Several Factors Affecting the Novel Synthesis of Mesoporous Aluminosilicate MCM-41 through Non-hydrothermal Conditions

Takayoshi SHINDO[*], Masayoshi KATO[*], Shigeaki KITABAYASHI[*] and Sentaro OZAWA[*]

[*]Department of Materials-process Engineering and Applied Chemistry for Environments,
Faculty of Engineering and Resource Science, Akita University,
1-1 Tegata Gakuen-cho, Akita 010-8502, JAPAN

In order to elucidate the effect of synthesis conditions of Al-MCM-41 on the characteristics of the resultant samples, Al-MCM-41 samples were synthesized through non-hydrothermal reactions under diverse conditions. The following conditions were found to be favorable to prepare Al-MCM-41 with well ordered 2D-hexagonal structure from the reaction mixtures of lower Si/Al ratios: simultaneous addition of Si and Al sources into the solution containing both template of surfactant and anti-foaming agent, in neutral to acidic media (pH 3-7), at temperatures above Krafft point of the surfactant, and under vigorous stirring. These conditions may be associated with assembly of aluminosilicate sources with uniform composition (i.e., constant Si/Al ratio) around the template micelles, promoting hydrolysis and/or condensation of aluminosilicate and forming Al-MCM-41 with highly-ordered structures. Relatively weak acid sites are mainly consisted of Al-MCM-41 and similar distributions of acid strength are observed for the samples with different Si/Al species. Dealkylation reactions of 1,3,5-triisopropylbenzene, which are well known to proceed on Bronsted acid sites are catalyzed more effectively on Al-MCM-41 samples than on HY-zeolites. This means that at least, a part of Al was incorporated into the silica framework of MCM-41 structure as tetrahedrally coordinated species in Al-MCM-41 samples prepared in the present study.

Key Words : Mesoporous aluminosilicate MCM-41, Non-hydrothermal synthesis, Preparation conditions, Acidity, Dealkylation of 1,3,5-triisopropylbenzene.

1. Introduction

Mesoporous molecular sieve materials such as MCM-41 have attracted considerable attention because of their characteristics such as large channels in a hexagonal array, long-range order and surface area above $700 \, m^2 g^{-1}$. The incorporation of Al and transition metals within the silica framework has been studied to improve the acidity, catalytic activity, and adsorption properties of the mesoporous silica molecular sieves. There are many reports for the synthesis of Al-incorporated MCM-41 (Al-MCM-41). Originally, Al-MCM-41 was prepared through hydrothermal reactions of aluminosilicate gels at various Si/Al ratios, with different Al or Si sources in the presence of quaternary ammonium surfactants in the temperatures ranging from 373 to 423 K[1,2]. Further studies on the hydrothermal synthesis clarified that some precise conditions such as the careful control of the reaction temperature as well as pH and an extensive reaction time are required to prepare well ordered Al-MCM-41[3-14]. In addition, extensive investigations for the preparation of Al-MCM-41 revealed that room temperature synthesis was able to provide a convenient access to high-quality of Al-MCM-41 in a short period of time, although sources of Si and Al, and the order of addition of them into the surfactant solution, and pH of the reaction mixture were different depending on literatures[9, 15-17, 24]. Thus, effect of

factors in room-temperature synthesis on the properties of Al-MCM-41 has to be further elucidated. It is of great interest based on the concept of "Green Chemistry" that milder conditions and simplified procedures for the preparation of Al-MCM-41 are developed instead of conventional hydrothermal ones. In the present investigation, the non-hydrothermal synthesis of Al-MCM-41 was studied under various conditions to clarify the effect of the adding order of Si and Al sources to the surfactant solution, pH of the reaction mixture, and the utilization of an anti-foaming agent on the properties of the resultant Al-MCM-41. The acidity and the catalytic activity of Al-MCM-41 for the dealkylation reactions of 1, 3, 5-triisopropylbenzene (TIPB) were also studied.

2. Experimental

2.1 Materials

The sources of aluminosilicate were sodium silicate powder (Kishida chemical), containing 50 - 55% SiO_2, and sodium aluminate powder (Kanto chemical), containing 34-39% Al_2O_3. The surfactant used to prepare the template was cetyltrimethylammonium bromide (Tokyo kasei kogyo). An anti-foaming agent was non-ionic emulsifiers, ANTIFORM A emulsion (Sigma). Hydrochloric acid (35%) was obtained from Nacalai tesque. TIPB was purchased from Tokyo kasei kogyo. These reagents were used without further purification.

Table 1 Characteristics of AL-MCM-41 samples prepared under various conditions

No.	Type[a]	Si/Al[b]	Agitation / rpm	pH	Aging temp. / K	Additives	S_{BET}[d]/ m^{2}g^{-1}	d_{100}[e]/ nm	D[f]/ nm	V_p[g]/ cm^{3}g^{-1}	w[h]/ nm
1	(MCM-41)	∞	300	10-11	293	-	1215	3.71	2.45	0.90	1.83
2	[1]	30	300	10-11	293	-	886	3.53	2.20	0.52	1.88
3	[2]	50	300	10-11	293	-	842	3.53	2.40	0.71	1.68
4	[3]	30	300	10-11	293	-	976	3.29	2.05	0.65	1.75
5	[3]	30	15	10-11	293	-	821	3.47	2.15	0.55	1.86
6	[4]	30	400	3-5	323	-	1154	3.80	2.32	0.89	2.07
7	[4]	30	400	5-7	323	-	987	3.77	2.12	0.79	2.23
8	[4]	30	400	7-10	313	-	972	3.86	2.32	0.90	2.14
9	[4]	30	400	5-7	293	AF[c]	1069	3.78	2.32	0.80	2.05
10	[4]	30	400	5-7	293	-	1054	3.73	2.32	0.82	1.99
11	[4]	20	400	5-7	323	AF[c]	1064	3.61	1.90	0.76	2.27
12	[4]	20	400	5-7	323	-	917	-	2.52	0.97	-
13	[4]	10	400	5-7	323	AF[c]	916	3.55	2.12	0.56	1.98
14	[4]	10	400	5-7	313	-	706	-	2.12	0.47	-
15	[4]	5	400	5-7	293	AF[c]	751	3.80	2.32	0.71	2.07
16	[4]	5	400	5-7	313	-	590	-	2.12	0.58	-

a) Methods of addition of Si and Al sources to the template solution described in the text.
b) Si/Al atomic ratio of feed.
c) Anti foaming agent
d) Specific surface area by BET method
e) Basal spacing by XRD
f) Pore diameter by DH method
g) Pore volume by DH method
h) Wall thickness determined by $w = (2d_{100}/\sqrt{3}) - D$

