

Supplementary Information for
**Preparation of highly ordered aluminum-planted mesoporous silica
catalyst active for Biginelli reaction and formyl C-H insertion reaction
with diazoester**

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1. Experimental

General.

Unless specified, all starting materials and solvents were of purchased commercial reagents. Urea (**4a**) was recrystallized from MeOH, and the other reagents and solvents were purified by respective literature procedures. Ethyl diazoacetate (**2a**) was prepared by the reported manner.^{S1} GC analyses were performed on an HP 6890 gas chromatograph equipped with an HP-5MS column (30 m × 0.25 mm × 0.25 μm) and an HP 5793 mass selective EI detector. High resolution mass spectra (HRMS) data were obtained on a JEOL JMS-700 spectrometer. The amounts of carbon and hydrogen were analyzed in a usual manner with a CHNS-932 system of LECO Corporation. Melting point was measured by using a DTG-60 apparatus (Shimadzu). NMR spectra were measured on an AVANCE-400 (Bruker) spectrometer. Chemical shifts of the organic compounds were quoted in ppm from internal TMS. ²⁷Al MAS NMR spectra of Al-planted MCM-41s were recorded at a frequency 104.2 MHz, a spinning rate of 12 kHz, a pulse length of 4.0 μs, a delay time of 1.0 s and 12000 scans. Al-M41s were hydrated in an air chamber saturated with water vapour at room temperature before measurement. γ-Al₂O₃ was used as a reference of chemical shifts (3.94 ppm). Powder X-ray diffraction (XRD) patterns of catalysts were recorded on a RINT2000 diffractometer with Cu K_α radiation (40 kV, 40 mA). N₂ sorption isotherms were obtained on a BELSORP 28SA volumetric adsorption analyzer at 77 K. An OPTIMA 3200XL ICP was used to determine the contents of metal ions in MCM-41s.

Preparations of catalysts.

All M41s were prepared by using C₁₂H₂₅NMe₃Br and colloidal silica (Snow Techs 20, Nissan chemical Industries, Ltd.) as the template and the silica source. Al-M41-a,^{S2} -b,^{S3} and -c^{S4} were prepared by post synthesis methods in which the parent M41 was separately prepared^{S5} and the Al sources employed were described in the respective literatures. Al-M41-d,^{S6} -e,^{S7} and -f^{S8} were prepared by sol-gel methods. In preparation of Al-M41-[z], Al was planted onto the parent M41^{S5} by the template-ion exchange (TIE) method^{S9} with Al(NO₃)₃. All of the resulting materials were calcined at 873 K for 6 h in air. The catalysts were characterized by XRD, ICP, and N₂ absorption measurements as described above and applied for the catalytic reaction after being evacuated at 373 K for 1 h.

Typical procedure of Biginelli reaction.

3-Oxo-hexanoic acid ethyl ester (**3b**, 1.0 mmol), *p*-tolualdehyde (**1b**, 1.0 mmol), urea (**4a**, 0.50 mmol), tetradecane (GC internal standard, 0.20 mmol), and octane (solvent, 1 mL) were added into a 40 mL test tube which contained in advance a selected amount of catalyst and a magnetic stirrer bar. The mixture was heated at 388 K under Ar atmosphere for 10 h. The reaction mixture was diluted with MeOH, and the catalyst was removed by filtration and washed with AcOEt. The filtrate was evaporated and analyzed by GC.

5-Pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-methylphenyl)-2-oxo-6-propyl-, ethyl ester (**5a**)^{S10}

White crystal. ¹HNMR (400 MHz, *d*₆-DMSO/TMS): δ_H 9.14 (br, 1H), 7.68 (br, 1H), 7.11 (d, *J* = 1.5, 4H), 5.12 (d, *J* = 3.3, 1H), 3.97 (q, *J* = 7.0, 2H), 2.63 (t, *J* = 7.3, 2H), 2.24 (s, 3H), 1.49-1.62 (m, 2H), 1.09 (t, *J* = 7.0, 3H), 0.90 (t, *J* = 7.1, 3H). ¹³CNMR (100 MHz, *d*₆-DMSO/TMS): δ_C 165.56, 152.86, 152.64, 142.47, 136.83, 129.36, 126.59, 99.66, 59.66, 54.08, 32.78, 22.10, 21.10, 14.50, 14.15. HRMS(FAB) Calcd for [C₁₇H₂₃N₂O₃⁺] 303.1709, Found 303.1701. Mp 140-144 °C

Procedude of formyl C-H insertion reaction (Fig. 3).

Ethyl diazoacetate (**2a**, 12 mmol) was added at a stroke at 298 K to the mixture of heptanal (**1a**, 8.0 mmol), tetradecane (GC internal standard, 1.6 mmol) and Al-M41 (20 mg) in 40 ml of CH₂Cl₂. Progress in the reaction was traced with the periodical GC analysis.

3-Oxo-nonanoic acid ethyl ester (3a)^{S11} Colorless oil. ¹HNMR (400 MHz, CDCl₃/TMS): δ_H 4.20 (q, *J* = 7.2, 2H), 3.43 (s, 2H), 2.54 (t, *J* = 7.4, 2H), 1.55-1.63 (m, 2H), 1.26-1.31 (m, 9H), 0.90 (t, *J* = 7.2, 3H). ¹³CNMR (100 MHz, CDCl₃/TMS): δ_C 203.08, 167.33, 61.43, 49.33, 43.07, 31.57, 28.70, 23.42, 22.49, 14.26, 14.04. Anal. Calcd for C₁₁H₂₀O₃: C, 65.97; H, 10.07. Found: C, 65.52; H, 9.93.

