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Highly ordered aluminium-planted mesoporous silica as active catalyst for Biginelli reaction and formyl C–H insertion reaction with diazoester†

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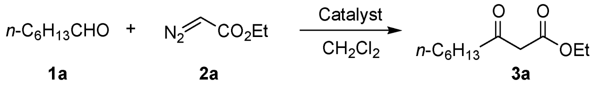
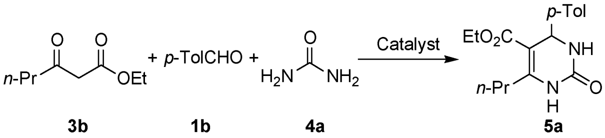
Al-planted MCM-41s (Al-M41s) with regular mesoporous structure and Si/Al ratio of 23–32 were successfully prepared by the template-ion exchange method in which the template/Si molar ratio and Si/Al ratio were adjusted at 1.44 and 5–15, and showed much higher catalytic activity for the titled reactions than the other types of Al-M41s prepared by post-synthesis or sol–gel methods.

Recently, Al-planted MCM-41 (Al-M41) catalysts prepared by template-ion exchange (TIE) method[1] were found to be very active for C–H insertion reaction of aldehyde with diazoester (the formyl C–H insertion reaction, Scheme 1)[2] and Biginelli dihydropyrimidinone (DHPM) synthesis (the Biginelli reaction, Scheme 2) by the present group.[3,4] In the latter reaction, the yield of desired DHPM **5a** showed a volcano-shaped dependence on the Si/Al atomic ratio of Al-M41 and the highest yield 75% was attained at Si/Al = 35 as shown in Fig. 3, open circle.[4] The decrease in the yield of **5a** at or below Si/Al = 30 was due to the partial collapse of the pore structure, that is, the drastic decrements in mesopore volume evaluated from N_2 adsorption isotherms with t-plot method (V_p), specific surface area calculated with BET method (S_{BET}), and intensity of XRD diffraction as shown in the previous study.

The incorporation of Al into silica-based mesoporous materials was frequently applied to prepare effective acid catalysts, and several preparation methods such as sol–gel method,[5] post-synthesis,[6] and the TIE method[1] were reported. However, the partial destruction of pore structure owing to too much Al contents and the resulting decrease in the catalytic activity were widely recognized in various reactions.[7] For example, the catalytic activity for the dehydrative dimerization of acetone or the reaction of formaldehyde with phenol was found to be maximized at Si/Al = 7[7a] or 70.[7b] The combination of highly loading of Al into the silica wall with the maintenance of the regular pore structure is one of the challenging research topics in the heterogeneous catalysis field.



Scheme 1 Formyl C–H insertion reaction of diazoester.



Scheme 2 Biginelli reaction.

Here we tried to prepare Al-M41 with ordered mesoporous structure and high Al contents by applying various preparation methods of the parent M41s and supporting methods of Al ions. The sol–gel and post-synthesis methods were used as well as the TIE method. The effect of the ratio of template/Si was also investigated in the preparation of the parent M41 on the basis of the finding that the high template/Si ratio in sol–gel synthesis resulted in the highly ordered Al-M41,[8] though the template/Si ratios were 0.1–0.3 in this experiments[8] while was 0.72 in our previous study.[4] The catalytic activity for the Biginelli reaction was mainly employed as the indicator of the effectiveness of each preparation method. The results reported here will show that Al-M41 samples with low Si/Al ratios and high regularity of pores could be prepared and both factors were indeed important for appearance of high catalytic activity.

