

Supporting Information

Supported Pd complex catalyst for allylation with allylic alcohols enhanced by aluminum-doped mesoporous silica support

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Experimental Section

Materials

Unless otherwise noted, all other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and Aldrich Inc. and used without further purification. In the catalytic reactions, 1,3,5-triisopropylbenzene was used as an internal standard.

NMR measurements

^1H and ^{13}C NMR spectra were recorded in CDCl_3 with an AVANCE 400 spectrometer (Bruker) operating at 400.0, 100.6, and 161.9 MHz, respectively. An AVANCE 500 spectrometer (Bruker) was also used, operating at 500.1 and 125.8 MHz for ^1H and ^{13}C , respectively.

Solid-state ^{29}Si DD/MAS NMR spectra [MAS rate = 10 kHz (^{29}Si)] were recorded with an AVANCE III spectrometer (Bruker) operating at 120 MHz. The accumulation number and delay time were approximately 2000 and 90 s respectively. The cross-polarization (CP) contact time for the ^{29}Si CP/MAS NMR measurements was 4.0 ms.

For solid-state ^{27}Al single-pulse MAS NMR measurements, ECA400 spectrometer (JEOL Ltd.) was also used [MAS rate = 5 kHz] operating at 104 MHz and delay time of 70 s.

Hexamethylcyclotrisiloxane (-9.66 ppm) and Al(NO₃)₃ solution (0 ppm) were used as external standards for the calibration of chemical shifts.

N₂ adsorption–desorption measurement

N₂ adsorption–desorption isotherms at 77 K were measured using a BELSORP mini (MicrotracBEL) system. Samples were prepared for N₂ adsorption measurements by outgassing at 473 K for 2 h under vacuum to a final pressure of 1 Pa. The BET surface areas were estimated over the relative pressure (P/P₀) range of 0.30–0.70. The pore size distribution was obtained from the analysis of the isotherms by using the Barrett–Joyner–Halenda (BJH) method.

XAFS data acquisition

XAFS was measured in transmission mode at the NW10 of PF-AR (proposal No. 2020G033 and 2022G033, KEK, Tsukuba, Japan) at room temperature. The electron storage ring was operated at 6.5 GeV and 60 mA. Synchrotron radiation from the storage ring was monochromatized with Si (311) channel-cut crystals. Ionization chambers filled with Ar gas and Kr were used as detectors for monitoring incident (I₀) and transmitted X-rays (I), respectively. The angle of the monochromator was calibrated using Pd foil, with

the inflection point at the edge set to 24352.6 eV. XAFS spectra were analyzed using Athena and Artemis[1] and REX2000 (for curve-fitting analysis, Rigaku. Co. Japan). The backscattering amplitude and phase shift of Pd-P/Cl were extracted from the PdCl₂(PPh₃)₂ complex. A goodness of curve fit was estimated using the following equation.

$$R_{factor} = \sqrt{\frac{k^n \chi_{exp}(k) - k^n \chi_{cf}(k)}{k^n \chi_{exp}(k)}}$$

where $\chi_{exp}(k)$, $\chi_{cf}(k)$ are the experimental data and theoretical curve-fitted data, respectively.

FT-IR measurements

FT-IR spectra were recorded from 4000-400 cm⁻¹, using a Shimadzu IR Tracer-100 spectrometer with TGS detector. Each spectrum was the average of 45 scans using a spectral resolution of 2 cm⁻¹. FT-IR pellets were prepared as follows: ca. 2.0×10⁻³ g of sample and 0.4 g of KBr were mixed. Then, the mixture was pressed. The pellet diameter S3 was 4 mm.

Preparation of catalyst

Preparation of Mesoporous Silica (MS)

MS-Al(C8, C10, C12, C18) supports with different pore diameters and doping amount (Si:Al = 15, 30, 75) were prepared by modified reported method using primary amine with C8 to C18 alkyl chain as a template molecule.[2] Typical preparation procedure is as follows. Dodecylamine (C12, 53.8 mmol) was dissolved in deionized water (100 g) and ethanol (82 g) solvent at room temperature. Then, tetraethoxysilane (TEOS, 200 mmol) and triethoxyaluminium (X mmol, in ratio of Si:Al) was added to the solution and vigorously stirred for 30 min at room temperature. The reaction mixture was aged at room temperature for 30 h. The obtained solid was filtrated, washed with deionized water, and air-dried. The template amine was removed by mixing in 200 mL of ethanol solution containing 0.1N HCl for 2 h at 60 °C, then the slurry was filtrated. This extraction procedure was reported three times, and the obtained solid was finally mixed in pure ethanol (200 mL) for 2 h at 60 °C, filtrated, and dried at 80 °C for 12 h, generating MS(C12).