2. ^1H and ^{13}C NMR spectra of 5a and 3a

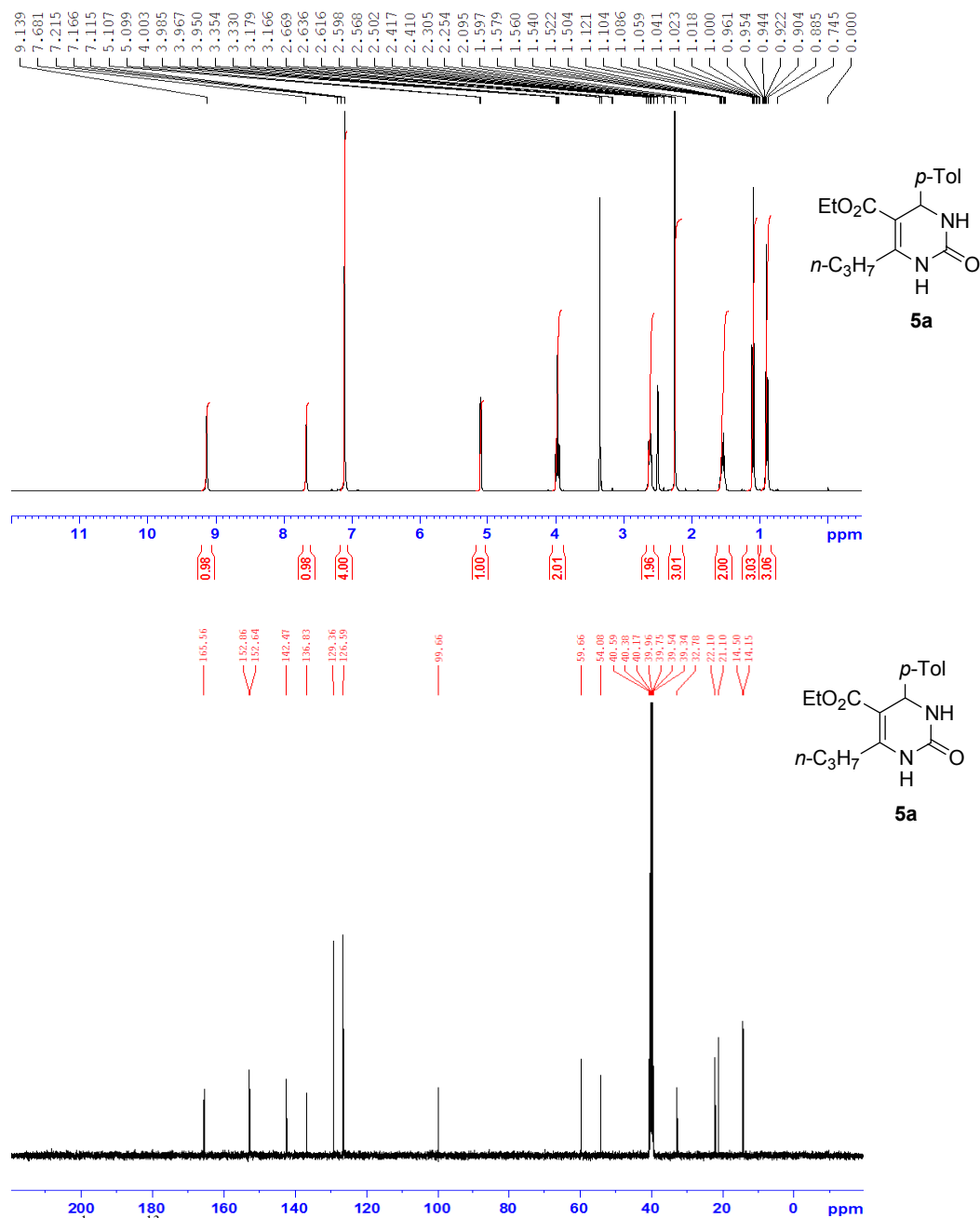


Fig. S1 ^1H and ^{13}C NMR spectra of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro -4-(4-methylphenyl)-2-oxo-6-propyl-, ethyl ester (**5a**).^{S10}

