

Acidic Property of FSM-16. 2. Generation of Lewis Acid Sites and Catalysis

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Catalysis over Lewis acid sites on siliceous mesoporous FSM-16 was confirmed. Acidic property of FSM-16 was studied by pyridine TPD measurements, and catalyses of α -pinene isomerization and methylamine synthesis. FSM-16 possess both Brønsted and Lewis acid sites, and another Lewis acid site formed on FSM-16 when a catalyst was pretreated above 873 K. α -Pinene isomerization was catalyzed over Brønsted acid sites, the activity of which is the highest when FSM-16 is pretreated at 673 K. Lewis acid sites on FSM-16 catalyze methylamine synthesis, and the initial rates are enhanced with increasing pretreatment temperature up to 1273 K. The structure of FSM-16 was completely retained throughout a pretreatment at 1273 K and a reaction procedure for methylamine synthesis at 673 K.

Introduction

Since the discovery of highly ordered mesoporous silica,^{1,2} mesoporous silicas such as MCM-41,^{2,3} HMS,^{4,5} and FSM-16⁶ have been investigated extensively.⁷ All three materials exhibit a similar structure to each other and possess high surface area, narrow pore size distributions, and high pore volume. Because siliceous mesoporous materials have been believed to be catalytically inert, preparation of Al-containing mesoporous materials has been attempted for the application to solid acid catalysis. Most commonly, an Al source was added into the starting materials before synthesis of the mesoporous materials.^{7–10} Impregnation methods of AlCl_3 ^{11,12} or $\text{Al}(\text{O}^i\text{Pr})_3$ ^{13,14} to synthesized mesoporous silica were also performed. In another way, preparation of heteropoly acid introduced MCM-41 was reported.¹⁵

In contrast to these efforts, catalyses of the acid-catalyzed reaction over siliceous mesoporous materials were reported by some researchers in 1997.^{13,16} However, they did not pay attention to catalyses by mesoporous silicas. In their reports, results over siliceous mesoporous silicas dealt with one of the reference catalysts or blank test. Sakata found thermal degradation of polyethylene proceeds over siliceous FSM-16 as fast as over silica–alumina.¹⁷ The yield of liquid products over FSM-16 was higher than that for silica–alumina. They concluded that the mesopore surrounded by silica sheets acts as a radical flask.

We have first reported the acid property of mesoporous silica in detail. FSM-16 catalyzes but-1-ene isomerization and α -pinene isomerization at 323 and 303 K, respectively.¹⁸ Subsequently, our results were confirmed and supported by a report of the catalyses over siliceous MCM-41 about acetalization of aldehydes and ketones.¹⁹ The activities of FSM-16 depend on pretreatment temperatures, and were the highest when the catalyst was pretreated at 673 K. The acidity of FSM-16 is much reduced by calcination at a higher temperature, but restores by

water treatment at 353 K as long as the FSM-16 retains its structure. We have concluded from IR characterizations that the active sites for the two reactions are weakly perturbed silanol groups which act as Brønsted acid sites. However, FTIR characterization of adsorbed pyridine on FSM-16 revealed that a majority of the acid sites were Lewis acid sites. Furthermore, the peak intensity assigned to the 8a mode of Lewis pyridine (1624 cm^{-1}) on FSM-16 pretreated at 1073 K was much stronger than that on FSM-16 pretreated at 673 K.¹⁸ In the previous work, no evidence was obtained about catalyses over Lewis acids.

In the present study, we focused on the Lewis acid property of FSM-16. The property was evaluated with pyridine TPD measurement and a catalysis for methylamine synthesis. Methylamine synthesis from methanol and ammonia is known to be a typical acid-catalyzed reaction, which proceeds over many solid acid catalysts having Lewis and/or Brønsted acid sites.²⁰ Segawa et al. reported that $\gamma\text{-Al}_2\text{O}_3$ (JRC-ALO-4) catalyzes methylamine synthesis from methanol and ammonia, and the initial rate was higher than those of amorphous silica–alumina (JRC-SAL-2; $\text{Al}_2\text{O}_3 = 13\text{ wt } \%$) and HZSM-5 ($\text{Si}/\text{Al} = 12.5$).²¹ It has been concluded from IR spectra of adsorbed pyridine that the acid site of $\gamma\text{-Al}_2\text{O}_3$ is only Lewis acid sites.^{22–24} Therefore, the reaction catalyzed over $\gamma\text{-Al}_2\text{O}_3$ is considered to be a Lewis acid promoted reaction and is expected to proceed over FSM-16 pretreated above 1073 K.

Experimental Section

Materials. FSM-16 was synthesized according to the literature,²⁵ and the procedure was previously reported in detail.¹⁸ The grade of water glass used for FSM-16 synthesis is as follows: Fuji Silysia Co., Ltd, $\text{SiO}_2 = 15.3\text{ wt } \%$, $\text{Na}_2\text{O} = 6.1\text{ wt } \%$, $\text{Al} = 0.6\text{ ppm}$, $\text{Fe} = 0.4\text{ ppm}$; Osaka Keiso Co., Ltd, $\text{SiO}_2 = 31.93\text{ wt } \%$, $\text{Na}_2\text{O} = 15.37\text{ wt } \%$, $\text{Al} = 98\text{ ppm}$, $\text{Fe} = 28\text{ ppm}$. The Cu K α XRD pattern of synthesized FSM-16 exhibits typical d_{100} , d_{110} , d_{200} , and d_{210} reflections at $2\theta = 2.3^\circ$, 4.1° , 4.7° , and 6.3° , respectively.