2.2 Synthesis

Al-MCM-41 samples were synthesized basically according to the literature described elsewhere[15] with some modifications. Sodium silicate (42 - 50 mmol of Si) dissolved in 9.4 ml of distilled water and sodium aluminate (1.0 - 8.3 mmol of Al) dissolved in 9.4 ml of distilled water were added to the aqueous solution of the surfactant (6.0 mmol of the surfactant in 100 ml of distilled water) at 313 K with various agitation modes. Molar ratio of surfactant/(Si + Al) was fixed to 0.12. The pH of the reaction mixture (pH 3 - 11) was adjusted with diluted hydrochloric acid. The acid was basically poured into the aqueous solution of the surfactant before adding Si and Al sources. HCl was also added to the solution which was under addition of Si and Al sources into the surfactant solution, if necessary. The reaction mixture was aged under stirring at 313 - 323 K or at ambient temperature for 3 h to prepare the solid product. The obtained solid product was filtrated and washed with an excess amount of distilled water. The solid product was dried at 383 K for 16 h and calcined at 823 K for 6 h to prepare Al-MCM-41. The most important modification in the synthesis of Al-MCM-41 samples was the method of addition of Si and Al sources into the solution of the surfactant. Both sources were added dropwise to the template solution by using individual burettes made of polyethylene. Four types of additions were employed in the present study. In type [1], 9.4 ml of Al-source was added into the surfactant solution before equal volume of Si-source was titrated. In type [2], 9.4 ml of Si-source was firstly mixed with the solution of the surfactant followed by the addition of equal volume of Al-source. In type [3], 1.0 ml of Al-source and 1.0 ml of Si-source were added one after the other into the template solution, and that was repeated until total volume of each source reached 9.4 ml. Sources of Si and Al were added simultaneously to the surfactant solution which contains an appropriate amount of the anti-foaming agent if necessary in type [4].

2.3 Analysis

Powder X-ray diffraction patterns were obtained by a Rigaku RAD-C system. Adsorption isotherms of N_2 at 77 K were measured on a Japan Bell BELSORP 18 automated sorption apparatus. Dead volume was determined by using helium gas (purity 99.99%). Chemical analysis of samples was performed by a Horiba energy dispersive X-ray analyzer EMAX-2770WR. Acidity and acid strength of the samples were measured by means of NH_3 temperature programmed desorption (NH_3-TPD). Samples were pretreated at 523 K for 2 h under vacuum, then preadsorbed NH_3 at 373 K under 5.7×10^3 Pa for 45 min, and evacuated at 373 K for 45 min to remove physically adsorbed NH_3. The samples were then subjected to the TPD operation with a ramping rate of 10 K min^{-1}. The amount of desorbed NH_3 was recorded on a ULVAC quadrupole mass analyzer MSQ-150A.

2.4 Catalytic dealkylation of TIPB

The dealkylation reactions of TIPB were carried out using a conventional fixed bed flow type reaction system at 513 - 533 K under atmospheric pressure with WHSV of 4.2 - 25.3 h^{-1}. Al-MCM-41 and other catalysts were activated in situ at 623 K for 2 h in a stream of helium. The reaction products were analyzed by a Shimazu GC-14 gas chromatograph equipped with FID and using a MEGABORE DB-1 column.

3. Results and discussion

3.1 Effect of synthesis conditions

Effect of adding order of Si and Al sources : Four types of different methods were investigated to elucidate the effect of adding order of Al and Si sources into the solution of the surfactant on the characteristics of Al-MCM-41 samples. Characteristics of the samples prepared under various conditions were listed in Table 1. XRD patterns, adsorption isotherms and pore size distributions of the samples were depicted in Figures 1 - 3. The Dollimore-Heal method was used to calculate the pore size

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distribution, since this method considers the thickness of multilayer adsorption and provides similar evaluation to that of the BJH method[21, 22]. The sample (No. 8) prepared by type [4] preparation gave larger specific surface area, pore volume and rather intense (100) XRD peak as well as a narrow pore size distribution in mesopore region than those obtained from type [1], [2], and [3] preparations, i.e. samples Nos. 2, 3, and 4, respectively. Adsorption isotherms showed the character of type IV in BDDT classification, which is a typical one for MCM-41.
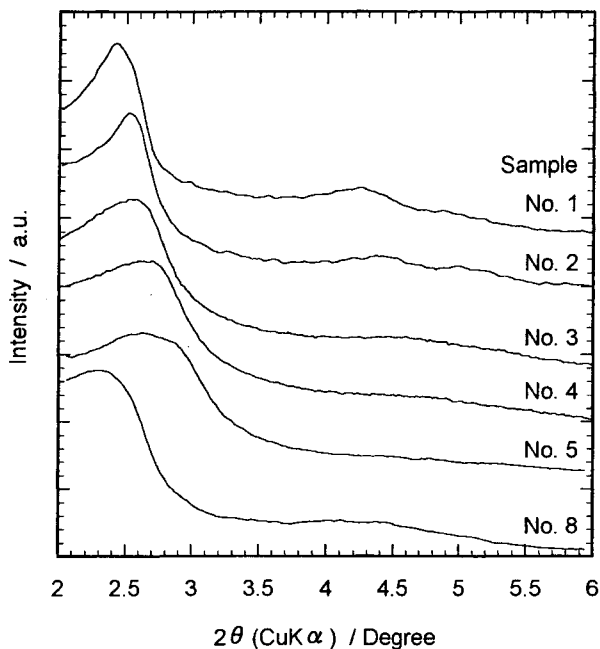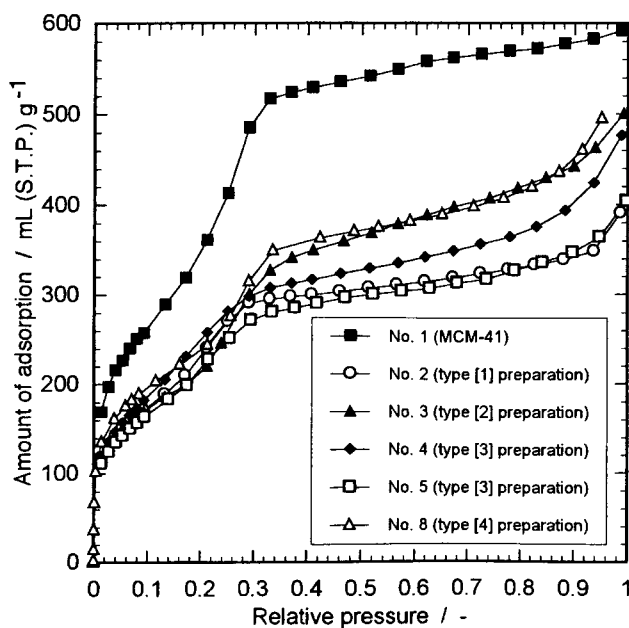
Namely, a steep rising in the amount of adsorption was observed at relative pressures of 0.2 - 0.3, which indicated capillary condensation of nitrogen in the mesopores of approximately 2 - 3 nm diameter. The degree of stepwise increase of adsorption depended on the adding order of Si and Al sources into the surfactant solution. The degree of the rising was found to decrease as follows: type [4] > type [2] > type [3] > type [1].