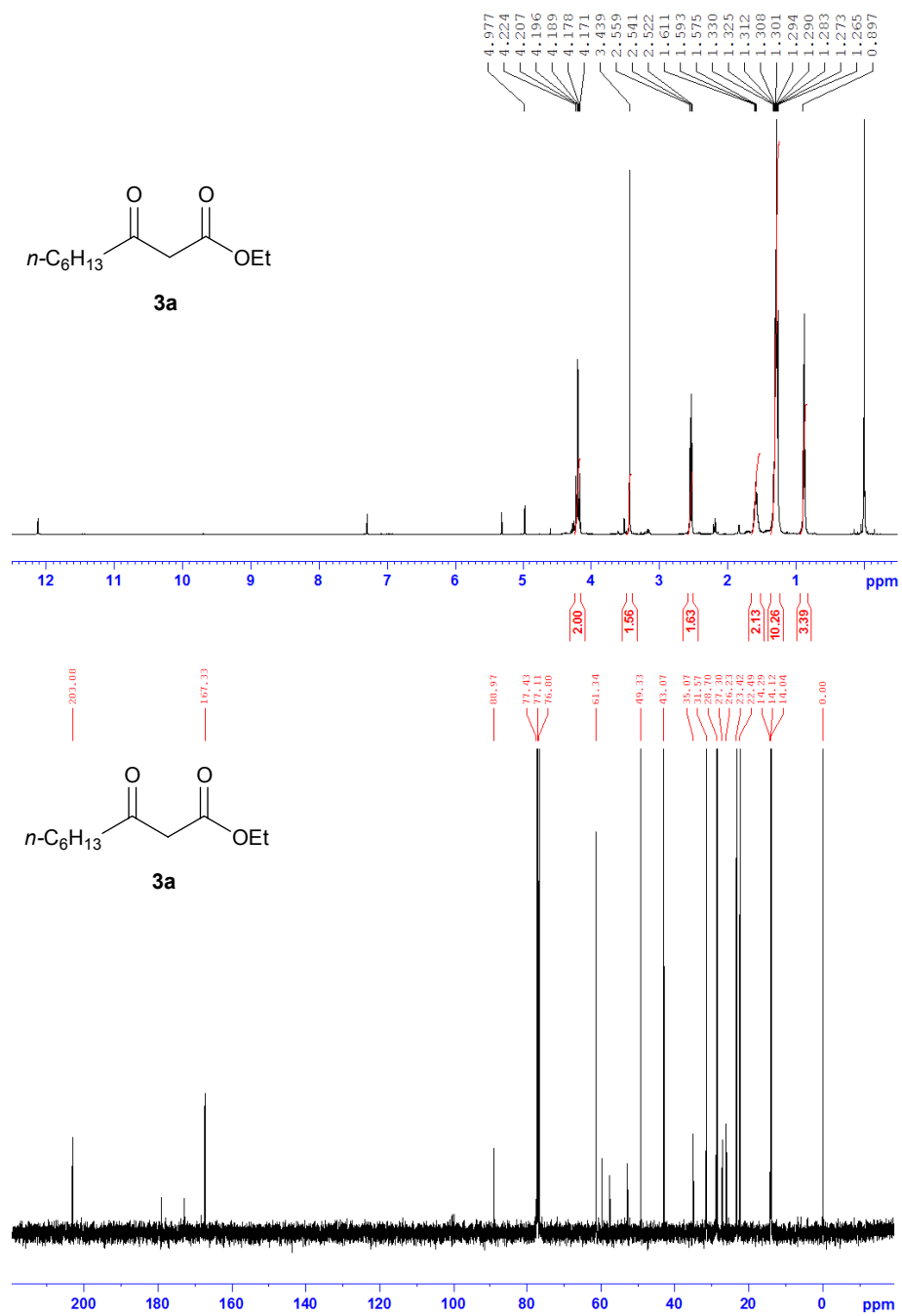


Fig. S2 ¹H and ¹³C NMR spectra of 3-oxo-nonanoic acid ethyl ester (**3a**).^{S11}

3. N₂ absorption isotherms of Al-MCM-41s

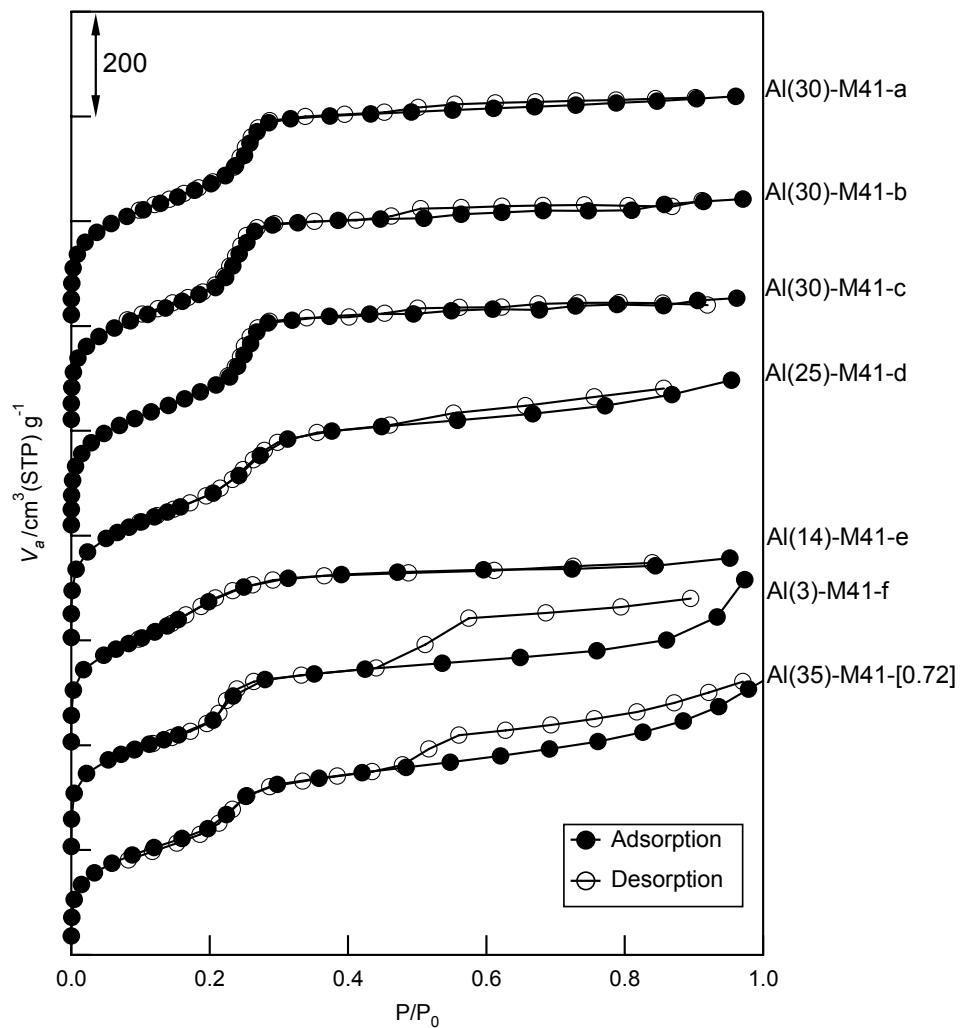


Fig. S3 N₂ adsorption-desorption isotherms of Al-MCM-41s (Table 1).

