

Acidic Property of FSM-16

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Siliceous FSM-16 possesses acid sites to catalyze but-1-ene isomerization to produce but-2-ene (cis/trans = 1.4–1.7) at 323 K and 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (α -pinene) isomerization at 303 K. Catalytic activity was dependent upon heat treatment and reached a maximum at 673 K. The maximum acid strength was invariably $H_0 = -3.0$ independent of the pretreatment temperatures. The acidity was much reduced by calcination at higher temperatures, but restored by water treatment at 353 K as long as the FSM-16 retained its structure.

Introduction

FSM-16,¹ MCM-41,^{2,3} and HMS⁴ are mesoporous silicas with narrow pore size distribution, high specific surface area, and high thermal stability up to 1273 K. These materials, synthesized with cetyltrimethylammonium salts, have a quite similar structure, a unique adsorption isotherm of nitrogen, high BET specific surface area, a narrow pore size distribution, and a high pore volume, although the XRD pattern of HMS is slightly different from the others. While XRD patterns of FSM-16 and MCM-41 may exhibit up to four well-defined peaks, that of HMS exhibits only one broad peak attributed to the 100 reflection.⁵ The main difference between FSM-16 and MCM-41 is the synthesis procedure and formation mechanism. Mobil researchers proposed the formation mechanism of M41S materials, such as MCM-41, based on a liquid crystal templating model. The folding sheets mechanism was proposed for FSM-16: intercalation of surfactants to layered polysilicate kanemite with a primary d spacing of 10 Å and then the folding of layers to form the specific hexagonal structure. On the other hand, Monnier et al. proposed a layered intermediate with a primary d spacing of 31 Å for the formation of MCM-41.⁶ In fact, an in situ XRD study showed that the intermediate lamellar silica-surfactant intercalate was formed during the synthesis of FSM-16 from kanemite, whereas no intermediate phases were observed during the formation of MCM-41.⁷

Silica is a generally catalytically inert material, and the surface silanol groups are very weakly acidic in nature.⁸ Therefore, FSM-16 and MCM-41 themselves are considered inactive catalytically, and the introduction of Al to the framework was often performed to generate acidity.^{3,6,9–13} Other metals or cations are also added to FSM-16 and MCM-41 to generate catalytic activity, as exemplified by incorporation of transition metal cations such as Ti to the framework,^{5,14–16} introduction of metal cations by ion exchange,¹⁷ direct incorporation of novel metals via synthesis gel,¹⁸ and introduction of catalytically active species into pores,^{19–23} and so forth.

Here, we report that siliceous FSM-16 catalyzes isomerization of but-1-ene and 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (α -pinene) at 323 and 303 K, respectively. Isomerizations of terpenes such as the rearrangement of α -pinene to 2,2-dimethyl-

3-methylenebicyclo[2.2.1]heptane (camphene)²⁴ and the migration of olefinic bonds of 1-methyl-4-(1-methylethynyl)cyclohexene (limonene)²⁵ were known to be acid-catalyzed reactions. In contrast, solid bases such as CaO and SrO catalyze isomerization of α -pinene to produce 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (β -pinene), selectively.²⁶ Therefore, isomerization of α -pinene is an excellent test reaction for acid-base properties of a catalyst.

Recently, catalysis by siliceous mesoporous materials was reported. The selective dehydration of 2-methylbut-3-yn-2-ol to 2-methylbut-3-yn-1-ene proceeded at 453 K over MCM-41.²⁷ Cumene cracking was catalyzed over FSM-16 at 673 K.²⁸ Furthermore, Yoshida et al. reported that FSM-16 evacuated at 873 K catalyzes metathesis of propene under photoirradiation.²⁹ However, the first two papers did not focus on the catalytic properties of siliceous mesoporous materials. There have been no reports discussing the acidic properties of siliceous mesoporous materials.