Simultaneous addition of Si and Al sources into the solution of the surfactant which is similar to type [4] in the present study was applied to the room-temperature synthesis[15, 17] and hydrothermal synthesis[9]. This type of method seems to produce Al-MCM-41 with ordered structure compared with other methods adopted in the room temperature[9, 16, 24] as well as the hydrothermal[2, 4-8, 10] preparations of Al-MCM-41 samples. Therefore, these results indicate that both sources of Si and Al should be added into the solution of surfactant (template) keeping the value of Si/Al ratio constant during the synthesis, in order to prepare Al-MCM-41 samples of highly ordered structure.

Effect of agitation : As shown in Table 1 and Figures 1 - 3, comparing the characteristics of No. 4 and No. 8 with those of No. 5, it is noted that a vigorous stirring is essential for the samples to have characters such as large specific surface area, large pore volume, well ordered 2D-hexagonal structure, and sharp distributions in mesopore region. This result suggests that one of the most important points is to maintain the local homogeneity of template and inorganic species such as silicate and aluminate ions.

Effect of pH : XRD patterns, adsorption isotherms, and pore size distributions of the samples synthesized under different pH ranges were shown in Figures 4 - 6. In comparison with No. 8 produced under basic media, both No. 6 and No. 7 which were prepared under neutral to acidic conditions gave large specific surface areas and rather sharp diffraction peaks, indicating that the reactions in neutral to acidic media are favorable for the formation of the Al-MCM-41 samples with well ordered structures. These results are in agreement with those reported by Yu et al.[24] who prepared the aluminosilicate mesoporous materials in the pH range of 5 - 6.

Figure 1   XRD profile of Al-MCM-41 and MCM-41

Figure 2   Adsorption isotherms of N_2 at 77 K of samples prepared under various adding orders of Si and Al sources into surfactant solution in basic media
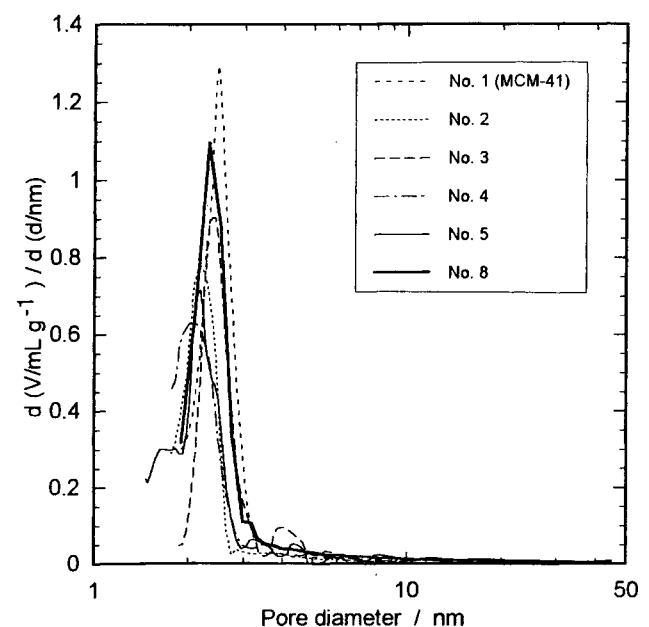