The effect of preparation method was first studied. Six kinds of Al-M41s were prepared according to the previous studies reporting Al-M41s with high S_{BET} and high Al content (Table 1).[9,10] The sample name Al(x)-M41-y or -[z] in this paper shows the conditions of initial Si/Al ratio in the preparation (x), preparation method (y), and template/Si ratio in preparation of the parent (z). Al-M41-a, -b and -c were synthesized by post-synthesis methods using Al(Oi-Pr)$_3$, Al(acac)$_3$ and AlMe$_3$ as Al sources.[9] Al-M41-d, -e and -f were prepared by sol–gel methods with $NaAlO_2$, Al(Oi-Pr)$_3$ and $Al(OH)_3$.[10] In all experiments $C_{12}H_{25}NMe_3Br$ was employed as a template in order to minimize the influence of surfactant on the catalytic activity. The high S_{BET} and V_p could be obtained in all experiments as shown in entries 1–6 of Table 1. All of them showed catalytic activity for the Biginelli reaction of **3b**, **1b** and **4a** (Scheme 2). The yields of **5a**, however, were lower than that of Al(35)-M41-[0.72] prepared by the TIE method (entry 7). It follows that the situations of Al ions loaded by various methods would be strongly dependent on the preparation methods; for example, the sol–gel Al-M41s (entries 5 and 6 in Table 1) would have Al species buried in the silica wall, while the TIE method would give Al species separately supported on the wall, though there was no direct evidence for the speculation at the present. The preparation conditions of TIE were therefore investigated in more detail to enhance the catalytic activity, though the characterization of respective Al ions remained to be clarified in near future.

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† Electronic supplementary information (ESI) available: Nitrogen adsorption isotherms, XRD patterns and ^{27}Al NMR spectra of the catalysts and correlations between catalytic activity and physicochemical properties. See DOI: 10.1039/c0cp00565g

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Table 1 Physicochemical properties and catalytic activity of Al-M41s prepared by post, sol–gel, or TIE methods

Entry	Catalyst[a]	Method	Al source	Ref.	Physicochemical properties [Al]/mmol g^{-1}	Si/Al	S_{BET}/m^2 g^{-1}	V_p mm^3 g^{-1}	D^b/nm	$Int_{100}{}^c$/10^3 cps	GC yield[d](%)
1	Al(30)-M41-a	Post	Al(O*i*-Pr)$_3$	9a	0.35	25	1012	566	2.2	29	38
2	Al(30)-M41-b	Post	Al(acac)$_3$	9b	0.35	25	968	532	2.3	29	47
3	Al(30)-M41-c	Post	AlMe$_3$	9c	0.40	34	1011	606	2.3	28	45
4	Al(25)-M41-d	Sol–gel	NaAlO$_2$	10a	0.62	20	969	570	2.5	11	48
5	Al(14)-M41-e	Sol–gel	Al(O*i*-Pr)$_3$	10b	1.2	12	825	488	1.9	7.2	38
6	Al(3)-M41-f	Sol–gel	Al(OH)$_3$	10c	3.3	3.2	799	453	2.2	18	49
7	Al(35)-M41-[0.72]	TIE	Al(NO$_3$)$_3$	1	0.38	35	896	406	2.2	24	75

[a] Numbers in the parentheses indicate initial Si/Al atomic ratios and those in the square brackets initial $C_{12}H_{25}NMe_3Br/SiO_2$ molar ratios. [b] Estimated from the N_2 desorption isotherms with the 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. [c] Relative intensities of X-ray (100) diffraction. [d] *Reaction conditions*: catalyst 50 mg, **3b** 1.0 mmol, **1b** 1.0 mmol, **4a** 0.50 mmol, octane 1.0 mL, 388 K, 10 h.

The correlation of the template/Si molar ratio with the regularity of pores or the catalytic activity was examined. Three types of parent M41s were prepared on the conditions of the template/Si ratios 0.36, 0.72 and 1.44. It should be noted that the experiment with template/Si ratio of 1.8 did not give correct results because of insufficient dissolving of template ion. The TIE treatment was carried out at the initial Si/Al ratio of 30 (Table 2, entries 1–3). The pore structure and catalytic activity were measured after the TIE treatment and calcination at 873 K for 6 h. The S_{BET} and XRD peak intensities of the samples were in the order Al(30)-M41-[1.44] > Al(30)-M41-[0.72] > Al(30)-M41-[0.36] (Fig. 1). The catalytic activity were Al(30)-M41-[1.44] = Al(30)-M41-[0.72] > Al(30)-M41-[0.36] within the experimental errors. The M41 prepared at template/Si = 1.44 was mainly employed as the parent for the following study.