Experimental Section

Materials. FSM-16 was synthesized according to Inagaki's method.³⁰ Prior to calcination, the Si/Na atomic ratio of water glass (Osaka Keiso Co., LTD; SiO₂ = 31.93, Na₂O = 15.37, Al = 0.0098, Fe = 0.0028 wt %; Si/Al = 1463 atomic ratio) was adjusted to 1.00 by addition of NaOH solution (Wako Pure Chem. Ind., LTD). During synthesis, water glass successively changed to δ -Na₂Si₂O₅, kanemite (NaHSi₂O₅·3H₂O), and finally FSM-16 via three steps. [C₁₆H₃₃(CH₃)₃N]Br (Tokyo Chem. Ind. Co., LTD) was used as a template. The ion exchange of kanemite to produce FSM-16 was carried out as follows. At the beginning of ion exchange of kanemite, the concentration of template was 0.10 M and a molar ratio of the template to Si of kanemite was adjusted to 0.2. The ion exchange was carried out at 343 K for 3 h with stirring. After cooling to room temperature, the solid was filtered off and then dispersed in distilled water again. After adjustment of the pH to 8.5 with 2 M HCl, it was heated to 343 K and stirred for 6 h while maintaining pH at 8.5. Finally, ion-exchanged kanemite (FSM-16) was calcined in a dry air stream at 823 K for 6 h. The yield of FSM-16 based on SiO₂ was 24%. After calcination, FSM-16 was ground to powder under 100 mesh. The XRD pattern (d_{100} ; 38 Å), the BET specific surface area (1078 m²

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TABLE 1: Elemental Analysis of Catalysts^a

catalyst	elements (mass%)						Si/Al atomic ratio
	Na	Al	Ca	Fe	Mg	Ti	
FSM-16	0.008	0.061	0.012	0.023	0.003	0.032	735
FSM-1173H ^b	0.017	0.062	0.012	0.021	0.003	0.029	723
FSM-1373H ^c	0.021	0.071	0.014	0.031	0.004	0.035	631
FSM-16 ^d	0.01	0.14		0.02			320
H ₂ Si ₂ O ₅	0.005	0.008	0.006	0.002	0.001	0.007	5612
SiO ₂ gel	0.002	<0.001	0.001	<0.001	<0.001	<0.001	

^a Analyzed by ICP (inductively coupled plasma) and atomic absorption spectroscopy. ^b Hydrated at 353 K for 4 h followed by calcination at 773 K for 5 h. Before hydration, FSM-16 was calcined in a dry air stream at 1173 K for 2 h. ^c Hydrated at 353 K for 4 h followed by calcination at 773 K for 5 h. Before hydration, FSM-16 was calcined in a dry air stream at 1373 K for 2 h. ^d Supplied by Toyota Central R&D Labs., Inc. (lot no. NG78-550).

g⁻¹), the N₂ adsorption isotherm, the pore volume (0.73 cm³ g⁻¹; estimated by *t*-plot), and the pore diameter (27.6 Å; estimated by the Clanston–Inkley method) were quite similar to those reported in the literature.^{30,31}

Calcined and rehydrated FSM-16 was also prepared because a hydration state of FSM-16 is closely related to catalytic activities, as would be described below. Rehydrated catalysts were prepared via two steps. Before rehydration, FSM-16 was calcined once in a dry air stream at 1173 or 1373 K for 2 h (FSM-1173, FSM-1373). At the next step, the calcined FSM-16 was treated with water at 353 K for 4 h with stirring, followed by calcination at 773 K for 5 h (FSM-1173H, FSM-1373H).

Silicon oxide hydrate (H₂Si₂O₅) was synthesized from kanemite,³² which was the same material as used for FSM-16 synthesis. Kanemite dispersed in distilled water was converted to H₂Si₂O₅ keeping the pH at 1.2 at room temperature. Adjustment of the pH was performed with 2 M HCl, and the condition was maintained for 24 h with stirring. The precipitate was washed with distilled water until Cl⁻ was free based on AgNO₃ test. It was dried at 343 K for 12 h followed by calcination at 773 K for 5 h. Formation of H₂Si₂O₅ crystal was confirmed by XRD (JCPDS file No. 27-606) for the dried sample, which became amorphous upon calcination at 773 K. TG-DTA analysis showed that H₂Si₂O₅ released the interlayer water molecules around at 473 K, and the loss of interlayer water should account for the loss of crystallinity. This phenomenon was consistent with previous works.³³ Al-doped δ-Na₂Si₂O₅ and H₂Si₂O₅ were also synthesized. To adjust the Si/Al atomic ratio to be 16, whose value was to form 5 wt % of Al₂O₃ containing SiO₂–Al₂O₃ as a starting material, NaAlO₂ was added to water glass.

