-Al(3)LDH$ forms SiO_2 core – LDH shell like structure with Si-O-Al and Si-O-Mg covalent bonds, indicating LDH crystal is immobilized on SiO_2 surface. Additionally, in comparison with various type of Mg-Al(3)LDHs prepared with different SiO_2 size and/or preparation method, the $\text{SiO}_2(40\text{nm})@Mg-Al(3)LDH$ prepared by co-precipitation method has the smallest LDH crystallite and gave the highest catalytic activity among all. Accordingly, we concluded that utilization of spherical $\text{SiO}_2(40\text{nm})$ seeds in co-precipitation method effectively generate the fine-crystallized LDH nanocrystal with high activity for base catalysis, because the high surface area and abundant Si-O sites derived from SiO_2 seeds gave highly-dispersed starting points of LDH crystal growth on SiO_2 surface.

In this paper, we successfully obtained highly active fine-crystallized LDHs *via* co-precipitation method with coexistence of SiO_2 sphere seeds, and improved the base catalysis of LDHs. The obtained $\text{SiO}_2@LDH$ materials are composed of SiO_2 cores and fine-crystallized LDH shells, the former acts as a carrier for dispersion and immobilization of LDH and the latter as a highly active base catalyst. Spectroscopic studies well supported that the addition of small

SiO₂ sphere seeds was crucial factor to generate the starting growth points serving fine-crystallized LDHs as highly active solid base catalyst in accordance with our strategy. Thus, this approach based on material chemistry would open significant avenues to generate fine-crystallized LDH materials for versatile practical applications.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Results of nitrogen sorption, XPS spectra, Knoevenagel condensation over M²⁺-M³⁺(1)LDHs and SiO₂(40nm)M²⁺-M³⁺(1)LDHs, XRD patterns, TEM images, assignments of ²⁹Si CP-MAS NMR, Amount of LDH, and Relation between crystallite size and reaction rate (PDF)

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 61. The BET specific surface area values of SiO₂(40nm)@Mg-Al(3)LDH and Mg-Al(3)LDH were 409 m² g(cat)⁻¹ and 150 m² g(LDH)⁻¹, respectively. On the basis

of Si content in SiO₂(40nm)@Mg-Al(3)LDH (12.3 wt%, ICP-AES), the specific surface area of Mg-Al(3)LDH itself prepared on SiO₂(40nm) surface tentatively calculated to be above 168 m² g(LDH)⁻¹, which was higher value than Mg-Al(3)LDH prepared without SiO₂ seeds.

62. To examine the actual morphology of SiO₂ in the SiO₂(40nm)@Mg-Al(3)LDH, SEM images after treatment with 1 M HCl dissolving the LDH layers of SiO₂(40nm)@Mg-Al(3)LDH were monitored. As shown in Fig. S6, the presence of shapeless SiO₂ cores was also observed in the present catalyst.