The effect of the concentration of Al(NO$_3$)$_3$ in the TIE treatment was next studied. As shown in Table 2, entries 4–6, the amounts of Al added in the solution little affected the Si/Al ratios of the resulting Al-M41s, while surprisingly increased greatly the V_p values in spite of the approximately constant S_{BET}. The V_p values of Al(5)-M41-[0.72], Al(15)-M41-[1.44] and Al(5)-M41-[1.44] were 601–639 mm^3 g^{-1}, which can be compared with the values of 340–379 of entries 1–3. This is clearly shown in Fig. 2 where the amounts of nitrogen adsorbed at P/P_0 = 0.23 onto the Al(5)-M41s were much greater than those of Al(30)-M41s (Fig. 2). The results were sufficiently reproducible within the respective error shown in the table.[11] Two findings/discussion should be noted here. The small change in S_{BET} and great increase in V_p indicate the increase in internal surface area of pores, which was confirmed in the separated experiments as shown later. The second point is the question which the increment in V_p resulted from the high Al concentration or the low pH of the solution, since the pH values in entries 4–6 were lower than those of entries 1–3. This subject would also be studied later. Before the detailed structural studies, the catalytic activities for the Biginelli reaction were compared. The yields of DHPM on Al(5)-M41-[0.72], Al(15)-M41-[1.44] and Al(5)-M41-[1.44] were 75, 88 ± 2 and 87 ± 1%, respectively. Clearly the

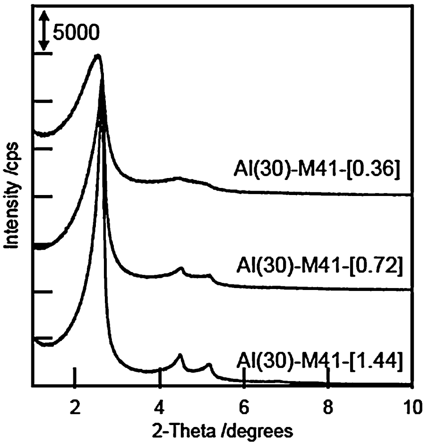

Fig. 1 X-Ray diffraction patterns of Al(30)-M41s prepared at various template/Si molar ratios.

Table 2 Effects of template/Si molar ratio and initial Si/Al atomic ratio on physicochemical properties and catalytic activity

Entry	Al-M41[a]	pH[b]	[Al]/mmol g^{-1}	Si/Al	S_{BET}/m^2 g^{-1}	V_p/mm^3 g^{-1}	D^c/nm	Int$_{100}{}^d$/10^3 cps	GC yield[e] (%)
1	Al(30)-M41-[0.36]	6.9	0.38	30	731	340	2.3	15	29
2	Al(30)-M41-[0.72]	7.0	0.44	29	791	379	2.0	22	66
3	Al(30)-M41-[1.44]	7.2 ± 0.4	0.45 ± 0.03	29 ± 0	832 ± 38	375 ± 14	2.1 ± 0.0	28 ± 2	60 ± 1
4	Al(5)-M41-[0.72]	3.2	0.32	38	1009	601	2.2	25	75
5	Al(15)-M41-[1.44]	3.4 ± 0.1	0.44 ± 0.02	29 ± 0	892 ± 34	639 ± 15	2.3 ± 0.1	26 ± 2	88 ± 2
6	Al(5)-M41-[1.44]	3.0 ± 0.1	0.48 ± 0.05	26 ± 3	1057 ± 16	617 ± 9	2.2 ± 0.1	31 ± 2	87 ± 1
7	Al(30)-M41-[1.44]-pH	3.0 ± 0.1	0.26 ± 0.03	57 ± 4	899 ± 32	598 ± 41	2.2 ± 0.2	31 ± 3	66 ± 5

[a] Numbers in the parentheses indicate initial Si/Al atomic ratios and those in the square brackets initial $C_{12}H_{25}NMe_3Br/SiO_2$ molar ratios. [b] pH values of TIE solution. [c] Estimated from the N_2 desorption isotherms with the 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. [d] Relative intensities of X-ray (100) diffraction. [e] *Reaction 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.