SiO₂ gel was synthesized from tetraethyl orthosilicate (Nacalai tesque, EP-grade, once distilled) by hydrolysis in a water–ethanol mixture at boiling point followed by calcination at 773 K for 5 h in a dry air stream.³⁴ Before calcination, a dried sample was ground to powder under 100 mesh. No crystalline phases of SiO₂ were detected by XRD analysis.

Other silicas used were Japan Reference Catalyst (JRC-SIO-5, JRC-SIO-7), supplied by the Committee on Reference Catalyst, Catalysis Society of Japan. JRC-SIO-5 contains 134 ppm Na, 122 ppm Al, 40 ppm Ca, 57 ppm Fe, and 100 ppm Mg. JRC-SIO-7 contains 135 ppm Na, 195 ppm Al, 36 ppm Ca, 72 ppm Fe, and 117 ppm Mg. The BET specific surface area of JRC-SIO-5 and JRC-SIO-7 is 192 and 86 m² g⁻¹, respectively. They were precalcined in dry air at 773 K for 3 h.

Reference catalysts used for α-pinene isomerization were HZSM-5 (JRC-Z5-25H, -70H, -1000H; Si/Al atomic ratio are 12.3, 40.0, 623, respectively), NaY (JRC-Z-1), γ-Al₂O₃ (JRC-ALO-4), ZrO₂ (JRC-ZRO-1), TiO₂ (JRC-TIO-4), Mg(OH)₂ (Rare Metallic Co., 99%), Ca(OH)₂ (Nacalai, GR), Nb₂O₅·nH₂O (CBMM), and NiSO₄·nH₂O (Nacalai, GR).

Characterization. NH₃-TPD measurements were carried out by a quadrupole-type mass spectrometer at a heating rate of 5 K min⁻¹. Before TPD measurements, each 100 mg of sample was evacuated 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 sample was exposed to 500 μmol of NH₃ at room temperature for 0.5 h followed by evacuation at the same temperature for 1 h. The amount of desorbed gases (NH₃; *m/e* = 16) was normalized with that of introduced Ar (*m/e* = 40) as an internal standard.

FTIR spectra were recorded with a Perkin-Elmer Paragon 1000 spectrometer in a transmission mode at room temperature. IR spectra of adsorbed pyridine were recorded with a resolution of 4 cm⁻¹. Each sample (20–80 mg) was pressed into a self-supporting wafer (20 mm in diameter) with a pressure of 100 kg cm⁻² for 10 s. The wafer was pretreated in the same way as that for NH₃-TPD measurements and exposed to 27 Pa of pyridine vapor at 423 K for 5 min followed by evacuation at the same temperature for 1 h. The other spectra were recorded with a resolution of 2 cm⁻¹.

Thermogravimetric analysis was carried out with Rigaku Thermoflex TG 8110 in a dry N₂ stream at a heating rate of 5 K min⁻¹.

X-ray diffraction patterns of samples were obtained with a Rigaku Geigerflux diffractometer using Ni-filtered Cu Kα radiation (1.5418 Å).

The acid strength of catalysts was measured by various Hammett indicators. The indicators used for the titration method were 0.1 wt % benzene solution of methyl red (*H*₀ = +4.8), *p*-dimethylaminoazobenzene (+3.0), benzenazodiphenylamine (+1.5), dicinnamalacetone (−3.0), and benzalacetophenone (−5.6).

Catalysis. But-1-ene isomerization was carried out in a closed circulation system (dead volume, 200 cm³). Prior to each run, 50 mg of FSM-16 was evacuated at a prescribed temperature 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 amount of substrate was 400 μmol, and the reaction temperature was 323 K.

α-Pinene isomerization was carried out under dry N₂ atmosphere using a stirred batch reactor at 303 or 353 K. The pretreatment procedure was the same as mentioned above. In a typical experiment, the reactor was loaded with 2 mL (12.6 mmol) of α-pinene (Nacalai, EP, 99.8%) and 50 mg of catalyst.