Figure 3   Pore size distributions of MCM-41 and Al-MCM-41 samples

Lower pH may enhance the kinetics of silica polymerization[24]. It was reported, however, that strong acidic conditions such as pH below 3 result in the dissolution of aluminum from the samples[15]. As described later, Figure 11 shows that Si/Al ratios of the samples produced in the basic and neutral media are smaller than
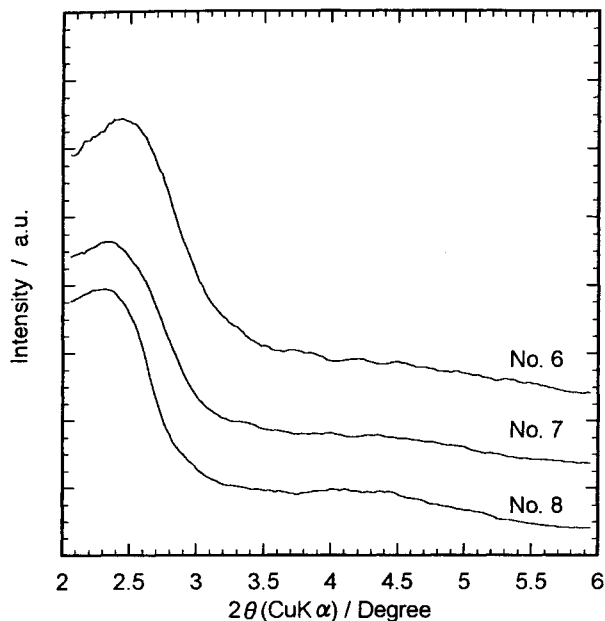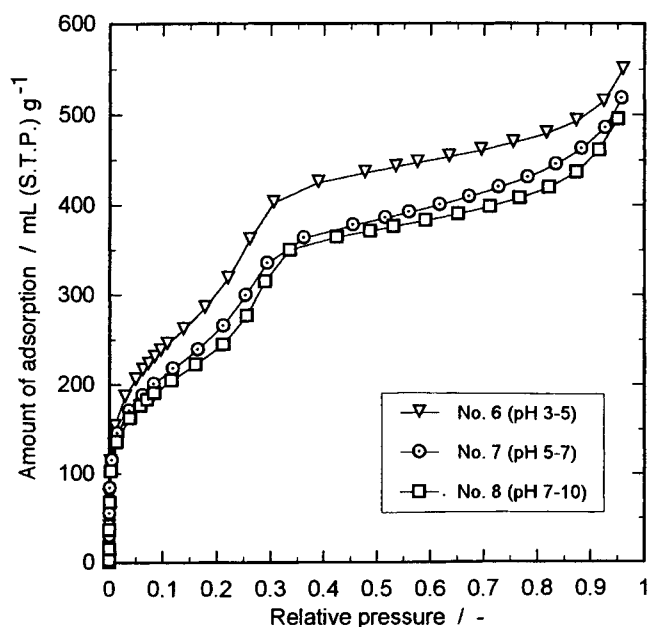
those of the reactants, while those of the sample and the reactant solution in the acidic media are similar. These results indicate that equilibrium between Al-MCM-41 phase and the solution of the reactants is affected by pH and that the solubility of Si in basic media is rather high in comparison with those in neutral and acidic media, which is probably due to the decrease in regularity of the structure for the resultant Al-MCM-41 samples in the basic media.

Effect of aging temperature : Comparison of the characteristics of sample No. 10 with those of No. 7 suggests that the effect of the aging temperature is not significant. This implies that during the dropwise addition of Al and Si sources into the solution of the template, temperature of the reaction mixture should be kept above Krafft point of the surfactant to assemble sources of aluminosilicate and templates, i.e., rod-like micelles into nucleuses of Al-MCM-41. It also may be suggested that the aging temperature is not necessarily higher than Krafft point, provided the temperature of the solution is kept above Krafft point during addition of Al/Si sources into the surfactant solution.

Effect of anti-foaming agent : Effect of the anti-foaming agent was not significant for the samples prepared under higher Si/Al ratio (Si/Al = 30), comparing sample No. 9 with sample No. 10. In contrast, samples synthesized under lower Si/Al ratios using the anti-foaming agent showed typical characters of MCM-41, i.e., 2D-hexagonal structure, type IV isotherm, and sharp distribution in mesopore region, while those produced under similar conditions without the anti-foaming agent did not give any typical features of MCM-41. These results support that the anti-foaming agent apparently acted as a promoter to produce Al-MCM-41 with regularly ordered 2D-hexagonal structures under relatively lower Si/Al ratios. This effect of the anti-foaming agent was also reported in hydrothermal synthesis of Al-MCM-41[14]. It is considered that the anti-foaming agents suppress the formation of bubbles and foam and decrease the population of them during vigorous agitations, contributing to keep the homogeneity of the reaction mixtures.
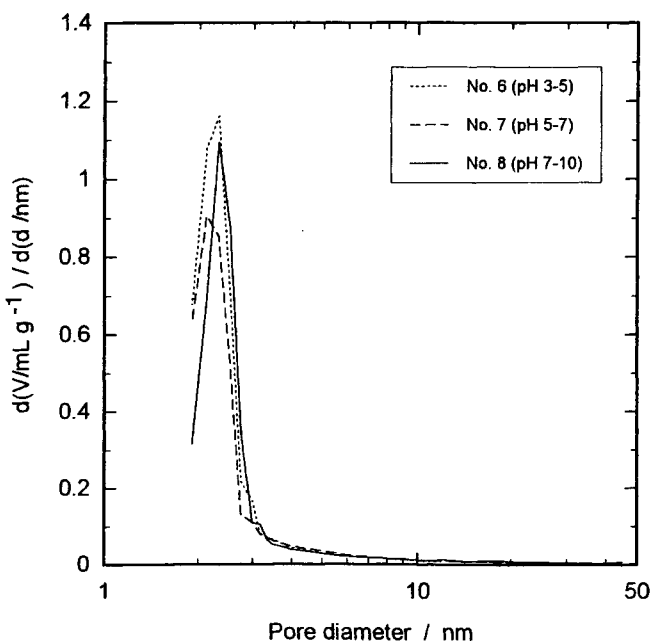

Figure 4   XRD profile of Al-MCM-41 samples prepared under different pH ranges

No. 6 (pH 3-5)
No. 7 (pH 5-7)
No. 8 (pH 7-10)

Figure 5   Adsorption isotherms of N₂ at 77 K of samples prepared under various pH ranges

Figure 6   Pore size distribution of Al-MCM-41 samples synthesized under differet pH ranges