Pyridine adsorption FT-IR experiment

The testers were mixed with pyridine and stirred vigorously for 5-10 minutes prior to the removal of pyridine by constant vacuum treatment for 4 hours at room temperature,

which was to ensure that the physically adsorbed pyridine was eliminated. Then, the absorbance spectra from FT-IR showed the acid sites on the surface of both supporting materials and immobilized catalysts.

Catalytic allylation procedure

Allylation with allyl alcohol using a MS-supported Pd catalyst

The mesoporous silica supported-Pd catalyst (Pd: 8 μmol), K_2CO_3 (0.50 mmol), nucleophile (1.0 mmol) and allyl alcohol (2.5 mmol) were added into a 20 mL Schlenk flask under Ar protection, and then stirred at assigned temperature. After the reaction, the 1,3,5-triisopropylbenzene was added as an internal standard and the reaction mixture was diluted by CDCl_3 for NMR sample. A portion of the solution was pipetted through a dropper into an NMR tube. The yield of reaction was analyzed by ^1H NMR after the addition of CDCl_3 as solution. All products are identified by reported ^1H and ^{13}C NMR and Mass data.[3,4] After the filtration of reaction mixture through a membrane filter under reduced pressure, collected filtrate was used as catalysts for reuse experiments.

Table S1. Elemental analysis results of prepared catalyst samples.^a

Catalyst	Pd (mmol g ⁻¹)	Pd wt%	Si (mmol g ⁻¹)	Al (mmol g ⁻¹)	Si : Al
MS(C12)-Al-15/PP-Pd	0.376	4.00	8.11	0.299	27 : 1
MS(C12)-Al-30/PP-Pd	0.389	4.14	10.44	0.236	44 : 1
MS(C12)-Al-75/PP-Pd	0.389	4.14	9.54	0.142	67 : 1
MS(C12)/PP-Pd	0.379	4.03			
MS(C12)-cal/PP-Pd	0.335	3.56			

^a Determined by ICP-AES analysis.

Table S2. Curve-fitting analysis of the EXAFS spectra for the fresh supported Pd catalysts on Pd-P/Cl shell.

Sample	N^b	R (Å) ^c	DW factor(Å) ^d	ΔE_0 (eV) ^e	Rf (%) ^f
MS(C12)-Al-30/PP-Pd	3.0	2.27	0.09	-4.97	3.06
	(fix)	±0.01	±0.01	±2.33	
MS(C12)-Al-75/PP-Pd	3.0	2.27	0.09	-4.72	1.92
	(fix)	±0.01	±0.01	±2.32	
MS(C8)-Al-15/PP-Pd	3.0	2.28	0.09	-4.67	2.35
	(fix)	±0.01	±0.01	±2.32	
MS(C10)-Al-15/PP-Pd	3.0	2.28	0.09	-4.37	1.82
	(fix)	±0.01	±0.01	±2.32	
MS(C18)-Al-15/PP-Pd	3.0	2.28	0.09	-4.85	1.60
	(fix)	±0.01	±0.01	±2.33	
PdCl₂(PPh₃)₂^g	2 (Pd-P)	2.34			
	2 (Pd-Cl)	2.30			

^a Fourier transform and Fourier-filtering regions were limited, with $\Delta k \approx 3.0\text{--}12 \text{ \AA}^{-1}$ and $\Delta r \approx 1.0\text{--}2.2 \text{ \AA}$, respectively. ^b Coordination number. ^c Bond distance between the absorber and backscattering atoms. ^d Debye-Waller (DW) factor relative to the reference. ^e Inner potential correction to account for the difference in the inner potentials of the sample and the reference. ^f Goodness of curve fit. ^g Average values of crystallographic data have been reported.

Table S3. Peak area ratio of Q², Q³ and Q⁴ sites in ²⁹Si DD/MAS NMR spectra.

Sample	Q ²	Q ³	Q ⁴
MS(C12)-Al-15	7.9	34.8	57.3
MS(C12)-Al-15/PP-Pd	5.8	29.8	64.5

Table S4. Physicochemical properties of synthesized MS supports

MS Support	Surface area [m ² g ⁻¹] ^[a]	Pore size [nm] ^[b]	Pore volume [ml/g] ^[b]
MS(C8)-Al-15	1327.2	1.32	0.616
MS(C10)-Al-15	1778.6	1.74	0.812
MS(C12)-Al-15	1320.0	2.14	0.973
MS(C12)-cal	1159.5	2.09	0.693
MS(C18)-Al-15	1081.2	2.56	1.022

[a] Determined by N₂ adsorption-desorption isotherm measurement. [b] Determined by BJH method.