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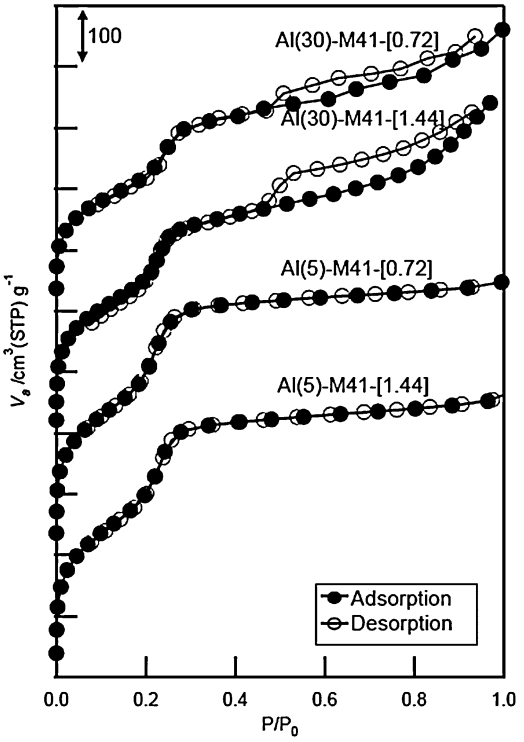

Fig. 2 N_2 adsorption–desorption isotherms of Al(30)-M41-[0.72], Al(30)-M41-[1.44], Al(5)-M41-[0.72] and Al(5)-M41-[1.44].

preparation with high-Al-solutions was very effective for enhancement of the catalytic activity, though the amounts of Al loaded on the silica surface did not increase.

The reason for the increments in pore volume and catalytic activity in entries 4–6, Table 2 was studied. The pH value of TIE solution was adjusted at 3.0 by addition of an aq. HNO_3 solution in entry 7 of Table 2 where the initial Si/Al ratio was adjusted at 30. The Si/Al ratio of the resultant sample was 57 ± 4. The higher Si/Al values than those of the usual treatment would be due to the presence of much amount of proton as already reported in the literature.[1] On the other hand, the V_p values of Al(30)-M41-[1.44]-pH was comparable to those of entries 4–6, clearly indicating that the treatment of the parent M41 with an acidic solution resulted in the higher regularity of pore structure. The yield of DHPM **5a**, however, was lower than those in entries 4–6. This would be due to the low Al contents as shown in the next paragraph. All results obtained on Al-M41s newly prepared in the present work and those reported in the previous work[4] were plotted in Fig. 3 as a function of the Si/Al ratio.[11] Closed circles and open triangles show the results on Al-M41-[1.44] and Al-M41-[1.44]-pH. Open circles are those on Al-M41-[0.72]. It follows that the volcano-shaped correlation between the Si/Al ratio and the catalytic activity, the solid line, could be improved to the level of the dotted line through the present preparation method.

To reveal the factors controlling the catalytic activity, the yields of **5a** were plotted as a function of the V_p values, the intensity of (100) XRD peak (Int_{100}), and the S_{BET} values.[12] No correlation between the Int_{100} or S_{BET} values and the yields could be observed. The long-range regularity of Al-M41, measured by Int_{100}, would not be significant for the appearance of catalytic activity. The total surface areas S_{BET} would not be the good index of the present catalysis because the values are the sum of outer and inner surface areas of mesoporous structure. In contrast, the very good relationship between the V_p values and the yield of **5a** could be recognized. Fig. 4 shows the dependence of the yield of **5a** on the Si/Al ratio and the V_P value. The Al-M41s having given the 85% or more yields were plotted by closed circles in the figure. They were located at the positions of low Si/Al ratios and large mesopore volumes. The results indicate that the reaction took place in the pores of M41 and the important factor for the high catalytic activity would be maintenance of pore structures and the high Al contents. This was further confirmed by the S_{int} of Al-M41s which could be calculated from the difference between S_{BET} and the external surface area (S_{ext}) determined by the t-plot method. Similar correlation could be observed (Fig. S11 in ESI).† The reason why high template/Si ratio and high Al concentration was essential for the high catalytic activity should be resolved in the near future.