SiO_2 gel was synthesized from tetraethyl orthosilicate (Nacalai tesque, EP-grade, singly distilled) by hydrolysis in a water–

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TABLE 1: Elemental Analysis of Catalysts

sample	catalyst	elements (mass%)						Si/Al ^a
		Na	Al	Ca	Fe	Mg	Ti	
1	FSM-16	0.008	0.061	0.012	0.023	0.003	0.032	735
2	FSM-16	0.013	0.110	0.009	0.012	0.007	<0.001	408
3	SiO ₂ -gel	0.002	<0.001	0.001	<0.001	<0.001	<0.001	
4	<i>p</i> -silica ^b	0.003	0.004	<0.001	<0.001	<0.001	<0.001	11226

^a Atomic ratio. ^b Precipitated silica.

ethanol mixture at the boiling point, followed by calcination at 773 K for 5 h.²⁵

Precipitated silica was prepared from silicic acid, by calcination at 773 K for 5 h. Silicic acid was obtained by mixing of water glass (Fuji Silysia Co. Ltd.) and 2 M HCl at room temperature, followed by washing with 0.2 M HNO₃ until Cl⁻ was free based on AgNO₃ test.

Reference catalysts used were Japan Reference Catalyst (JRC-ALO-4, JRC-SAL-2), supplied by the Committee on Reference Catalyst, Catalysis Society of Japan. JRC-ALO-4 is γ -Al₂O₃, which contains 0.01% of Fe₂O₃, SiO₂, and Na₂O. JRC-SAL-2 is amorphous silica-alumina which contains 0.02% Fe, 0.012% Na₂O, 0.33% SO₄, and 13.75% Al₂O₃. The BET specific surface areas of JRC-ALO-4 and JRC-SAL-2 are 177 and 560 m² g⁻¹, respectively.

Characterization. Elemental analysis was carried out by inductively coupled plasma (ICP) with Shimadzu ICPS-2000, and the results are shown in Table 1. The N₂ adsorption-desorption isotherm measurement was carried out with BELSORP 28SA (BEL Japan, Inc.) at 77 K. The specific surface area was calculated by BET method. The pore size distribution was estimated by the Clanston-Inkley method. The pore volume and outer surface area were estimated by *t*-plot using a N₂ adsorption isotherm of nonporous silica as a standard.²⁷

Pyridine temperature-programmed desorption (TPD) experiments were performed at a heating rate of 10 K min⁻¹ and quadrupole-type mass spectrometer (MASSMATE-100, UL-VAC) was used as a detector.²⁸ Before TPD measurements, each 100 mg of sample was preevacuated at 673 K for 0.5 h and calcined under 6.66 kPa of O₂ for 1 h, followed by evacuation at the same temperature for 1 h. The pretreated sample was exposed to 80 μ mol of pyridine at 373 or 423 K for 10 min, followed by evacuation at the same temperature for 1 h. The amount of desorbed pyridine was normalized to that of introduced Ar (*m/z* = 40) as an internal standard. Because the most intense signal for the pyridine mass spectrum was that of *m/z* = 52, we adopted profiles of *m/z* = 52 for acid properties of catalyst.

FTIR spectra were recorded using a Perkin-Elmer Paragon 1000 spectrometer with a resolution of 2 cm⁻¹. The 20 mg of FSM-16 was pressed into a self-supporting wafer (20 mm in diameter) with a pressure of 100 kg cm⁻² for 10 s and was mounted in an in situ IR cell equipped with BaF₂ windows. A wafer was evacuated at 673 or 1073 K for 1 h. After cooling to room temperature, each spectrum was recorded in a transmission mode.

Catalysis. α -Pinene isomerization was carried out under dry N₂ atmosphere using a stirred batch reactor at 303 or 353 K.¹⁸ Methylamine synthesis was carried out with a closed circulation system (dead volume, 200 cm³) at 673 K. The pretreatment procedure for both reactions was the same as in the TPD experiment. In a typical experiment for α -pinene isomerization, the reactor was loaded with 2 mL (12.6 mmol) of α -pinene (Nacalai, EP, 99.8%) and 50 mg of catalyst. The amounts of substrates used for methylamine synthesis were 200 or 800 μ mol

TABLE 2: Results of α -Pinene Isomerization^a

no.	catalyst	reaction temp (K)	conversion (%)	selectivity ^b (%)							
				1	2	3	4	5	6	7	8
1	FSM-16 ^c	303	44.6	tr	40	4	43	9	2	2	tr
1	FSM-16 ^d	353	97.4	tr	43	4	33	10	4	2	4
1	FSM-16 ^{c,e}	303	6.6	1	37	3	48	7	2	2	1
2	FSM-16	303	38.7	tr	38	4	44	8	2	2	2
3	SiO ₂ -gel ^{c,d}	353	0.0								
4	<i>p</i> -silica	353	0.0								
	γ -Al ₂ O ₃ ^{c,d}	353	3.4	33	44	2	17	2	1	1	tr
	silica-alumina	303	99.8	tr	43	3	26	14	6	4	4

^a α -Pinene: 2 mL (12.6 mmol). Catalyst: 50 mg. Reaction time: 0.5 h. Pretreatment temperature: 673 K. ^b (1) β -pinene; (2) camphene; (3) α -fenchene; (4) limonene; (5) terpinolene; (6) α -terpinene; (7) γ -terpinene; (8) others. ^c Taken from ref 18. ^d Catalyst: 100 mg. Reaction time: 3 h. ^e Pretreatment temperature: 1073 K.

of ammonia and 400 μ mol of methanol. Products were analyzed by FID gas chromatography (GC-14A, Shimadzu) with a CBP20-M25-025 capillary column (Shimadzu) for α -pinene isomerization and by GC-8A (Shimadzu) with an Unicarbon B-2000 column (GL Sciences, 2.6 i.d. \times 2 m) for methylamine synthesis.