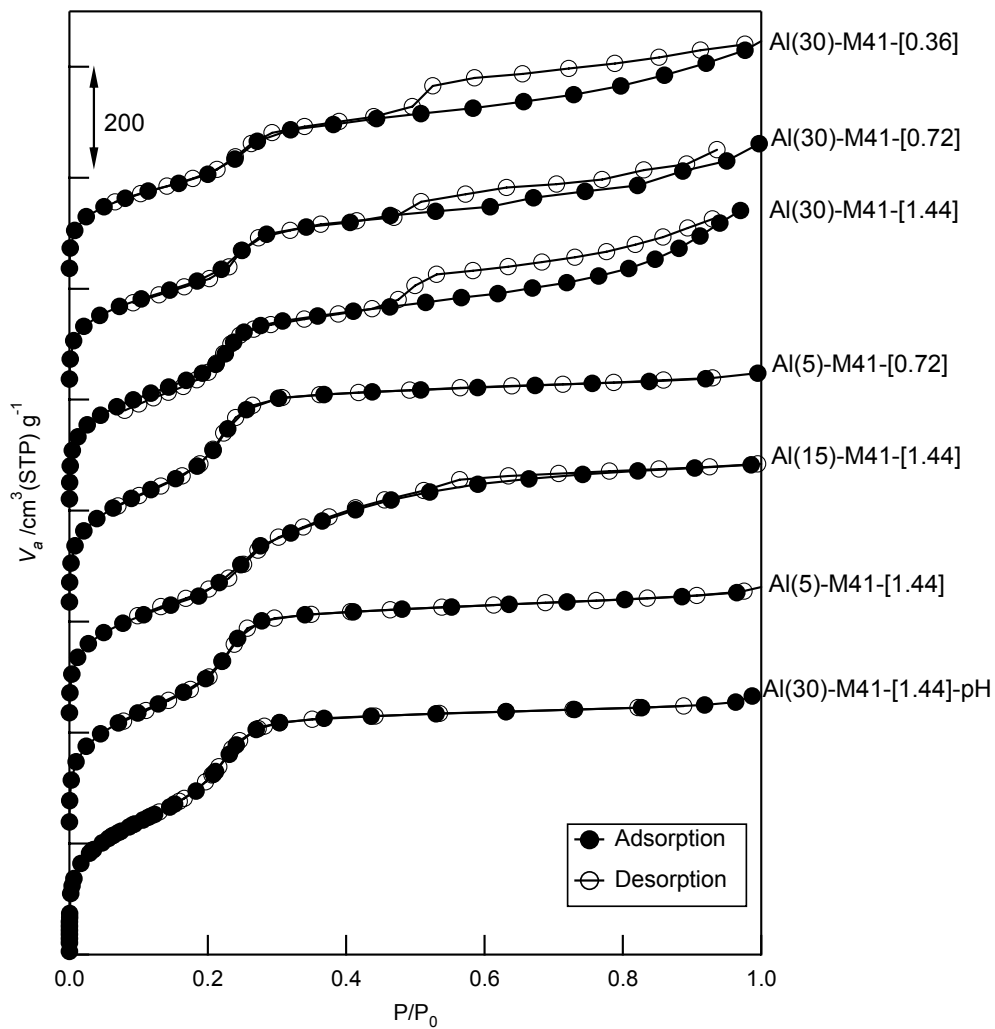


Fig. S4 N₂ adsorption-desorption isotherms of typical Al-MCM-41s (Table 2).

4. X-ray diffractions of Al-MCM-41s

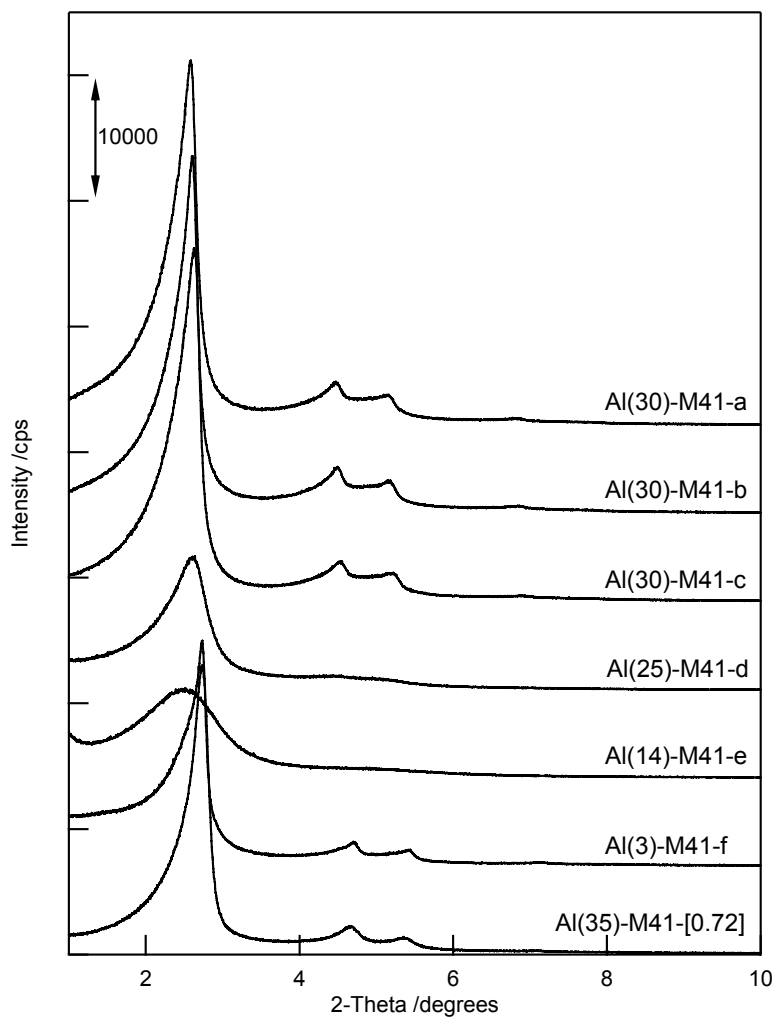


Fig. S5 X-ray diffraction patterns of Al-MCM-41s (Table 1).