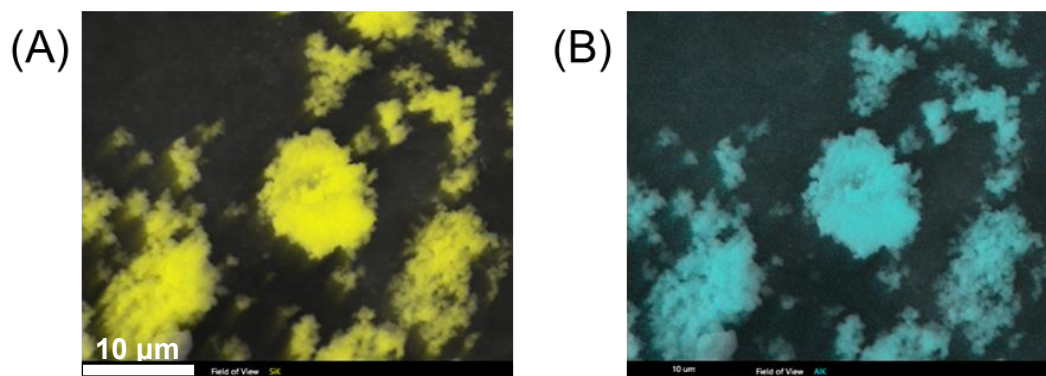


Figure S1. SEM-EDS mapping of MS(C12)-Al-15 for elements (A) Si and (B) Al.

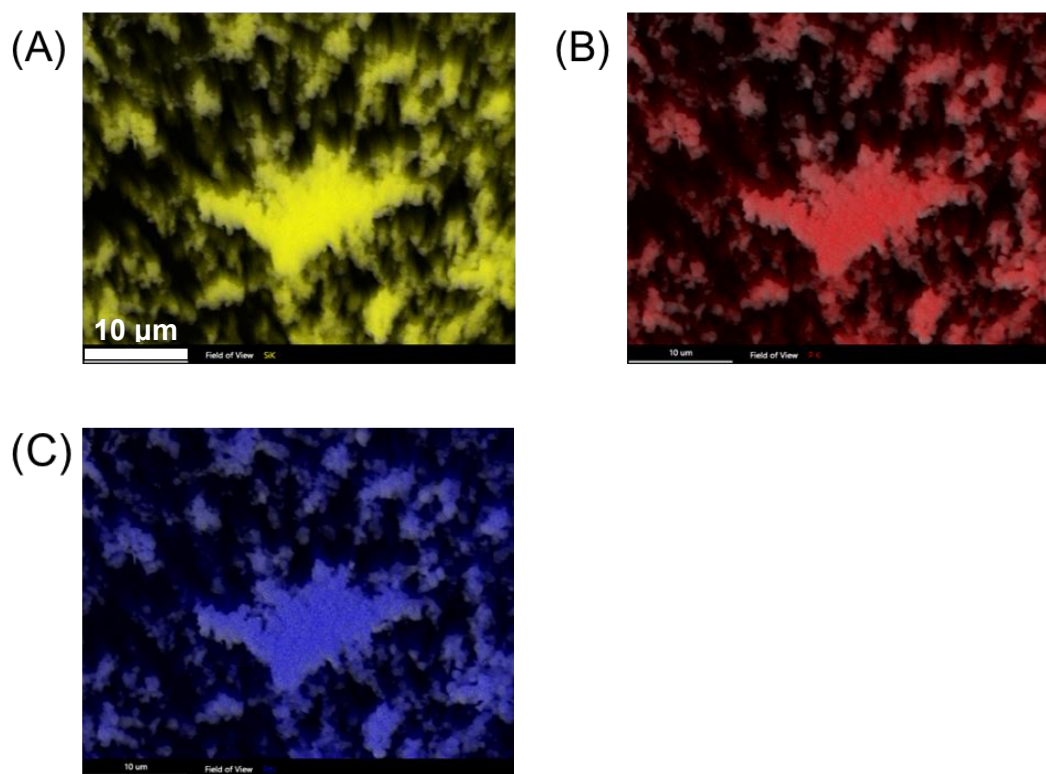


Figure S2. SEM-EDS mapping of MS(C12)/PP-Pd for elements (A) Si, (B) P, and (C) Pd.