Results and Discussion

Catalysis over Brønsted Acid Sites. From FTIR characterization, we have concluded that the active sites for but-1-ene and α -pinene isomerizations are Brønsted acid sites of weakly perturbed silanol groups. The 19b mode of Brønsted pyridine (1546 cm⁻¹) was observed on FSM-16 pretreated at 673 K, whereas it was not seen on FSM-16 pretreated at 1073 K.¹⁸ A trace amount of Al of FSM-16 did not affect the acidic property at all. To confirm this conclusion again, α -pinene isomerization was carried out with two kinds of FSM-16 which contain different concentration of Al. Results of the catalytic tests are summarized in Table 2. The selectivity was independent of Al concentrations as well, and camphene (ca. 39%) and limonene (ca. 43%) were produced. A rate for successive isomerization of limonene was low over FSM-16 even at 353 K. If Al-related sites on FSM-16 participate in the acidity, an obvious difference in the activity should have been observed between sample 1 and sample 2. As shown in Table 2, any evident relations between the catalytic activity and Al concentration in FSM-16 were not observed. It strongly suggests that the acid property of FSM-16 is not due to contamination of Al.

Over silica-alumina of strong solid acid, consecutive isomerization of limonene proceeded and the dehydrogenate product (*p*-cymene) and polymerized products were observed even at 303 K for 30 min. Effective acid strength for α -pinene isomerization was proposed to $H_0 \leq +3.3$.^{18,29} Although γ -Al₂O₃ possesses certain amounts of strong Lewis acid sites (580 μ mol g⁻¹), the maximum strength of which is over $pK_a \leq -5.6$,^{23,30} the activity was much less than that of FSM-16. It was proposed that the reaction rate for α -pinene isomerization over Lewis acid site is lower than that over Brønsted acid site.³¹ Low activity of γ -Al₂O₃ is due to scarce existence of Brønsted acid sites. Other silicas were inert for α -pinene isomerization at 353 K.

Temperature-Programmed Desorption Measurements of Pyridine. To clarify a change of acidic property of FSM upon thermal treatment, a pyridine TPD experiment was carried out. It was reported that a strained siloxane bridge was formed on silica evacuated above 673 K. The site reacts with NH₃ to produce SiNH₂ and SiOH even at room temperature, whereas the sites do not react with pyridine.^{32,33} Therefore, we adopted

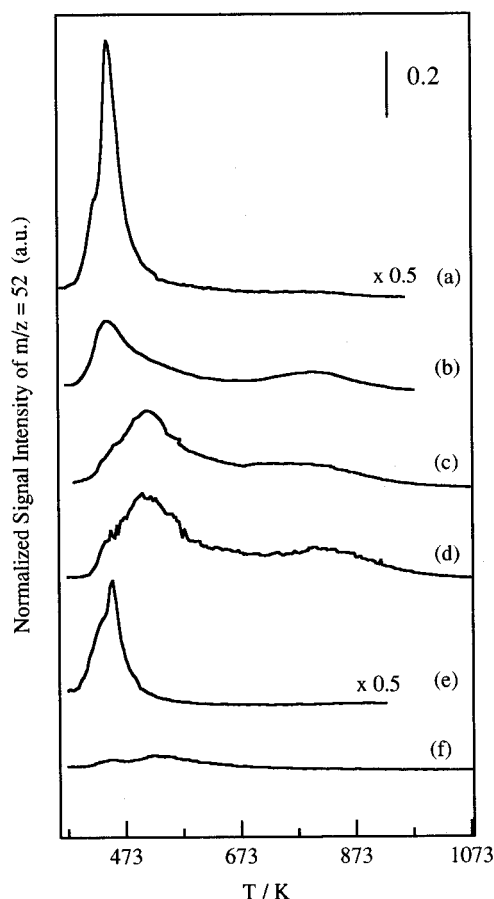


Figure 1. Pyridine TPD profiles of FSM-16 pretreated at 673 (a), 873 (b), 1073 (c), and 1273 K (d) and SiO₂ gel pretreated at 673 (e) and 1073 K (f). Adsorption temperature: 373 K. Rate: 10 K min⁻¹.

pyridine as a base molecule to evaluate the acidic property. The results of pyridine TPD experiments, each adsorption temperature of which was 373 K, are shown in Figure 1. TPD profiles of FSM-16 pretreated at 673 K exhibited a large desorption peak around 473 K and a faint peak around 800 K. With increasing pretreatment temperatures, the peak intensity around 473 K drastically reduced, whereas that around 800 K was almost constant. In the desorption profiles of FSM-16 pretreated at 1073 and 1273 K, a new desorption peak appeared around 510 K. The behavior of the desorption peak around 473 K upon pretreatment temperature is consistent with that of catalytic activities for but-1-ene and α -pinene isomerization. This pyridine adsorption site may be conjectured to be the active sites of FSM-16, which have been proposed to Brønsted acid. However, a pyridine TPD profile of SiO₂ gel pretreated at 673 K, which was inert for the two reactions, exhibited a large desorption peak around 473 K. When the pyridine adsorption procedure was carried out at 373 K, a large amount of hydrogen bonded pyridine adsorbed onto residual water molecules of both the catalysts. Therefore, the peak observed around 473 K is desorption pyridine from both hydrogen-bonded and Brønsted acid sites.