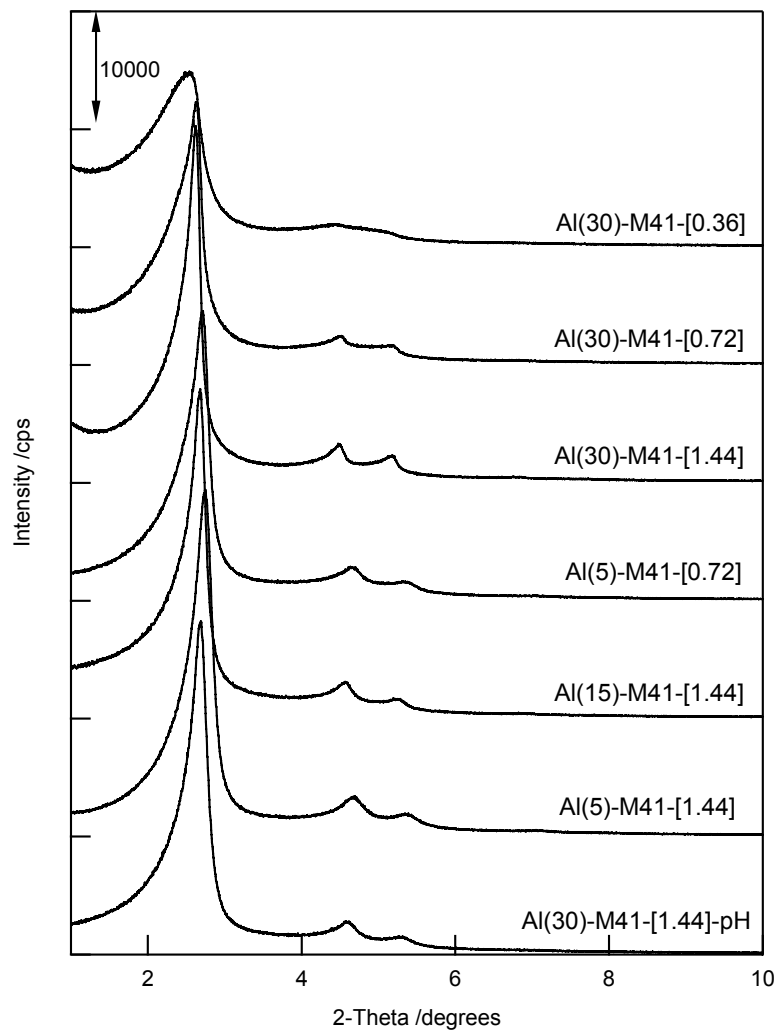


Fig. S6 X-ray diffraction patterns of typical Al-MCM-41s (Table 2).

5. Typical ^{27}Al NMR spectra of Al-planted MCM-41s

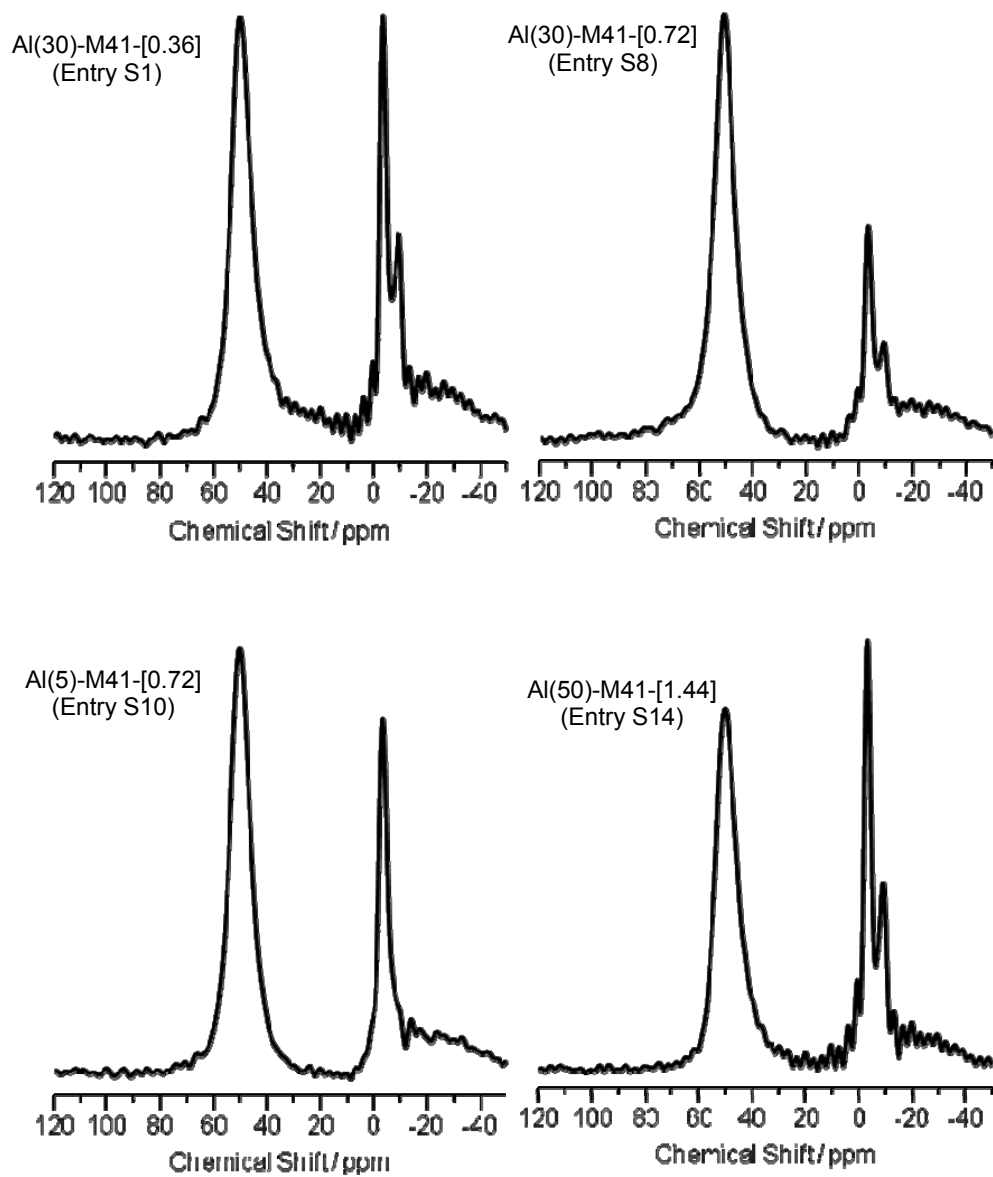


Fig. S7a Typical ^{27}Al NMR spectra of Al-MCM-41s.