Products were analyzed by GC and GC–MS (Shimadzu, GCMS-QP5050).

Results and Discussion

Elemental Analysis. Table 1 summarizes elemental analysis of prepared catalysts. Although the Si/Al atomic ratio of water

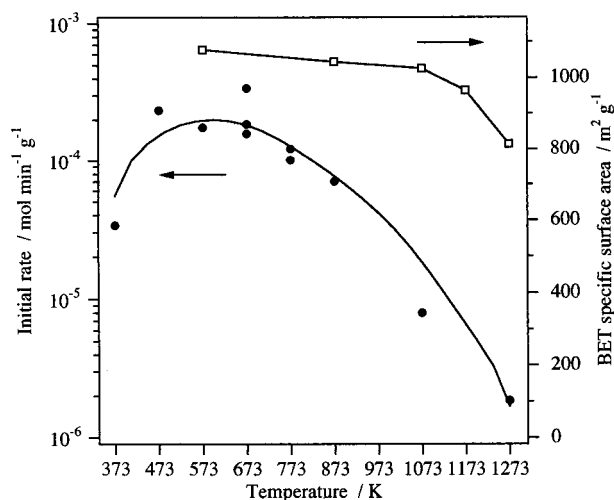


Figure 1. Plots of initial rates for but-1-ene isomerization over FSM-16 and BET specific surface area vs pretreatment temperatures. Dead volume, 200 cm³; catalyst, 50 mg; but-1-ene, 400 μ mol; reaction temperature, 323 K.

glass was 1463, that of synthesized FSM-16 was 735. This result shows that Al was slightly concentrated but the concentration was still quite low. Results of FSM-1173H and FSM-1373H show that no treatment changes the original elemental composition except for Na. Because H₂Si₂O₅ was treated with water of pH = 1.2 during synthesis, almost all of the trace elements were extracted off. SiO₂ gel contained little other elements.

Acidic Property. Figure 1 shows initial rates for but-1-ene isomerization over FSM-16 pretreated at various temperatures and BET specific surface areas of the FSM-16 samples. The initial rate strongly depended on the pretreatment temperature. Samples pretreated at temperatures from 473 through 673 K showed similar initial rates. Once pretreatments were performed at temperatures higher than 873 K, the initial rate drastically decreased, although BET specific surface areas remained high. No correlation between initial rates and surface areas was observed. For example, only a 5% difference in surface area was observed for the samples pretreated at 873 and 1073 K, but the initial rates differed by 1.5 orders of magnitude. In all cases, the ratios of the cis-isomer to the trans-isomer in produced but-2-enes were 1.4–1.7, indicating that this reaction was catalyzed by acids. No reaction proceeded over SiO₂ gel pretreated at 673 K.

A similar catalytic behavior was exhibited in isomerization of α -pinene (Figure 2), as summarized in Table 2. It should be noted that the selectivity did not change at all, whereas the catalytic activity was drastically changed depending upon pretreatment temperature. Main products were camphene and limonene, and the selectivity to these two products was around 40%. Products of α -pinene isomerization can be classified into three groups. The first group is β -pinene. Over solid base catalysts, only equilibrium between α -pinene and β -pinene would be observed.²⁶ The second group consists of bicyclic (camphene, α -fenchene, etc.) and tricyclic (tricyclene, etc.) products. The last group is composed of monocyclic products (limonene, terpinolene, α -terpinene, γ -terpinene, etc.). One remarkable result of the present study is that the formation of β -pinene was negligible over FSM-16. This result also revealed that few basic sites existed on FSM-16, and this reaction was catalyzed by acids. It was reported that monocyclic products were formed more preferentially than bi- or tricyclic products over strong acid catalysts.²⁴ The independence of selectivity