To reduce the effect of hydrogen-bonded pyridine in TPD experiments, the pyridine adsorption procedure was then performed at 423 K. The TPD profiles are shown in Figure 2. The TPD profile of FSM-16 pretreated at 673 K exhibited a small broad desorption peak around 600 K and a shoulder over 773 K. With increasing pretreatment temperature, a new desorption peak grew around 550 K. It is obvious that somewhat new acid sites are generated, the amount of which increased on

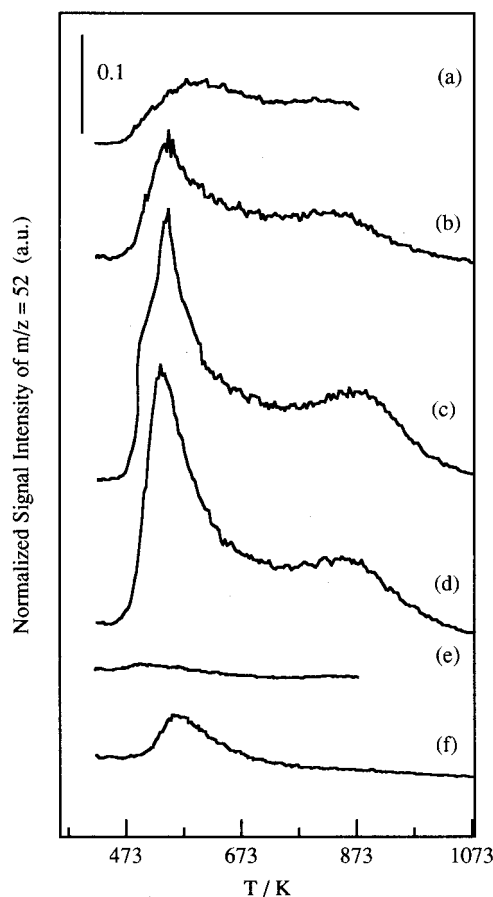


Figure 2. Pyridine TPD profiles of FSM-16 pretreated at 673 (a), 873 (b), 1073 (c), and 1273 K (d) and SiO₂ gel pretreated at 673 (e) and 1073 K (f). Adsorption temperature: 423 K. Rate: 10 K min⁻¹.

FSM-16 by thermal treatment. When pyridine was adsorbed at 373 K, FSM-16 pretreated at 673 K desorbed the largest amounts of pyridine. In contrast, FSM-16 pretreated at 1273 K desorbed the largest amounts when pyridine was adsorbed at 423 K. Similar phenomena were observed in pyridine TPD profiles of SiO₂ gel adsorbed at 423 K. Little pyridine was adsorbed on SiO₂ gel pretreated at 673 K. A new desorption peak was observed for SiO₂ pretreated at 1073 K as well; however, the intensity was much smaller than that of FSM-16. No desorption peaks were observed in those of SiO₂ gel above 673 K, in contrast to those of FSM-16.

When FSM-16 was pretreated above 1073 K, desorbed amounts of pyridine from FSM-16 were almost the same among the two different adsorption temperatures. IR spectra indicated that hydrogen-bonded silanol groups were absent on the surface of FSM-16 evacuated at 1073 K.¹⁸ As a result, hydrogen-bonded pyridine was absent on FSM-16 pretreated above 1073 K, and differences of TPD profiles were not observed among different adsorption temperatures. A pyridine TPD experiment on siliceous MCM-41 pretreated at 573 K was performed by Zhao.³⁴ Unfortunately, because the adsorption temperature on MCM-41 was 325 K, the differences of acidic property between FSM-16 and MCM-41 are not comparable. In conclusion, another kind of acid site is generated on FSM-16 pretreated above 873 K, and the effects of hydrogen-bonded pyridine are free if pyridine adsorption was carried out at 423 K.

Generation of Lewis Acid Sites. We have measured IR spectra of adsorbed pyridine on FSM-16 and estimated the ratio of Lewis and Brønsted acid sites ([L]/[B] ratio). Total amount of Lewis acid sites was much more than that of Brønsted acid

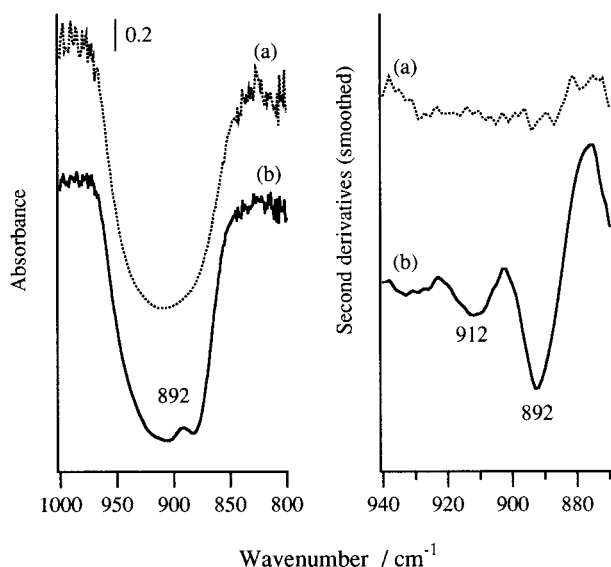


Figure 3. FTIR spectra of FSM-16 evacuated at 673 (a) and 1073 K (b) and their second derivatives.