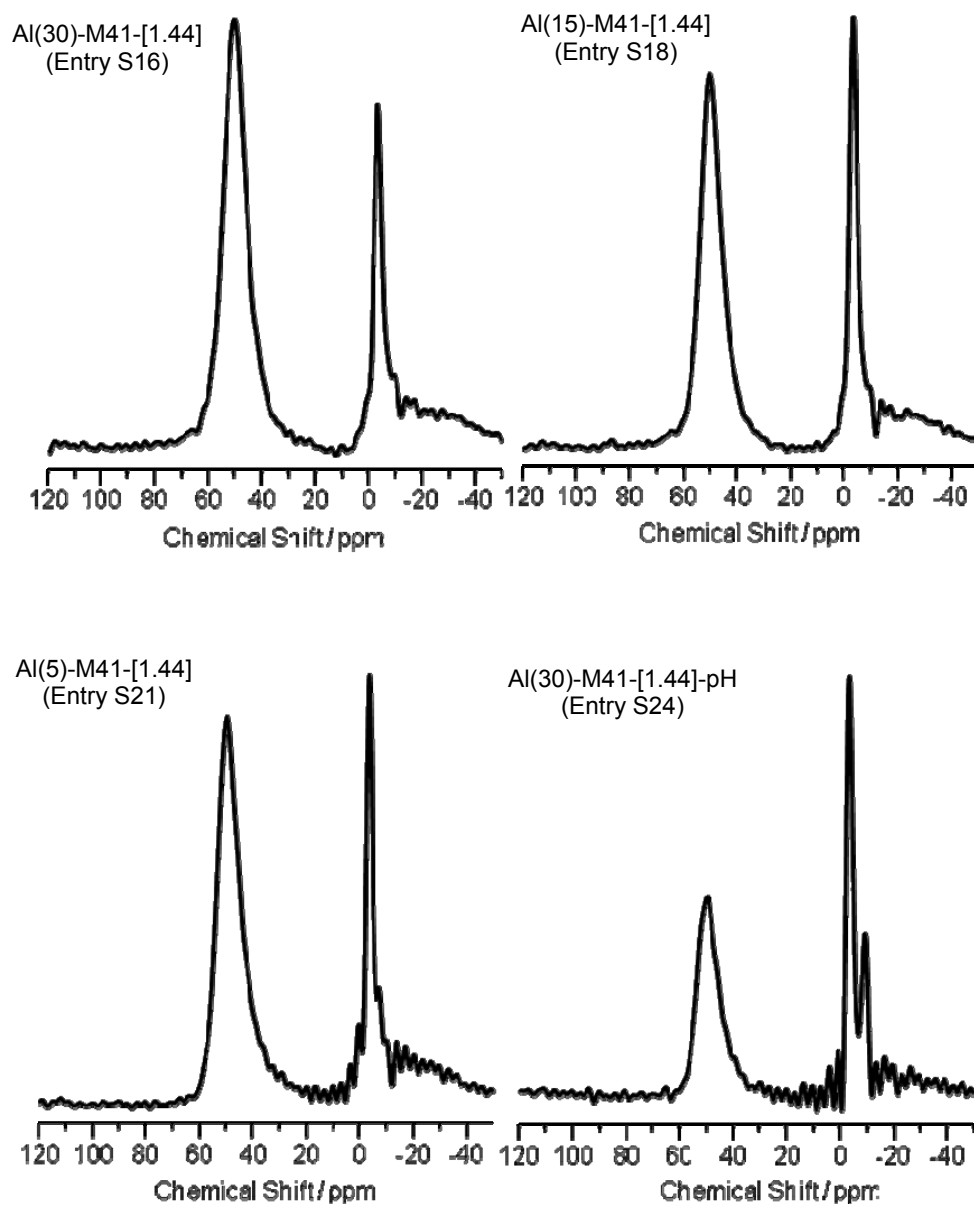


Fig. S7b Typical ^{27}Al NMR spectra of Al-MCM-41s.

6. Correlation between catalytic activity and physicochemical properties of Al-planted MCM-41s with Si/Al=23-38

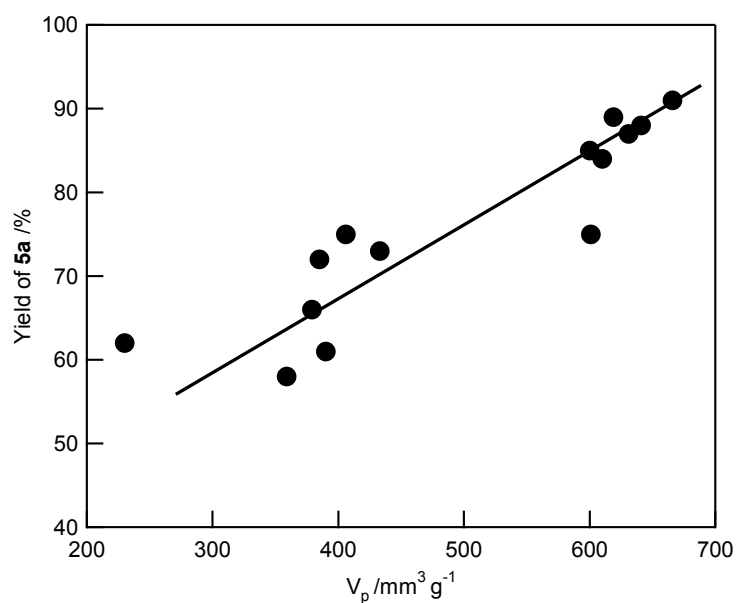


Fig. S8 Correlation between yields of 5a and mesopore volume of Al-M41s with 23-38 of Si/Al.