Effect of Si/Al ratio : As shown in Table 1 and Figures 7 - 9, specific surface area, pore volume, and intensity as well as sharpness of (100) peaks appeared in XRD patterns of the Al-MCM-41 samples de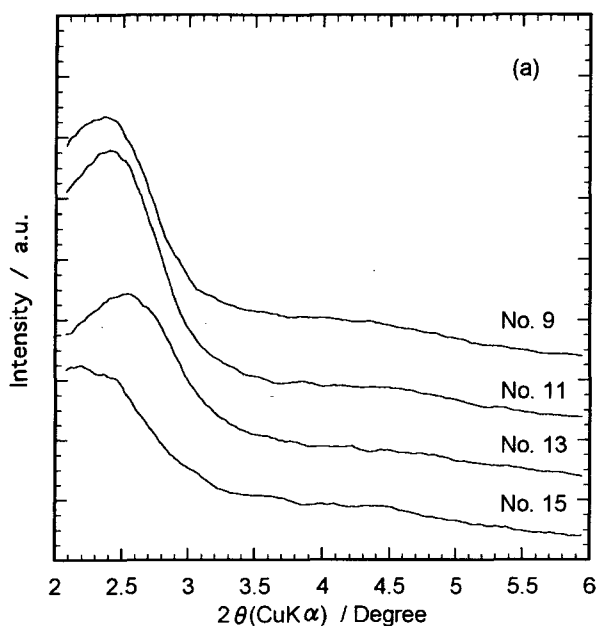creased as the Si/Al ratios of the reaction solutions decreased. Significant rise in isotherms at higher relative pressures was also noticed for the samples of smaller Si/Al ratios as shown in Figure 8. These tendencies were also reported in the literatures[4, 6, 10, 15]. It is considered that these features reflect the deterioration of the structural regularity for the resultant Al-MCM-41 samples with lower Si/Al ratios.

3.2 Acidic property

Profiles of NH_3-TPD for Al-MCM-41 samples with different Si/Al ratios were presented in Figure 10. Distributions and strengths of acid for individual samples seem to be almost similar, indicating that the locations of Al incorporated in the samples which directly affect the properties of the solid acids, are resemble and independent of the Si/Al ratios. Acidity of the samples calculated from the NH_3-TPD profiles increased as the decrease in Si/Al ratios as shown in Figure 11. Relatively weak acid sites are mainly consisted of the Al-MCM-41 samples. This feature of the Al-MCM-41 samples is quite different from that of HY-zeolites, which has a large amount of strong and weak acid sites.
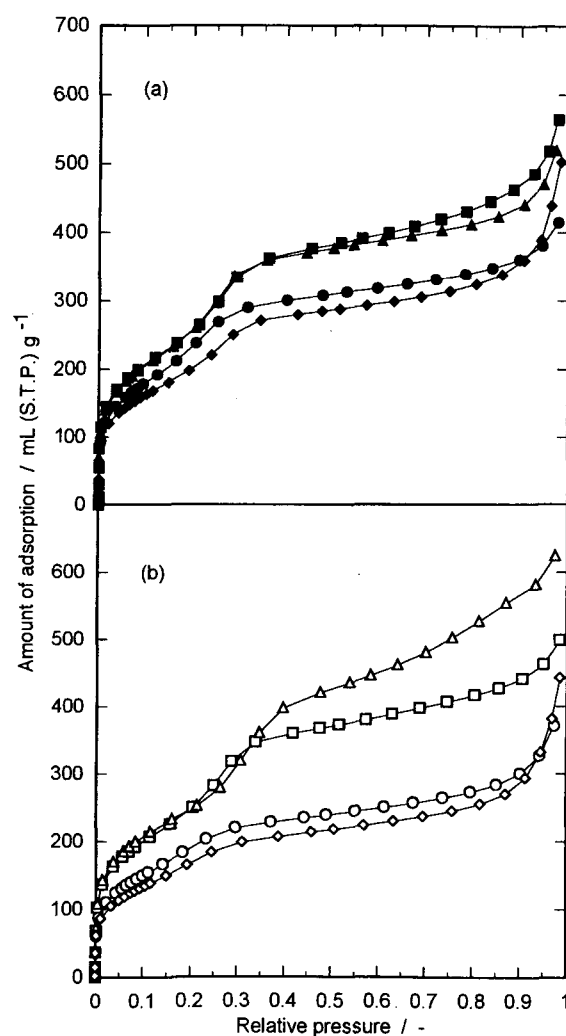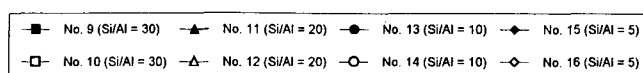
Figure 7(a)   XRD profile of samples synthesized with anti-foaming agent

No. 9 (Si/Al = 30), No. 11 (Si/Al = 20),
No. 13 (Si/Al = 10), No. 15 (Si/Al = 5)

Figure 8   Adsorption isotherms of N_2 at 77 K of samples synthesized under various Si/Al rations, (a) with anti-foaming agent, (b) without anti-foaming agent

Figure 7(b)   XRD profile of samples synthesized without anti-foaming agent

No. 10 (Si/Al = 30), No. 12 (Si/Al = 20),
No. 14 (Si/Al = 10), No. 16 (Si/Al = 5)

No. 9 (Si/Al = 30)   No. 11 (Si/Al = 20)   No. 13 (Si/Al = 10)   No. 15 (Si/Al = 5)
No. 10 (Si/Al = 30)   No. 12 (Si/Al = 20)   No. 14 (Si/Al = 10)   No. 16 (Si/Al = 5)

3.3 Dealkylation reactions of TIPB

Dealkylation reactions of TIPB were carried out to investigate activity and surface properties of the samples synthesized. Dealkylation reactions of TIPB were chosen as test reactions since these reactions were well known to proceed on Bronsted acid sites, and requires reaction spaces of mesopores larger than those of Y-zeolites because of bulkiness of reactant molecule[18, 25, 26].