sites. The [L]/[B] ratio of FSM-16 pretreated at 673 K was estimated to be 2.9, and that of FSM-16 pretreated at 1073 K was 5.6.¹⁸ In these spectra, the peak intensity assigned to the 8a mode of Lewis pyridine (1624 cm^{-1}) was enhanced by high-temperature pretreatment. The peak area on FSM-16 pretreated at 1073 K was 1.4 times as large as that on FSM-16 pretreated at 673 K. In cases of TPD experiments, accumulated amounts of desorbed pyridine in the range of 423–873 K differed by 2.2 times between the two FSM-16 samples of different evacuation temperatures. The tendency of the pyridine TPD profile adsorbed at 423 K is consistent with the results of IR spectra.

Figure 3 shows IR spectra of FSM-16 evacuated at 673 and 1073 K. In the range around 900 cm^{-1} , a new peak appeared at 892 cm^{-1} when FSM-16 was treated at 1073 K. In the second derivative spectra, an additional peak was confirmed at 912 cm^{-1} . On the other hand, any peaks were not present in the IR spectrum of FSM-16 treated at 673 K. This phenomena observed on FSM-16 is quite similar to those for amorphous silica. It is well-known that isolated surface silanol groups of silica are dehydroxylated to form a strained siloxane bridge over 900 K.³⁵ For dehydroxylated silica, two defect bands are observed at 888 and 908 cm^{-1} in the range of $800\text{--}1000\text{ cm}^{-1}$ which were assigned to edge-shared disiloxane ring.^{32,33,35–38} They are produced by dehydroxylation of isolated silanol groups, and can be classified to be Lewis acid.³⁸ In fact, dehydrogenation of ethanol is catalyzed over highly dehydrated silica, the active site of which was proposed to be Si–O–Si oxygen bridge.³⁹ However, the acid strength of SiO_2 pretreated at 1073 K was not very strong so that only hydrogen-bonded pyridine was detected with FTIR spectroscopy.⁴⁰ The newly formed acid sites on FSM-16 pretreated above 873 K are possibly due to silicon atoms of the strained siloxane bridge as well as amorphous silica. If one of the silicon–oxygen bonds of the siloxane bridge was prolonged, the silicon atom could be regarded as a pseudo-coordinated unsaturated site and the strength of the Lewis acidity remarkably should be enhanced. We speculate that such the pseudocoordinated unsaturated silicon species formed on FSM-16 pretreated at higher temperature. The rigid structure of FSM-16 permits the existence unstable species such as these. This might be the reason for the difference in acidity between FSM-16 and SiO_2 gel.

Catalysis over Lewis Acid Sites. As shown in Figure 2, the amount of Lewis acid sites on FSM-16 increases with raising pretreatment temperatures. As a test reaction for Lewis acid sites on FSM-16, methylamine synthesis was examined. If the Lewis acid sites on FSM-16 are effective for this reaction, the catalytic activity should be enhanced with increasing pretreatment temperatures.

Figure 4 shows a time course of methylamine synthesis over FSM-16. As expected, the initial rate for methanol conversion was highest when FSM-16 was pretreated at 1273 K. Figure 4b shows the selectivity for methylamine synthesis over 1273 K pretreated FSM-16. In the initial step, the selectivity for monomethylamine (MMA) was 90% and that for trimethylamine (TMA) was 10%. Formation of dimethyl ether was not observed. Ammonia was rapidly methylated to MMA over FSM-16; however, the rate for consecutive methylation was very slow. The amount of dimethylamine (DMA) formation was very small even when the reaction time was 180 min. The selectivities to each methylamine were unchanged by pretreatment temperatures, and no induction periods were observed in any case. Figure 5 summarizes initial rates for methylamine synthesis and activities of α -pinene isomerization over FSM-16 versus pretreatment temperature. Catalytic activity for α -pinene isomerization was dependent upon heat treatment and reached a maximum at 673 K, and the activity was drastically reduced when FSM-16 was pretreated above 1073 K. In contrast, methylamine synthesis was catalyzed by FSM-16 pretreated at 1273 K, the activity of which was higher than that of FSM-16 pretreated at 673 K. It clearly shows that methylamine synthesis proceeds over Lewis acid sites on FSM-16. These two reactions should be catalyzed by the different active sites on FSM-16.

Lewis acid sites on FSM-16 might change to Brønsted acid sites with water, which was formed by dehydration among methanol and ammonia. Hence, it is doubtful whether Lewis acid sites really participate in a catalysis for methylamine synthesis. If Brønsted acid sites were active sites, which were converted from the Lewis acid sites, an induction period should have been observed. Furthermore, the reaction rate over FSM-16 pretreated at 1273 K should never exceed that of FSM-16 pretreated at 673 K. However, present results of catalysis did not agree with these postulates. Therefore, it is obvious that the Lewis acid sites formed on FSM-16 act as active sites.