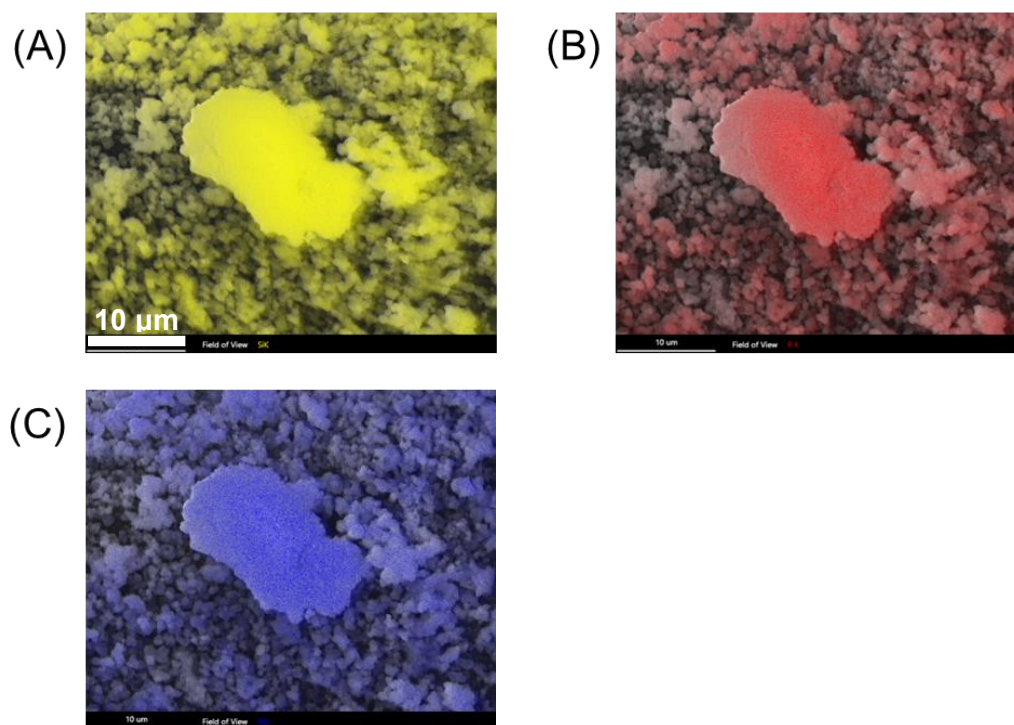


Figure S3. SEM-EDS mapping of MS(C12)-cal/PP-Pd for elements (A) Si, (B) P, and (C) Pd.