Effect of contact time on selectivity at 527 K using Al-MCM-41 (No. 11) as a catalyst was shown in Figure 12. Selectivity to diisopropylbenzenes (DIPB) extrapolated to the initial reaction time is almost 100%, indicating that DIPB is the initial reaction product and isopropylbenzene (IPB) and benzene (B) are produced consecutively in the succeeding reactions. Effect of conversion on the yield of the products was depicted in Figure 13. Plots of yield of each product and conversion of TIPB observed through the reactions at 523 K lay on the straight lines passing through the origin, regardless the Si/Al ratios of the catalysts. This may reflect the similarity of acidic characters of the catalysts even if the Si/Al ratios of the catalysts are quite different. These tendencies were also observed for the reactions at other temperatures. The apparent activation energy of the reaction

ranged from 22 to 47 kJ mol^{-1}. Dealkylation reactions of TIPB did not proceed on active alumina under the similar conditions as expected. Therefore, in every Al-MCM-41 catalyst, it is concluded that some Al species were incorporated into siliceous framework of Al-MCM-41 as tetrahedrally coordinated Al species, which
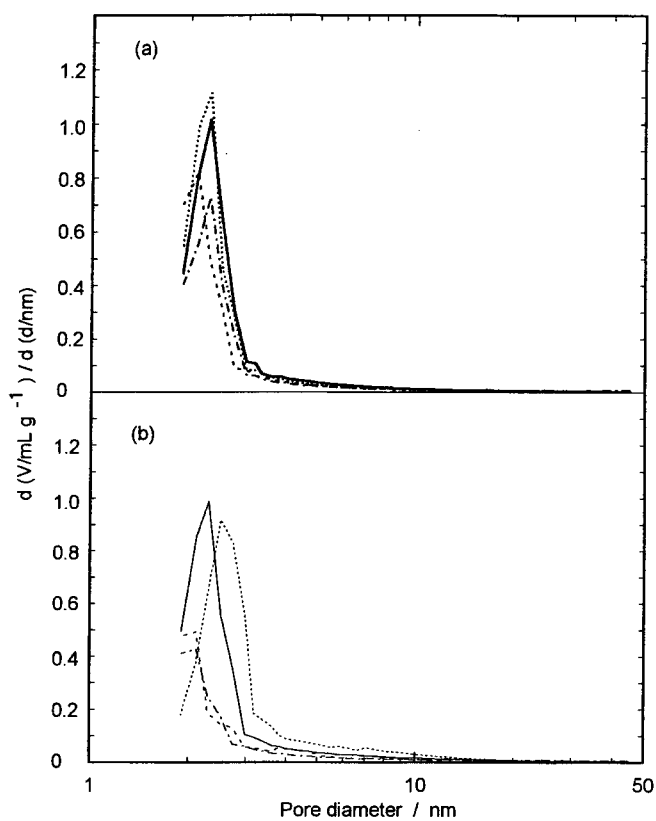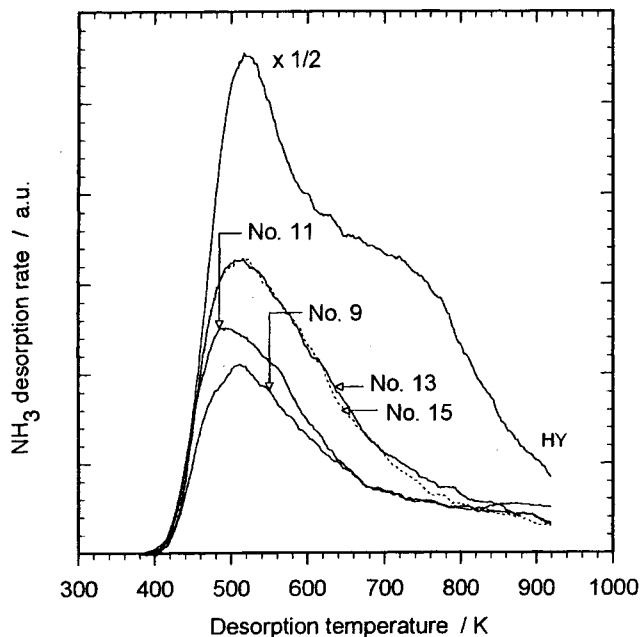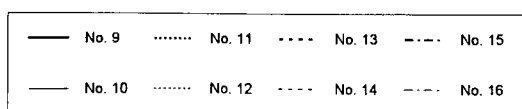
Figure 10   NH₃-TPD profile of Al-MCM-41 samples and HY-zeolite

Sample No.   9 : Si/Al = 30
No. 11 : Si/Al = 20
No. 13 : Si/Al = 10
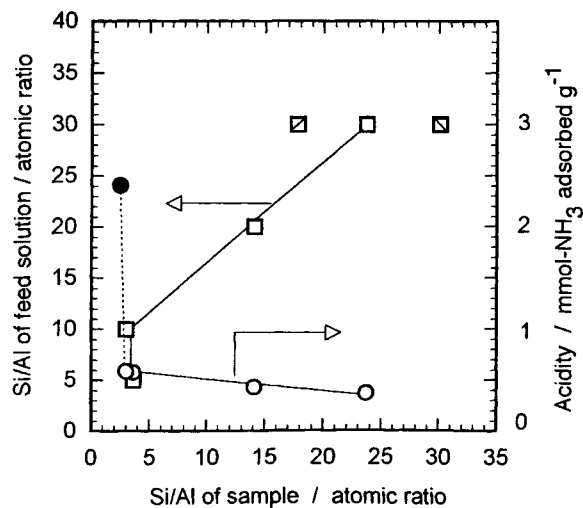No. 15 : Si/Al = 5
HY : HY-zeolite

Figure 9   Pore size distribution of samples synthesized under various Si/Al ratios

(a) with anti-foaming agent, (b) without anti-foaming agent

——— No. 9   ········ No. 11   ‑‑‑‑ No. 13   —·—· No. 15

——— No. 10   ········ No. 12   ‑‑‑‑ No. 14   —·—· No. 16

Figure 11   Relation between Si/Al of samples and that of feed solutions, and acidity of samples

◩ : pH 3-5,   □ : pH 5-7,   ◨ : pH 7-10,   ○ : Al-MCM,   ● : HY

directly lead to create Bronsted acid sites[19, 20] that are responsible for the dealkylation reactions of TIPB. Comparison of catalytic activities of various catalysts was shown in Figure 14. This figure was based on conversion per unit area and acidity per unit area. Activities of MCM-41 and Al-MCM-41 of various Si/Al ratios increase linearly with the increase in acidity of the relevant catalysts. In contrast, activity of HY-zeolite was not high and stayed in the range of Al-MCM-41 catalysts despite that HY-zeolite had a large amount of stronger acid sites. This may reflect the fact that the size of TIBP is too large to diffuse into the internal spaces of micropores of HY-zeolite[18, 25, 26], although TIPB mole-

cules easily diffuse into mesopores of Al-MCM-41. It also means that only external surfaces of HY-zeolite are utilized, while internal surfaces of mesoporous Al-MCM-41 are available for the reactions of TIPB, which may cause relatively high activity of Al-MCM-41.