From the results that H-type MFI, Y, and Mordenite zeolites exhibit higher activities for methylamine synthesis than those of each Na-type zeolite,^{21,41} it is concluded that not only Lewis but also Brønsted acid sites catalyze this reaction. In addition, reaction mechanisms catalyzed by Brønsted acid sites have been proposed.²⁰ We cannot conclude whether the active sites of FSM-16 for methylamine synthesis were Brønsted and/or Lewis acid sites. However, we say again that Lewis acid sites on FSM-16 participate in this catalysis.

When the reaction was carried out with $400\text{ }\mu\text{mol}$ of methanol and $200\text{ }\mu\text{mol}$ of NH_3 , an evident difference in initial rates was observed on FSM-16 pretreated at various temperatures. In contrast, the differences in activities to pretreatment temperatures were small when the reaction was performed with $400\text{ }\mu\text{mol}$ of methanol and $800\text{ }\mu\text{mol}$ of NH_3 . The reaction rates for methanol conversion were not so different by N/C (ammonia to methanol) ratios, however, the rate of TMA formation increased in a case $N/C = 2$. FSM-16 catalyzed methylamine synthesis to produce MMA readily, but the rate of consecutive methanation was relatively slow in all reaction conditions. As a result, reaction

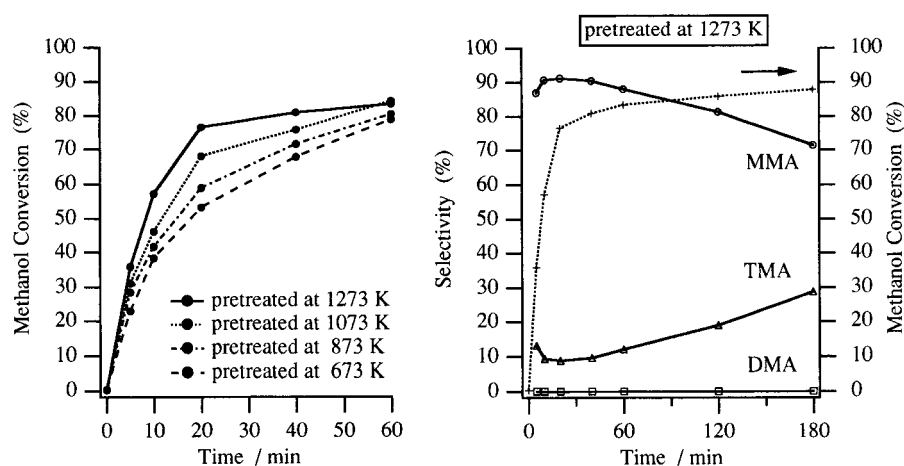


Figure 4. Time course of methylamine synthesis over FSM-16 pretreated at various temperatures. Methanol: 400 μmol . Ammonia: 200 μmol . Catalyst: 100 mg. Reaction temperature: 673 K. Dead volume: 200 cm^3 .

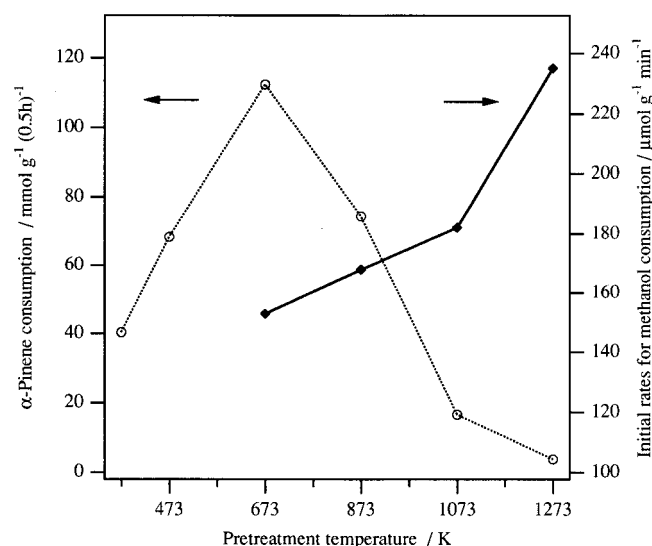


Figure 5. Effects of pretreatment temperature on catalytic properties of FSM-16. Dotted line: α -pinene isomerization at 303 K. Reproduced from ref 18. Solid line: methylamine synthesis at 673 K. $N/C = 0.5$.

rates for methanol consumption were not influenced by the reaction condition of different N/C ratios.

To compare the catalytic activity of FSM-16 with other catalysts, methylamine synthesis was carried out with various reference catalysts. No products other than methylamines were formed in all cases. The time courses of methanol consumption are shown in Figure 6. Activities of silica–alumina and $\gamma\text{-Al}_2\text{O}_3$ were higher by 1 order of magnitude than that of FSM-16. $\gamma\text{-Al}_2\text{O}_3$ exhibited the largest initial rates in the catalysts. SiO_2 gel pretreated at 1073 K was not active for this reaction at all. The activity of FSM-16 (sample 1) was slightly lower than that of FSM-16 (sample 2). The amounts of contained Al were 610 ppm for FSM-16 (sample 1) and 1100 ppm for FSM-16 (sample 2). The difference of catalytic activities between FSM-16 (sample 1) and FSM-16 (sample 2) was much less than that of contained amounts of Al impurities. Although FSM-16 was less active than silica–alumina and $\gamma\text{-Al}_2\text{O}_3$, the point we emphasize is that not only Brønsted but also Lewis acid sites on FSM-16 participate in certain kinds of catalyses.