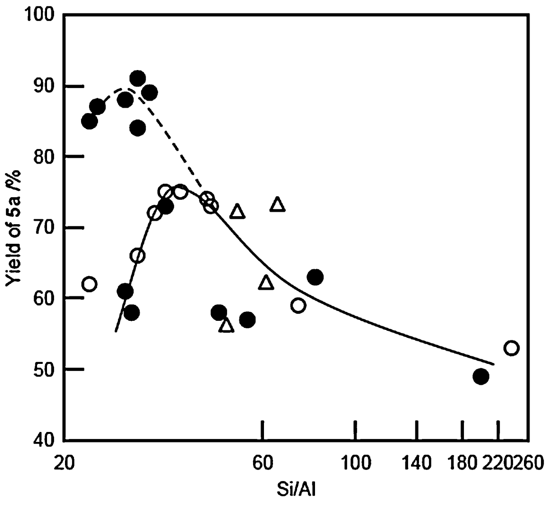

Fig. 3 Dependence of yield of **5a** on Si/Al ratio of Al-M41 catalysts prepared by the TIE method. Open circle, Al-M41-[0.72]. Closed circle, Al-M41-[1.44]. Open triangle, Al(30)-M41-[1.44]-pH.

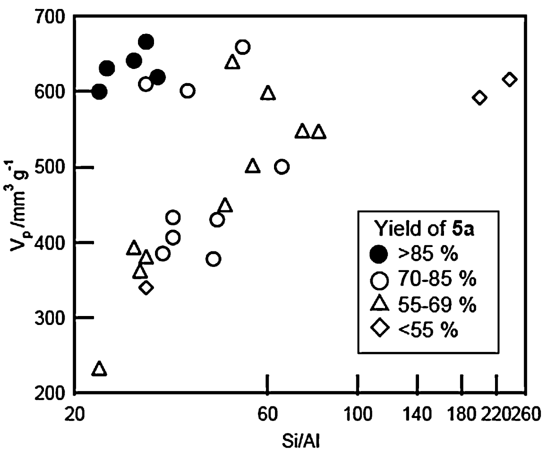

Fig. 4 Effect of Si/Al ratio and mesopore volume V_p on the catalytic activity of the Al-M41s.

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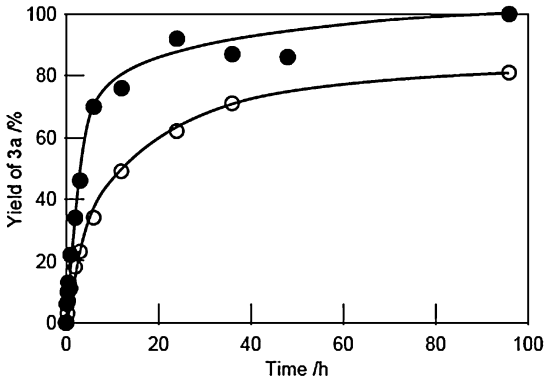

Fig. 5 Yields of the formyl C–H insertion reaction on Al(5)-M41-[1.44] (closed circle) and Al(30)-M41-[0.72] (open circle). *Reaction conditions*: Al-M41 20 mg, **1a** 8.0 mmol, **2a** 12 mmol, CH_2Cl_2 40 mL, 298 K. Determined by GC analysis.

The effect of coordination of Al ions was studied by using the solid-state ^{27}Al-MAS NMR technique because tetrahedrally coordinated Al (AlO_4) ion is often suggested as an important acidic site.[13] Both of AlO_4 and AlO_6 species could be observed on the present samples but no significant correlation with the catalytic activity was recognized (Fig. S12 in ESI).† The results observed in Table 1 and Fig. 4 clearly show the importance of coordination state of aluminium on the silica wall but they were still unclear.

The catalytic activity of the present Al-M41 for the formyl C–H insertion reaction[2] were compared with the previous catalyst in Fig. 5, in which the reaction of *n*-heptaldehyde (**1a**) with ethyl diazo acetate (**2a**) was selected as the model reaction. The reaction rate on the Al(5)-M41-[1.44] catalyst was two times greater than that on the reported one (Al(30)-M41-[0.72]) as shown in Fig. 5. The amount of Al(5)-M41-[1.44] employed was only 2.5 mg per mmol of **1a** and the yield reached to 100%. As long as we know, the amount of catalyst used in the figure is the least among those of the reported heterogeneous catalysts.[14,15]

In summary, the enhancement of catalytic activity of Al-M41 was achieved by improvement of the TIE method. The parent M41 should be prepared at template/Si = 1.44. The TIE treatment in a low pH solution with high Al contents was also the key. The resulting Al-M41s with the Si/Al ratio of 20–30 have the large pore volumes and showed high catalytic activity for the Biginelli reaction and the formyl C–H insertion reaction.

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