4. Conclusion

Results reported in the present work indicate that in the synthesis of Al-MCM-41 with lower Si/Al ratios through non-hydrothermal reactions, following conditions are important for the formation of the samples which have typical characters of well ordered 2D-hexagonal structure: simultaneous addition of Si and Al sources into the solution containing both template of the surfactant and the anti-foaming agent in neutral to acidic media (pH 3 - 7), at temperatures above Krafft point of the surfactant, and under vigorous agitations. These conditions may be associated with assembly of aluminosilicate sources with uniform composition (i.e., constant Si/Al ratio) around the template micelles, promoting hydrolysis and/or condensation of aluminosilicate and forming Al-MCM-41 with highly ordered structures. Relatively weak acid sites are mainly consisted of Al-MCM-41 and similar distributions of acid strength are observed for the samples with different Si/Al species. Dealkylation reactions of TIPB, which are known to proceed on Bronsted acid sites are catalyzed more effectively on Al-MCM-41 samples than on HY-zeolites. This means that at least, a part of Al was incorporated into the silica framework of MCM-41 structure as tetrahedrally coordinated species in Al-MCM-41 samples prepared in the present work.

Reference

1) J.S.Beck, J.C.Vartuli, W.J.Roth, M.E.Leonowicz, C.T.Kresge, K.D.Schmitt, C.T-W.Chu, D.H.Olson, E.E.Sheppard, S.B.McCullen, J.B.Higgins, J.L.Schlenker, "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates", J. Am. Chem. Soc., 114, 10834 (1992).
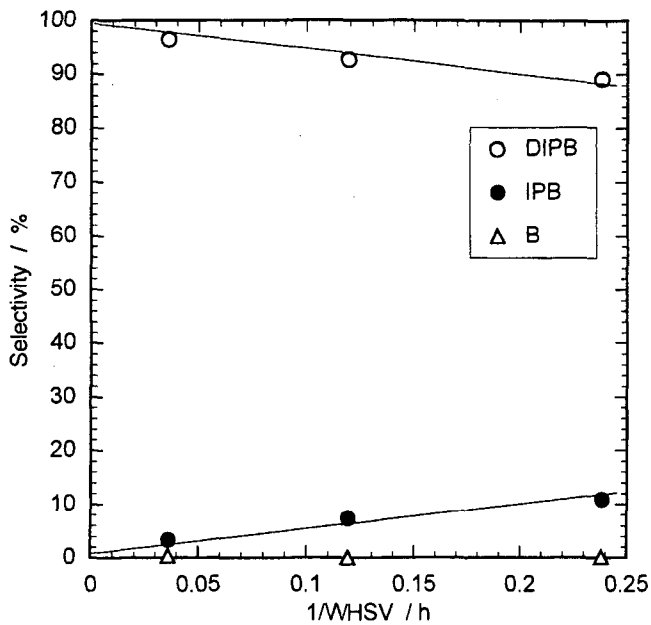
Figure 12   Effect of contact time on selectivity of Al-MCM-41 (Sample No. 11)
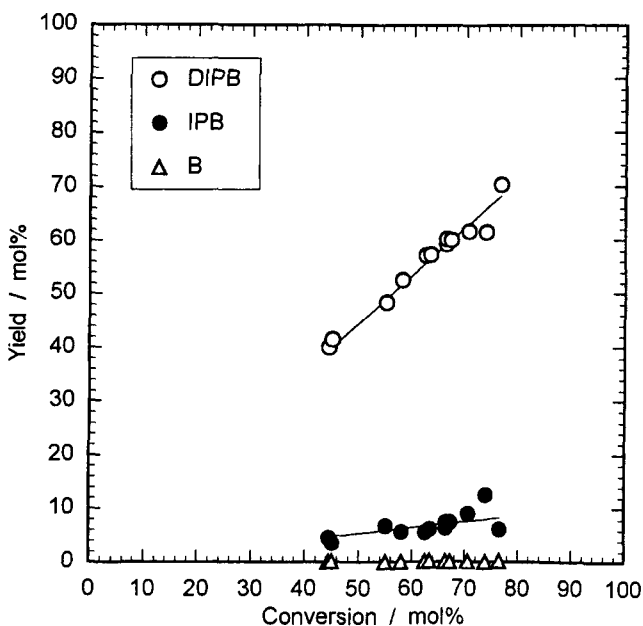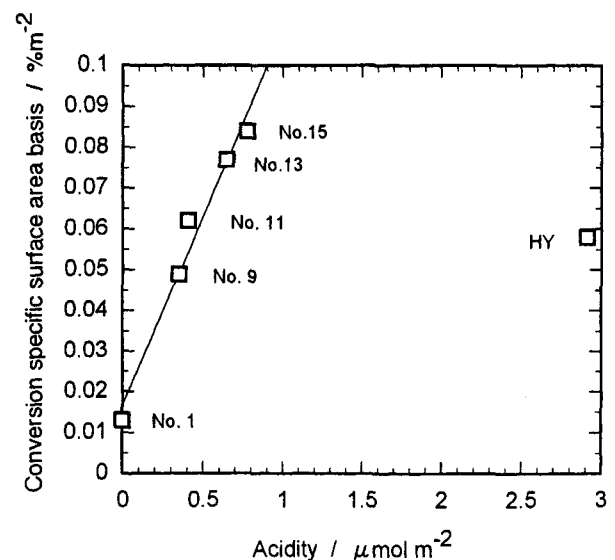

Figure 13   Effect of conversion on yield of products

Figure 14   Comparison of catalytic activity of various catalysts reacted at 523 K under WHSV = 8.4 h^{-1}

2) C.T.Kresge, M.E.Leonowicz, W.J.Roth, J.C.Vartuli, J.S.Beck, "Ordered mesoporous molecular sieves synthesized by a liquid crystal template mechanism", *Nature*, **359**, 710 (1992).