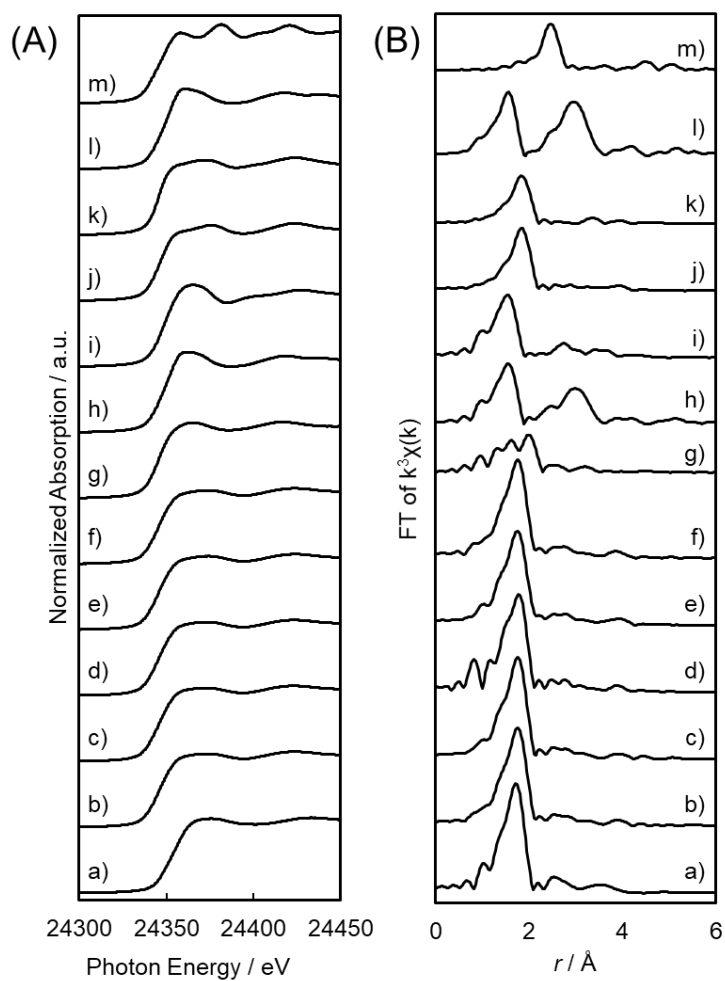


Figure S4. (A) Pd K-edge XANES and (B) k^3 -weighted FT-EXAFS spectra of (a) MS(C12)-Al-15/PP-Pd used, (b) MS(C12)-Al-30/PP-Pd, (c) MS(C12)-Al-75/PP-Pd, (d) MS(C8)-Al-15/PP-Pd, (e) MS(C10)-Al-15/PP-Pd, (f) MS(C18)-Al-15/PP-Pd, (g) PdCl(allyl)₂, (h) Pd(NO₃)₂, (i) Pd(OAc)₂, (j) PdCl₂(PPh₃)₂, (k) PdCl₂, (l) PdO