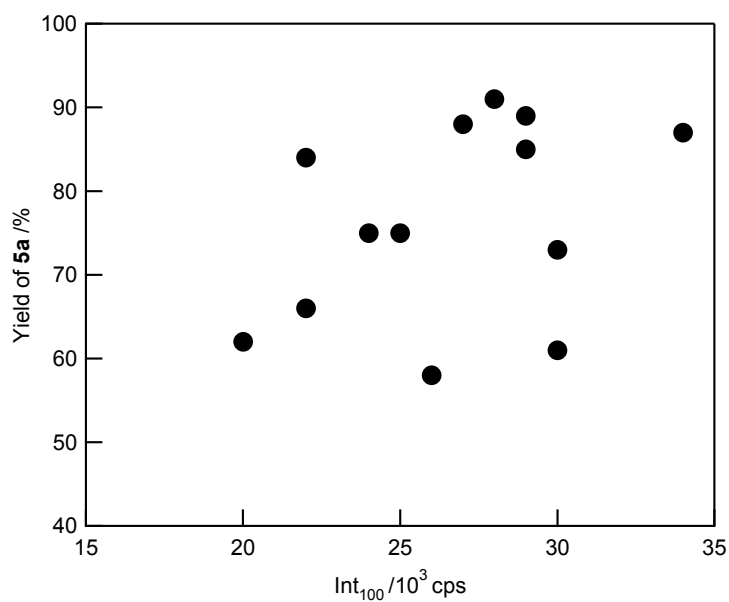


Fig. S9 Correlations between yields of 5a and peak intensity of XRD (100) of Al-M41s with 23-38 of Si/Al.

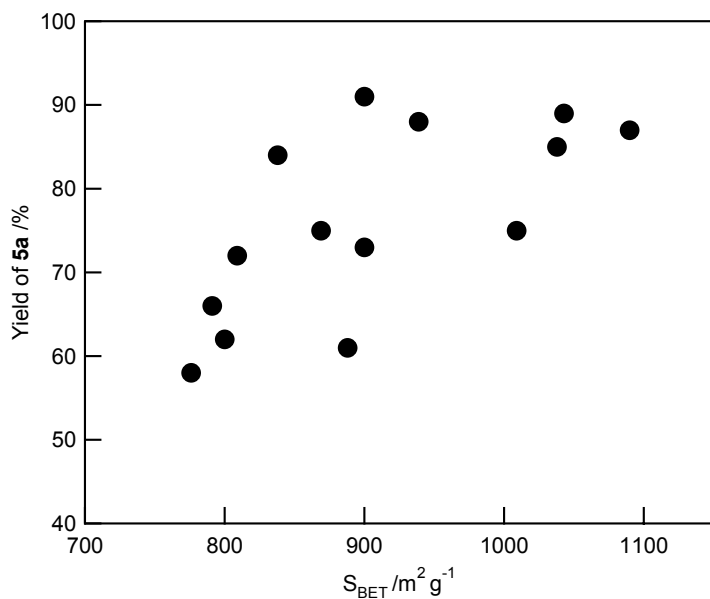


Fig. S10 Correlations between yields of **5a** and BET surface areas of Al-M41s with 23-38 of Si/Al.

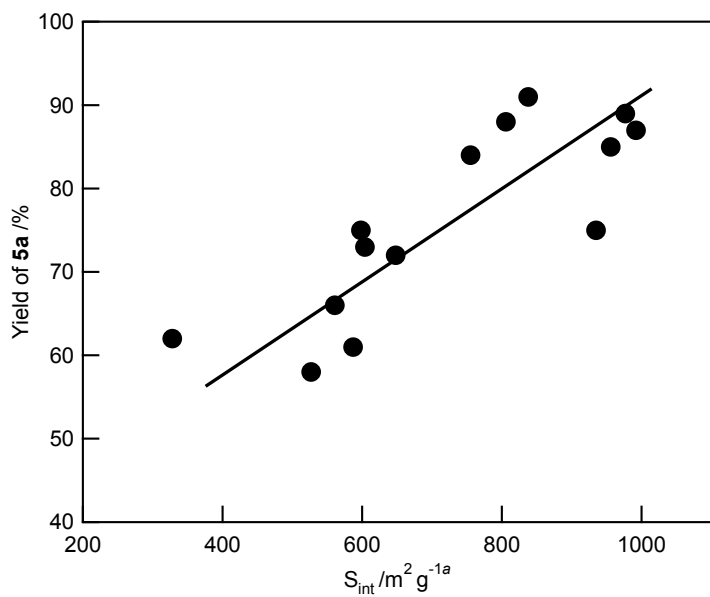


Fig. S11 Correlations between yields of **5a** and internal surface areas of Al-M41s with 23-38 of Si/Al ^aCalculated from the difference between S_{BET} and extent surface area determined by t-plot method.