The results of methylamine synthesis are summarized in Table 3. Consecutive methylation over FSM-16 was accelerated in a reaction condition of $N/C = 2$ more than in $N/C = 0.5$. The equilibrium concentrations of methylamines (MMA/DMA/TMA) are 5:25:70 for $N/C = 0.5$, and 31:38:31 for $N/C = 2$ at

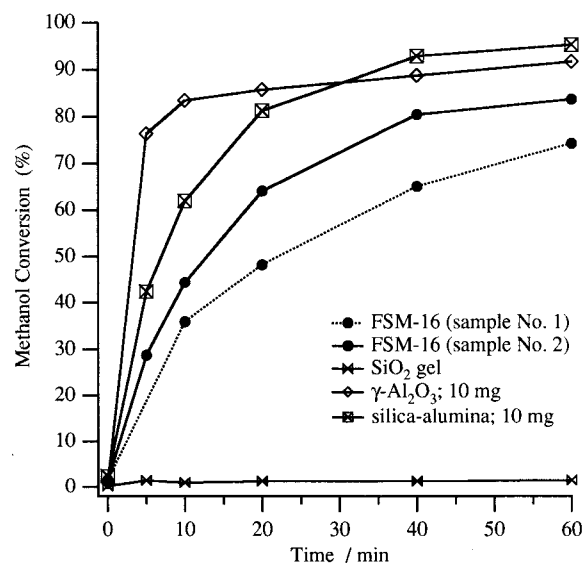


Figure 6. Time course of methylamine synthesis over FSM-16 and reference catalysts. Methanol: 400 μmol . Ammonia: 800 μmol . Catalyst: 100 mg. Reaction temperature: 673 K. Dead volume: 200 cm^3 .

TABLE 3: Results of Methylamine Synthesis at 673 K^a

catalyst	pretreatment temp (K)	N/C^b	conversion ^c (%)	selectivity (%)		
				MMA	DMA	TMA
FSM-16 ^d	673	0.5	78.7	88		12
	873	0.5	80.3	88		12
	1073	0.5	84.2	87		13
	1273	0.5	83.4	88		12
FSM-16 ^e	673	2	84.1	58	4	38
	1073	2	83.8	62	4	34
	1273	2	86.9	69	3	28
FSM-16 ^d	1073	2	74.3	71	3	26
SiO_2 gel	1073	2	1.3			
$\gamma\text{-Al}_2\text{O}_3^f$	673	2	83.5 ^g	90	5	5
		2	91.7	51	21	28
silica–alumina ^f	673	2	81.3 ^h	68	6	26
		2	95.3	50	8	42

^a Catalyst: 100 mg. Methanol: 400 μmol . Ammonia: 200 or 800 μmol . ^b Molar ratio of ammonia to methanol. ^c Reaction time: 1 h.

^d Sample 1. ^e Sample 2. ^f Catalyst: 10 mg. ^g Reaction time: 10 min.

^h Reaction time: 20 min.

673 K.²⁰ This suggests that FSM-16 possesses the acid sites to catalyze methylation of ammonia, the acid strength of which is not sufficient to reach the equilibrium of methylamines rapidly.

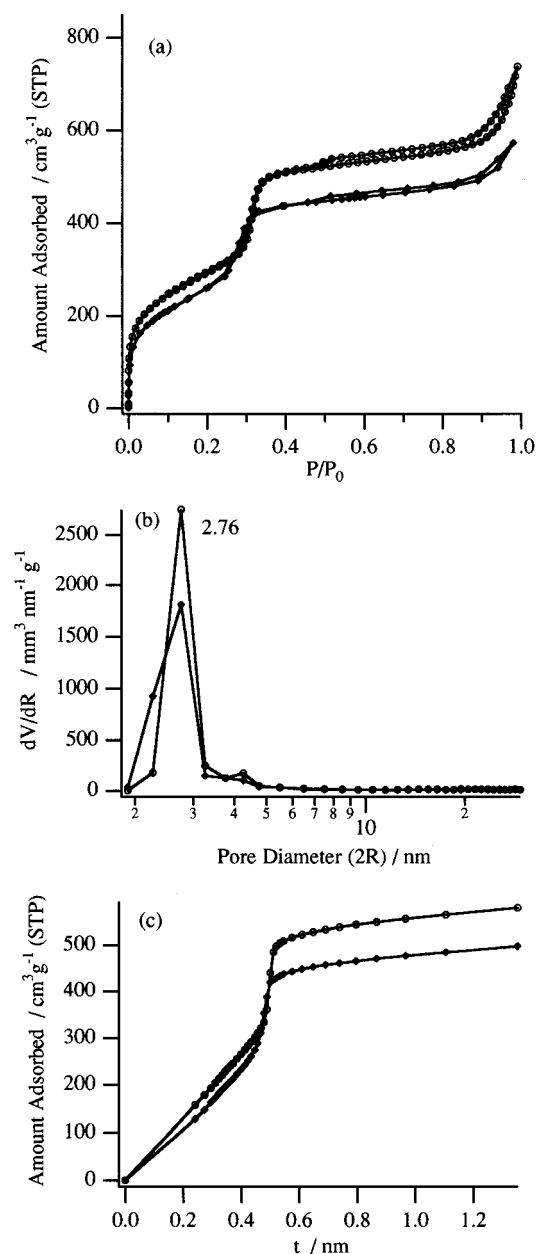


Figure 7. Results of N_2 adsorption/desorption isotherm measurements at 77 K: adsorption/desorption isotherms (a), pore size distribution curves (b), and t -plots (c). Circle: fresh FSM-16 (sample 2). Square: reacted FSM-16, which was pretreated at 1273 K and used for methylamine synthesis at 673 K for 3 h ($N/C = 2$).