and (m) Pd foil. The k range for FT was $\Delta k = 3.0\text{-}14.0 \text{ \AA}^{-1}$.

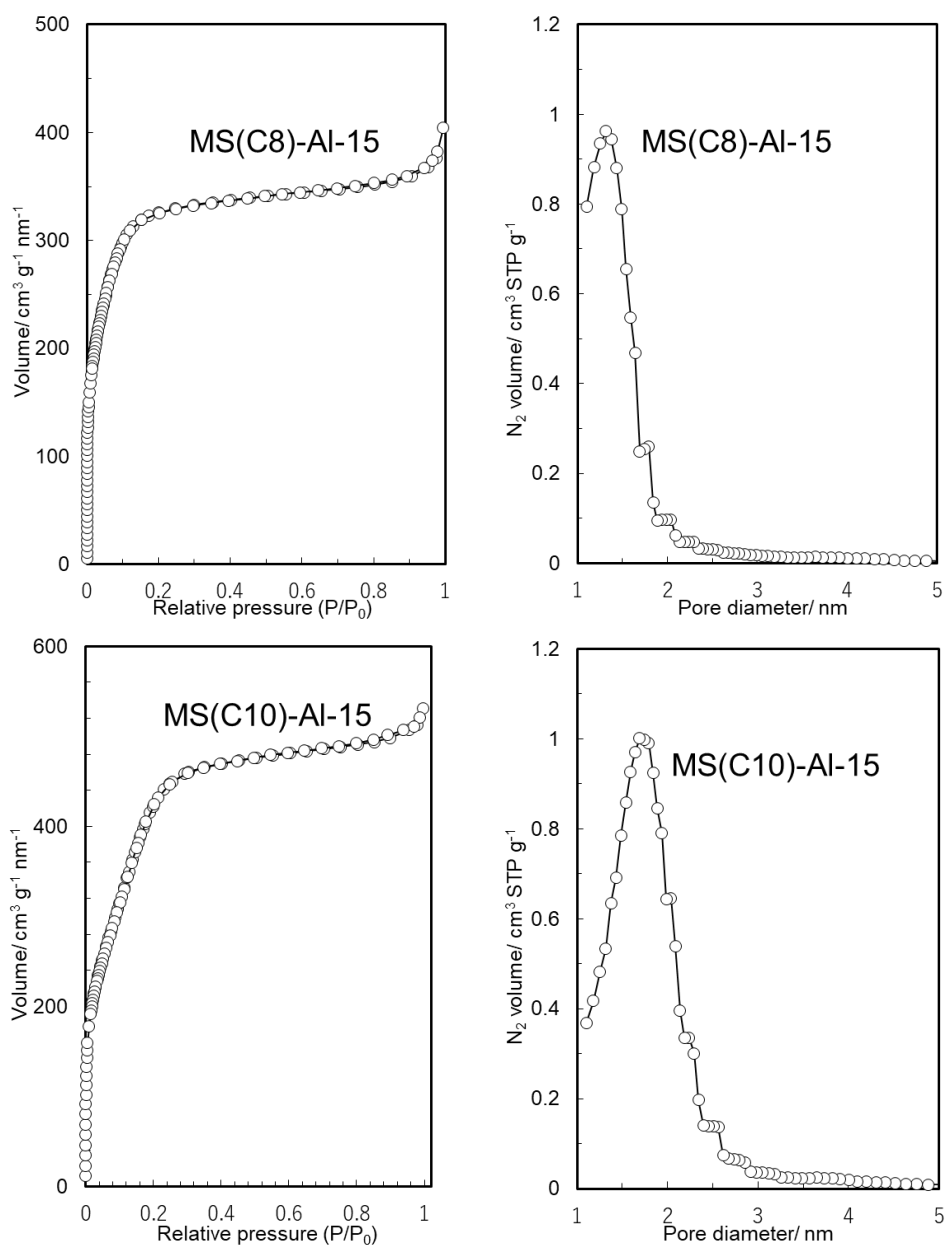
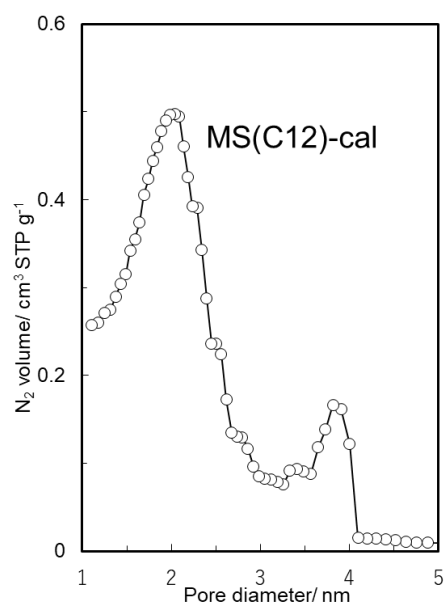
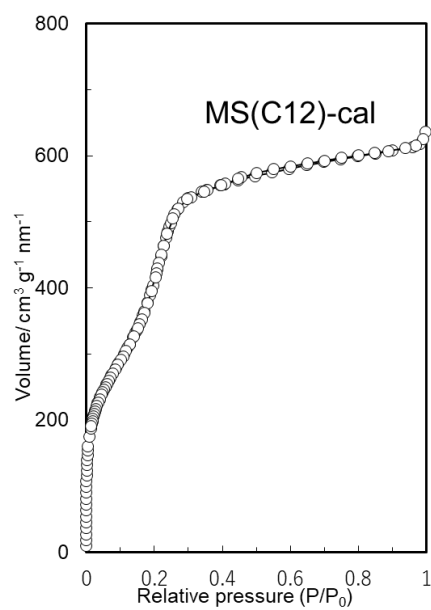
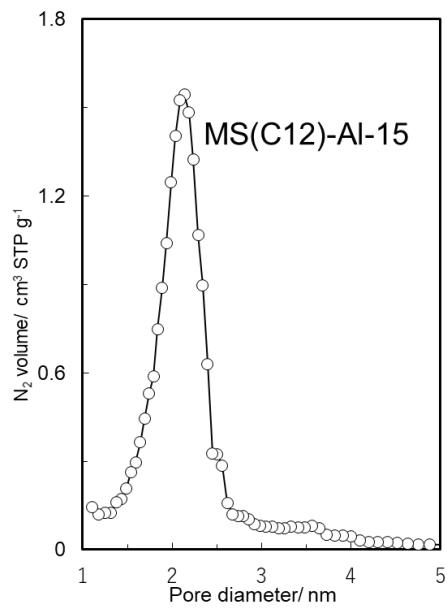
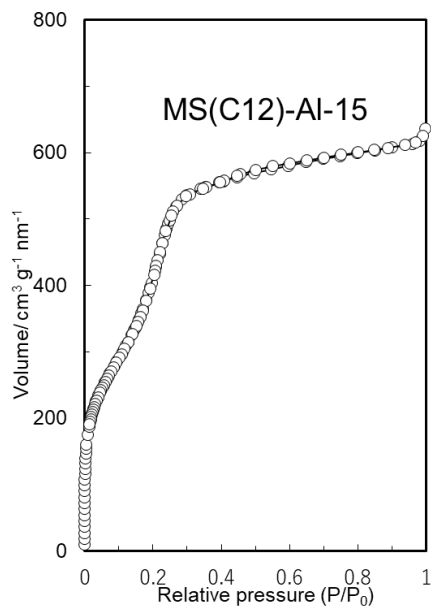