3) Z.Hurem, D.Vucelic, V.Markovic, "Synthesis of mordenite with different silica/alumina ratios", *Zeolites*, **13**, 145 (1993).

4) A.Corma, V.Fornes, M.T.Navarro, J.Perez-Pariente, "Acidity and Stability of MCM-41 Crystalline Aluminosilicates", *J. Catal.*, **148**, 569 (1994).

5) Z.Luan, C-F.Cheng, W.Zhou, J.Klinowski, "Mesoporous Molecular Sieve MCM-41 Containing Framework Aluminum", *J. Phys. Chem.*, **99**, 1081 (1995).

6) Z.Luan, H.He, W.Zhou, C.F.Cheng, J.Klinowski, "Effect of Structural Aluminium on the Mesoporous Structure of MCM-41", *J. Chem. Soc. Faraday Trans.*, **91**, 2955 (1995).

7) J.M.Kim, J.H.Kwak, S.Jun, R.Ryoo, "Ion Exchange and Thermal Stability of MCM-41", *J. Phys. Chem.*, **99**, 16742 (1995).

8) R.Ryoo, C.H.Ko, R.F.Howe, "Imaging the Distribution of Framework Aluminum in Mesoporous Molecular Sieve MCM-41", *Chem. Mater.*, **9**, 1607 (1997).

9) M.T.Janicker, C.C.Landry, S.C.Christiansen, D.Kumar, G.D.Stucky, B.F.Chmelka, "Aluminum Incorporation and Interfacial Structures in MCM-41 Mesoporous Molecular Sieves", *J. Am. Chem. Soc.*, **120**, 6940 (1998).

10) M.L.Occelli, S.Biz, A.Auroux, G.J.Ray, "Effect of the nature of the aluminum source on the acidic properties of some mesostructured materials", *Microporous and Mesoporous Mater.*, **26**, 193 (1998).

11) S.Cabrera, J.E.Haskouri, S.Mendioroz, C.Guillen, J.Latorre, A.Beltran-Porter, D.Beltran-Porter, M.D.Marcos, P.Amoros, "Towards the Loewenstein limit (Si/Al = 1) in thermally stable mesoporous aluminosilicates", *Chem. Commun.*, **1999**, 1679.

12) Z.Zhang, Y.Han, L.Zhu, R.Wang, Y.Yu, S.Qiu, D.Zhao, F.-S.Xiao, "Strongly Acidic and High-Temperature Hydrothermally Stable Mesoporous Aluminosilicates with Ordered Hexagonal Structure", *Angew. Chem.*, **113**, 1298 (2001)

13) D.Zhao, C.Nie, Y.Zhou, S.Xia, L.Huang, Q.Li, "Comparison of disordered mesoporous aluminosilicates with highly ordered Al-MCM-41 on stability, acidity and catalytic activity", *Catal. Today*, **68**, 11 (2001).

14) Y.Cesteros, G.L.Haller, "Several factors affecting Al-MCM-41 synthesis", *Microporous and Mesoporous Mater.*, **43**, 171

(2001).

15) Y.M.Setoguchi, M.Takahashi, I.Moriguchi, Y.Teraoka, S.Kagawa, N.Tomonaga, A.Yasutake, J.Izumi, "pH-Dependence of Room-Temperature Synthesis of Mesoporous (Alumino) silicates", *Proc. of ZMPS '97*, Tokyo, August 1997, 3-10.

16) M.Chatterjee, T.Iwasaki, H.Hayashi, Y.Onodera, T.Ebina, T.Nagase, "Room-temperature formation of thermally stable aluminium-rich mesoporous MCM-41", *Catal. Lett.*, **52**, 21 (1998).

17) A.Matsumoto, H.Chen, K.Tsutsumi, M.Grun, K.Unger, "Novel route in the synthesis of MCM-41 containing framework aluminum and its characterization", *Microporous and Mesoporous Mater.*, **32**, 55 (1999).

18) E.F.S.Aguiar, M.L.M.Valle, M.P.Silva, D.F.Silva, "Influence of external surface area of rare-earth containing Y zeolites on the cracking of 1,3,5-triisopropylbenzene", *Zeolites*, **15**, 620 (1995).

19) A.Corma, A.Martinez, V.Martinezsoria, J.B.Monton, "Hydrocracking of Vacuum Gasoil on the Novel Mesoporous MCM-41Aliminosilicate Catalyst", *J. Catal.*, **153**, 25 (1995).

20) M.J.Climent, A.Corma, S.Iborra, M.C.Navarro, J.Primo, "Use of Mesoporous MCM-41 Aluminosilicates as Catalysts in the Production of Fine Chemicals: Preparation of Dimethylacetals", *J. Catal.*, **161**, 783 (1996).

21) D.Dollimore, G.R.Heal, "An Improved Method for the Calculation of Pore Size Distribution from Adsorption Data", *J. Appl. Chem.*, **14**, 109 (1964).

22) D.Dollimore, G.R.Heal, "Pore-Size Distribution in Typical Adsorbent Systems", *J. Colloid Interface Sci.*, **33**, 508 (1970).

23) Y.M.Setogichi, Y.Teraoka, I.Moriguchi, S.Kagawa, N.Tomonaga, A.Yasutake, J.Izumi, "Rapid Room Temperature Synthesis of Hexagonal Mesoporous Silica Using Inorganic Silicate Sources and Cationic Surfactants under Highly Acidic Conditions", *J. Porous Mater.*, **4**, 129 (1997).

24) J.Yu, J.L.Shi, L.-Z.Wang, M.-L.Ruan, D.-S.Tan, "Room temperature synthesis of mesoporous aluminosilicate materials", *Ceram. Int.*, **26**, 359 (2000).

25) H.Koch, W.Reschetilowski, "Is the catalytic activity of Al-MCM-41 sufficient for hydrocarbon cracking?", *Microporous and Mesoporous Mater.*, **25**, 127 (1998).

26) L.Zhu, F.-S.Xiao, Z.Zhang, Y.Sun, Y.Han, S.Qiu, "High activity in catalytic cracking over stable mesoporous aluminosilicates", *Catal. Today*, **68**, 209 (2001).