In an initial period of methylamine synthesis over $\gamma\text{-Al}_2\text{O}_3$, MMA was selectively produced and the formation of TMA was scarce. In contrast, TMA was produced in an initial step over silica–alumina of strong solid acid.

We have estimated the maximum acid strength of catalysts with Hammet indicators. When pretreatment procedure was performed below 1073 K, FSM-16 exhibits medium acid strength of $H_0 = -3.0$. When FSM-16 was pretreated at 1273 K, the maximum acid strength was estimated to $H_0 = -5.6$.¹⁸ When FSM-16 was pretreated above 1073 K, catalytic activities for but-1-ene and α -pinene isomerization drastically reduced, despite the results that FSM-16 still exhibited solid acidity of medium acid strength. Therefore, we conclude that the Lewis acid site on FSM-16 possesses medium acid strength of $H_0^{\text{max}} = -3.0$ to -5.6 , which slightly catalyzes but-1-ene and α -pinene isomerization at 323 K.

TABLE 4: Surface Area and Porosity of Samples

sample	catalyst	S_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	V_p^b ($\text{cm}^3 \text{g}^{-1}$)	S_t^c ($\text{m}^2 \text{g}^{-1}$)	S_{out}^d ($\text{m}^2 \text{g}^{-1}$)	D^e (nm)
1	FSM-16	1059	0.721	1012	102	2.76
2	FSM-16	1068	0.762	948	97	2.76
3	FSM-16 ^f	924	0.642	888	94	2.76
4	SiO ₂ gel	637	0.683	582	59	4.26
5	<i>p</i> -silica ^g	464	0.266	477	14	(3.76)

^a BET specific surface area. ^b Pore volume estimated by t -plot. ^c Total surface area estimated by t -plot. ^d Outer surface area estimated by t -plot. ^e Tentative pore diameter estimated by Clanson–Inkley method. ^f After methylamine synthesis at 673 K for 3 h. The catalyst was pretreated at 1273 K. ^g Precipitated silica.

Thermal and Hydrothermal Stability of FSM-16. To examine the structural change of FSM-16 throughout a reaction, N_2 adsorption isotherms of fresh and reacted samples were measured. The reacted sample measured was FSM-16 (sample 2) which was pretreated at 1273 K, and the reaction was carried out at 673 K for 3 h ($N/C = 2$). Prior to measurement, reacted FSM-16 was calcined at 873 K for 2 h in a dry air, followed by evacuation at 673 K for 3 h. Figure 7 shows adsorption/desorption isotherms (a), t -plots (b), and pore size distribution curves (c) of fresh and reacted FSM-16. The estimated pore parameters are summarized in Table 4. The shape of the t -plot and estimated parameters for fresh FSM-16 are quite similar to those of FSM-16⁴² and that of MCM-41.^{43, 44}

Reacted FSM-16 retained 85% of the BET specific surface area ($924 \text{ m}^2 \text{g}^{-1}$) and total pore volume (0.642 mL g^{-1}), compared to those of fresh samples. The shape of the N_2 adsorption/desorption isotherm of reacted FSM-16 was retained with respect to that of the fresh sample. The ranges of capillary condensation were observed among $P/P_0 = 0.29\text{--}0.34$ and $0.25\text{--}0.32$, respectively. In the case of reacted FSM-16, the range of pore filling was slightly shifted to lower P/P_0 due to shrinkage of the lattice; however, its decay was almost the same as that of fresh FSM-16. It clearly shows that the crystallinity and pore uniformity of FSM-16 were retained in the pretreated and reacted sample. It was supported by the pore size distribution curves.

Under reaction conditions of a methylamine synthesis, H_2O is produced by dehydrative condensation among methanol and ammonia. As a result, catalysts were exposed to saturated water vapor at 673 K. Nevertheless, scarce reduction of the crystallinity occurred and no increase of outer surface area was observed throughout the reaction. Furthermore, FSM-16 has been pretreated at a high temperature of 1273 K prior to the reaction. The N_2 adsorption/desorption isotherm measuring experiments strongly demonstrate the excellent thermal and hydrothermal stability of FSM-16. It was consistent with the result that FSM-16 soaking into 353 K of water for 5 h retained the original structure, without reducing its crystallinity at all.¹⁸

Conclusion

Lewis acid sites formed on siliceous FSM-16 when the catalyst was pretreated above 873 K. Lewis acid sites on FSM-16 catalyzed methylamine synthesis at 673 K. The activity was enhanced with increasing pretreatment temperature up to 1273 K. The structure of FSM-16 was retained throughout a pretreatment at 1273 K and a reaction at 673 K. When FSM-16 was pretreated at 673 K, reactions catalyzed over Brønsted acid sites exhibit the highest rates. The rates of Lewis acid-catalyzed reactions were enhanced with increasing pretreatment temperature up to 1273 K.

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