Figure S5. N₂ adsorption-desorption isotherm and BJH pore size distribution of MS(C8)-Al-15 and MS(C10)-Al-15.



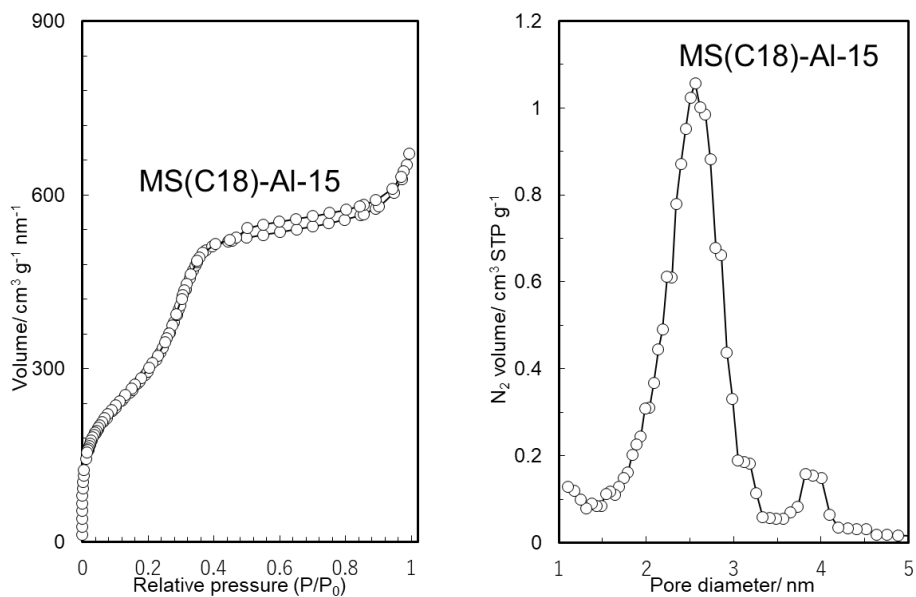


Figure S6. N₂ adsorption-desorption isotherm and BJH pore size distribution of MS(C12)-Al-15, MS(C12)-cal and MS(C18)-Al-15.

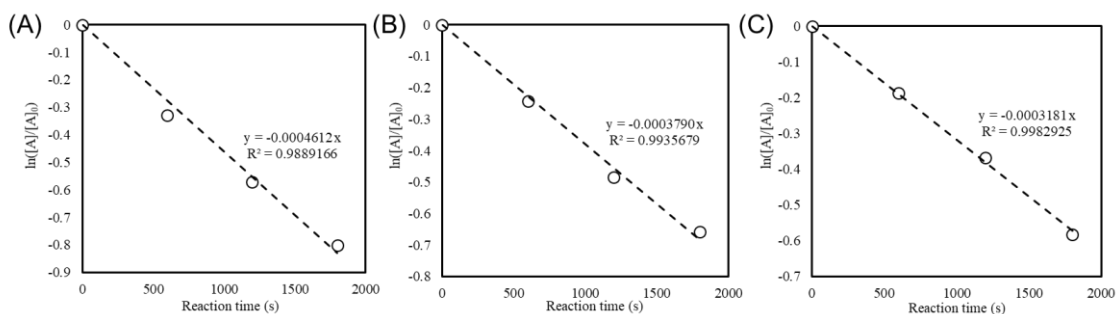


Figure S7. First order plot kinetic study for allylation of ethyl 2-oxocyclopentanecarboxylate with allylic alcohol catalyzed by (A) MS(C12)-Al-15/PP-Pd, (B) MS(C12)/PP-Pd, and (C) MS(C12)-cal/PP-Pd.

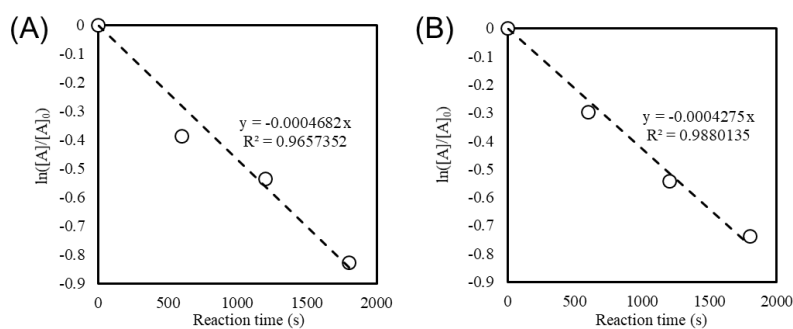


Figure S8. First order plot kinetic study for allylation of ethyl 2-oxocyclopentanecarboxylate with allylic alcohol catalyzed by (A) MS(C12)-Al-30/PP-Pd and (B) MS(C12)-Al-75/PP-Pd.

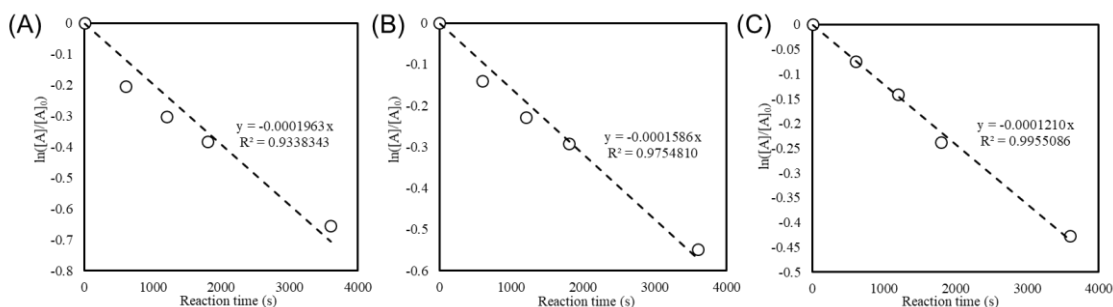


Figure S9. First order plot kinetic study for allylation of ethyl 2-oxocyclopentanecarboxylate with 1-butene-3-ol catalyzed by (A) MS(C12)-Al-15/PP-Pd, (B) MS(C12)/PP-Pd, and (C) MS(C12)-cal/PP-Pd.