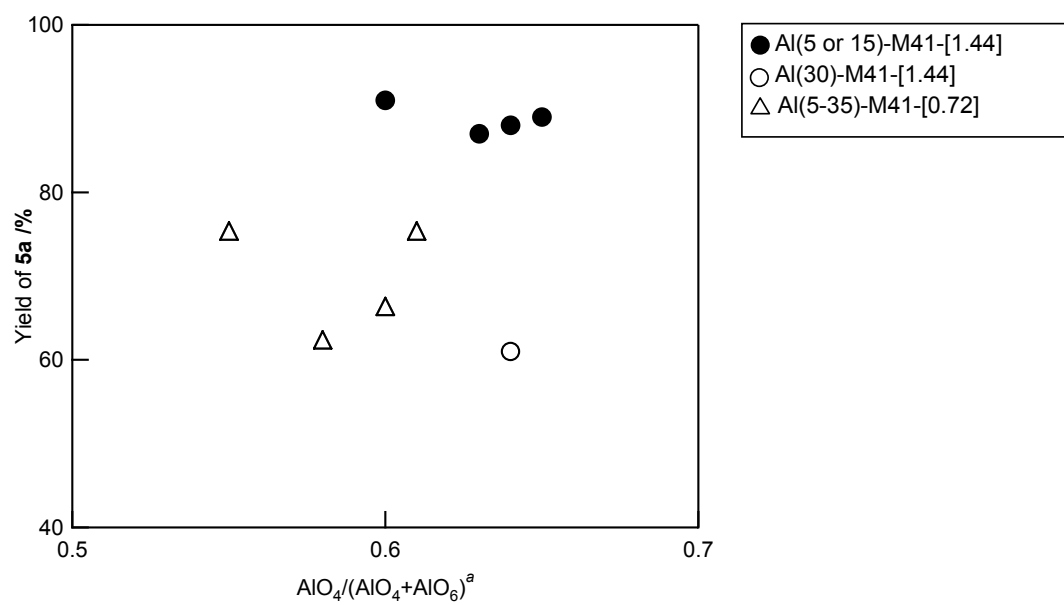


Fig. S12 Correlations between yields of **5a** and value of $\text{AlO}_4/(\text{AlO}_4+\text{AlO}_6)$ of Al-M41s. ^aCalculated from the ²⁷Al NMR spectra using the respective peak areas.

7. Summary of physicochemical properties and catalytic activities of individual Al-planted MCM-41s

Table S1. Physicochemical properties and catalytic activities of individual Al-planted MCM-41s

Entry	Al-M41 ^a	pH ^b	[Al] /mmol g ⁻¹	Si /Al	S _{BET} /m ² g ⁻¹	V _p /mm ³ g ⁻¹	S _{int} /m ² g ^{-1c}	D /nm ^d	Int ₁₀₀ ^e /10 ³ cps	GC yield /% ^f	AlO ₄ / (AlO ₄ + AlO ₆) ^g
1	Al(30)-M41-[0.36]	6.9	0.38	30	731	340	486	2.32	15	29	0.55
2	M41-[0.72]	^h	0.065	237	1010	616	925	2.12	29	53	0.57
3	Al(70)-M41-[0.72]	7.6	0.19	73	1002	545	823	2.12	29	59	0.72
4	Al(45)-M41-[0.72]	8.3	0.24	45	919	430	680	2.18	^h	73	^h
5	Al(40)-M41-[0.72]	6.3	0.44	44	904	445	696	2.12	^h	74	0.75
6	Al(35)-M41-[0.72]	7.7	0.38	35	869	406	598	2.12	24	75	0.61
7	Al(35)-M41-[0.72]	8.1	0.40	33	809	385	648	2.12	^h	72	^h
8	Al(30)-M41-[0.72]	7.3	0.44	30	791	379	561	2.02	22	66	0.60
9	Al(20)-M41-[0.72]	5.8	0.58	23	800	230	328	2.12	20	62	0.62
10	Al(5)-M41-[0.72]	3.2	0.32	38	1009	601	935	2.18	25	75	0.55
11	M41-[1.44]	^h	0.069	200	978	592	893	2.32	34	49	0.58
12	Al(100)-M41-[1.44]	9.5	0.16	80	852	544	802	2.24	35	63	^h
13	Al(50)-M41-[1.44]	8.8	0.36	47	949	447	761	2.16	29	58	^h
14	Al(50)-M41-[1.44]	7.6	0.44	55	875	499	655	2.08	28	57	0.53
15	Al(40)-M41-[1.44]	8.8	0.42	35	900	433	604	2.24	30	73	^h
16	Al(30)-M41-[1.44]	7.6	0.42	28	888	390	587	2.16	30	61	0.64
17	Al(30)-M41-[1.44]	6.8	0.48	29	776	359	527	2.08	26	58	^h
18	Al(15)-M41-[1.44]	3.7	0.39	30	900	666	838	2.32	28	91	0.60
19	Al(15)-M41-[1.44]	3.3	0.48	30	838	610	755	2.30	22	84	^h
20	Al(15)-M41-[1.44]	3.2	0.44	28	939	641	806	2.16	27	88	0.64
21	Al(5)-M41-[1.44]	3.2	0.38	32	1043	619	977	2.16	29	89	0.65
22	Al(5)-M41-[1.44]	2.9	0.54	23	1038	600	956	2.30	29	85	^h
23	Al(5)-M41-[1.44]	2.8	0.51	24	1090	631	992	2.16	34	87	0.63
24	Al(30)-M41-[1.44]-pH	3.1	0.24	52	978	659	949	2.32	29	72	0.50
25	Al(30)-M41-[1.44]-pH	3.0	0.27	60	859	596	820	2.18	39	62	0.41
26	Al(30)-M41-[1.44]-pH	2.9	0.32	49	896	637	868	2.20	30	56	0.49
27	Al(30)-M41-[1.44]-pH	2.8	0.19	65	862	500	817	1.96	26	73	0.85

^aNumbers in the parentheses indicate initial Si/Al atomic ratios and those in the square brackets initial C₁₂H₂₅NMe₃Br/SiO₂ molar ratios. ^bpH Values of TIE solution. ^cCalculated from the difference between S_{BET} and external surface area determined by t-plot method. ^dEstimated from the N₂ desorption branch with Barrett-Joyner-Halenda (BJH) method. The values estimated from the adsorption isotherms were almost the same as those listed in the table within the errors of 0.1 nm. ^eRelative intensities of X-ray (100) diffraction. ^fReaction conditions: Al-M41 50 mg, **3b** 1.0 mmol, **1b** 1.0 mmol, **4a** 0.50 mmol, octane 1.0 mL, 388 K, 10 h. ^gCalculated from the ²⁷Al NMR spectra and the peak area ratios of AlO₄ to (AlO₄+AlO₆). ^hNot determined.

8. References

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