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Supporting Information for

Fine-Crystallized LDHs Prepared with SiO₂ Sphere as

Highly Active Solid Base Catalyst

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Figure S1 Nitrogen sorption isotherm of spherical SiO₂(40 nm).

		$Si/(M^{2+}+M^{3+})$ ratio		M^{2+}/M^{3+} ratio	
Catalyst		Precursor	Obtained material	Precursor	Obtained material
Mg-Al(3)	LDH	_	_	3.0	2.8
	SiO ₂ @LDH	0.5	0.5	3.0	2.2
Ni-Al(3)	LDH		—	3.0	3.0
	SiO ₂ @LDH	0.5	0.4	3.0	3.1
Mg-Ga(3)	LDH	_	_	3.0	2.7
	SiO ₂ @LDH	0.5	0.6	3.0	2.3

Table S1 Chemical compositions of prepared $M^{2+}-M^{3+}(3)$ type LDHs estimated by ICP-AES.

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Figure S2 Survey XPS spectra of $M^{2+}-M^{3+}(3)LDHs$ and $SiO_2(40nm)@M^{2+}-M^{3+}(3)LDHs$.

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Figure S3 Activities of (\bigcirc) M²⁺-M³⁺(1)LDH and (\bigcirc) SiO₂(40nm)@ M²⁺-M³⁺(1)LDH with various metal compositions for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. *Reaction conditions*: benzaldehyde (0.5 mmol), ethyl cyanoacetate (0.6 mmol), catalyst (10 mg), toluene (3 mL), 313 K, N₂ flow (30 mL min⁻¹).

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Figure S4 XRD patterns of $M^{2+}-M^{3+}(1)LDHs$ and $SiO_2(40nm)@M^{2+}-M^{3+}(1)LDHs$.

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Figure S5 (A) TEM image and (B) SEM image of $SiO_2(40nm)$ treated in basic condition (pH = 10) for 1 h.



Figure S6 SEM image of $SiO_2(40nm)@Mg-Al(3)LDH$ treated with HCl solution (1 M) after 0.5 h.

Assignment	δ/ppm	References
Q^4	-105 ~ -120	54-56
$Q^4(1\mathrm{Al})$	-99 ~ -105	49, 57, 59
$Q^4(2\mathrm{Al})$	-94 ~ -99	57
$Q^4(3Al)$	-89 ~ -94	57
$Q^4(4\mathrm{Al})$	-84 ~ -85	57
Q^3	-87 ~ -102	49, 54-56, 58, 59
$Q^{3}(1Al)$	-85 ~ -88	58
$Q^{3}(2\mathrm{Al})$	-81 ~ -84	58
$Q^3(3Al)$	-73	58
$Q^3(1 \mathrm{Mg})$	-91 ~ -93	56, 60
Q^2	-73 ~ -93	54, 55
$Q^2(1 \mathrm{Mg})$	-84	56, 60
Q^1	-68 ~ -83	55
$Q^1(1Mg)$	-70	56
Q^0	-60 ~ -82	55

 Table S2
 Assignments of ²⁹Si CP-MAS NMR peaks.

	$S_{\rm BET}$ / m ² g ⁻¹	Assignment	δ / ppm	Percentage /%
SiO ₂ (40nm) sphere	1081	Q^4	-109	11
		Q^3	-100	70
		Q^2	-91	19
SiO ₂ (40nm)@LDH	409	Q^3	-101	14
		$\frac{Q^2}{Q^4(3\text{Al}), Q^3(1\text{Mg})}$	-92	31
		$Q^4(4\text{Al}), Q^3(1\text{Al}), Q^2(1\text{Mg})$	-85	37
		Q^1 and/or Q^0	-78	17
SiO ₂ (250nm) sphere	50	Q^4	-110	25
		Q^3	-101	60
		Q^2	-92	14
SiO ₂ (250nm)@LDH	133	Q^4	-110	18
		$\overline{Q^3}$	-100	60
		Q^2 Q^4 (3Al), Q^3 (1Mg)	-92	13
		$Q^4(4\text{Al}), Q^3(1\text{Al}), Q^2(1\text{Mg})$	-86	3
		Q^1 and/or Q^0	-77	5

Table S3 Surface area and silicon environments in the SiO₂ and SiO₂@LDH as determined by ²⁹Si CP-MAS NMR.

The degree of interactions between SiO₂ and LDH was defined as the total percentage of Si environmental which possesses Si-O-Mg and/or Si-O-Al covalent bonds.

	Amount of LDH ^a / wt%	Reaction rate ^{b}		
Type of Mg-AI(3)LDH		/ mmol g(cat) ⁻¹ h ⁻¹	/ mmol g(LDH) ⁻¹ h ⁻¹	
SiO ₂ (40nm)@LDH	73.6	116.7	158.4	
SiO ₂ (250nm)@LDH	71.1	59.5	83.7	
LDH(CP)	100	76.9	76.9	
LDH(com.)	100	13.6	13.6	
LDH(U-CP)	100	0.5	0.5	

Table S4 Catalytic activity of the LDH in various Mg-Al(3)LDHs.

^{*a*}The amount of LDH in the SiO₂@LDHs were calculated by ICP-AES with an assumption, that is all Mg-Al(3)LDHs are composed of only LDH structure or mixture of LDH and SiO₂. ^{*b*}Reaction rate for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.



Figure S7 Correlation between the crystallite sizes (\bigcirc : LDH(003) or \bigcirc : LDH(110) and the catalytic activity of LDH in the various Mg-Al(3)LDHs.