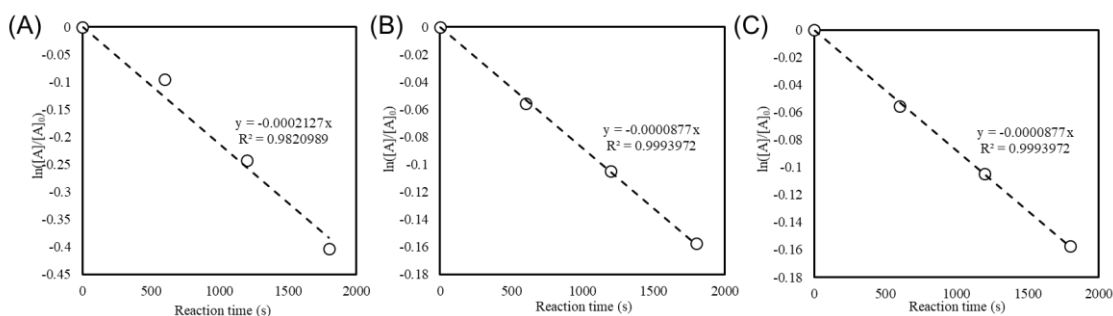


Figure S10. First order plot kinetic study for allylation of ethyl 2-oxocyclopentanecarboxylate with 1-pentene-3-ol catalyzed by (A) MS(C12)-Al-15/PP-Pd, (B) MS(C12)/PP-Pd, and (C) MS(C12)-cal/PP-Pd.

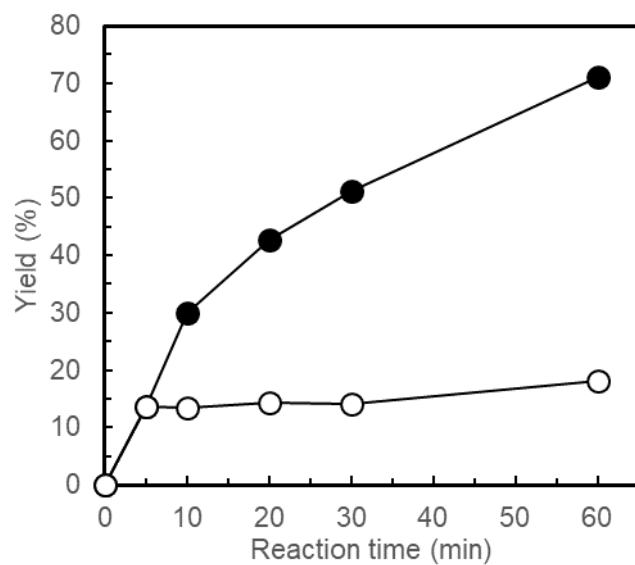


Figure S11. The hot filtration experiment on catalytic activity for allylation. Open circle: moiety without catalyst, separated liquid phase reactant, closed circle: moiety with catalyst. Reaction conditions: MS(C12)-Al-15/PP-Pd (Pd: 8 μmol), K_2CO_3 (0.50 mmol), 50 $^\circ\text{C}$.

Product Identification Reference

Table 2. Allylation of 2-phenylpropionaldehyde: reference [3]

Figure 5. Allylation of ethyl 2-oxocyclopentanecarboxylate: reference [4]

Table 3. Scope of nucleophiles: reference [3](aldehyde) and [4] (other nucleophiles)

Reference

- [1] (a) B. Ravel, M. Newville, *J. Synchrotron Rad.* **2005**, *12*, 537-541. (b) M. Newville, *J. Synchrotron Rad.* **2001**, *8*, 322-324.
- [2] P. T. Tanev, T. J. Pinnavaia, *Science* **1995**, *267*, 865-867.
- [3] Y. Bernhard, B. Thomson, V. Ferey, and M. Sauthier, *Angew. Chem. Int. Ed.* **2017**, *56*, 7460-7464.
- [4] K. Motokura, M. Ikeda, M. Kim, K. Nakajima, S. Kawashima, M. Nambo, W.-J. Chun, S. Tanaka, *ChemCatChem* **2018**, *10*, 4536–4544