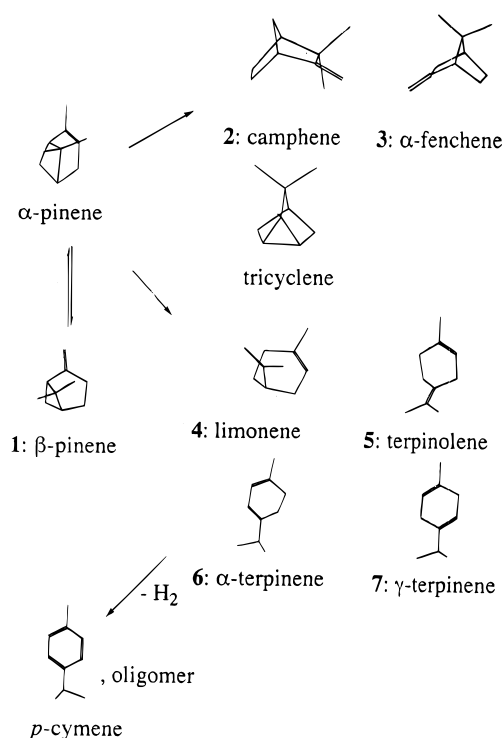


Figure 2. Scheme of α -pinene isomerization.

TABLE 2: Results of α -Pinene Isomerization at 303 K^a

catalyst	pretreatment temp/K	conversion (%)	selectivity ^b (%)							
			1	2	3	4	5	6	7	8
FSM-16	373	16.0	1	42	6	42	6	1	1	1
	473	27.1	1	40	5	44	7	1	1	1
	673	44.6	tr	40	4	43	9	2	2	tr
	873	29.5	tr	39	3	48	7	1	1	1
	1073	6.6	1	37	3	48	7	2	2	1
	1273	1.5	4	37	3	46	7	1	2	tr
FSM-16 ^c	673	52.9	tr	39	4	43	8	2	2	tr

^a α -pinene, 2 mL; catalyst, 50 mg; reaction time, 0.5 h. ^b 1, β -pinene; 2, camphene; 3, α -fenchene; 4, limonene; 5, terpinolene; 6, α -terpinene; 7, γ -terpinene; 8, others. ^c Supplied by Toyota Central Lab., Inc. (lot no. NG78-550).

for this reaction indicates that the maximum acid strengths were not changed by pretreatment temperatures.

As shown in Table 3, over SiO₂ gel, δ -Na₂Si₂O₅, H₂Si₂O₅, JRC-SIO-5 and JRC-SIO-7, α -pinene isomerization hardly took place even at 353 K. As-calcined H₂Si₂O₅ pretreated at 373 and 473 K, which remained as a crystal structure, was also inactive. The result of JRC-SIO-7 shows that silica containing 195 ppm of Al is not enough to catalyze this reaction at the temperature of 353 K. Furthermore, Al-doped H₂Si₂O₅ showed very low activity. Typical acid catalysts were also tested (Table 3). γ -Al₂O₃, TiO₂, Nb₂O₅·*n*H₂O, and NiSO₄·*n*H₂O were active for this reaction at 353 K, but activities were quite low compared to that of FSM-16. In the case of NiSO₄·*n*H₂O, a selectivity for bi- or tricyclic products was particularly high, 88%, which coincides with the previous reports.²⁴ It is very intriguing that HZSM-5, the Si/Al atomic ratio of which was 12.3, known as a strong acid catalyst, was less active than FSM-16 at least at a temperature of 303 K. It may be due to its small pore size. Although FSM-16 has a large mesopore of 28 Å, the MFI type zeolite has a micropore in which the three-dimensional channel system has straight 10-ring 5.2 × 5.7 Å channels connected by a zigzag structure like 5.3 × 5.6 Å channels. In the case of HZSM-5, a diffusion of substrates or products was suppressed

TABLE 3: Results of α -Pinene Isomerization at 353 K^a

catalyst	pretreatment temp/K (%)	conversion (%)	selectivity ^b (%)							
			1	2	3	4	5	6	7	8
FSM-16 ^c	673	77.8	0	41	4	41	9	2	2	1
SiO ₂ gel	673	0.0								
	1073	0.0								
δ -Na ₂ Si ₂ O ₅	673	0.0								
Al-doped Na ₂ Si ₂ O ₅ ^d	673	0.0								
H ₂ Si ₂ O ₅	673	0.0								
Al-doped H ₂ Si ₂ O ₅ ^d	673	1.7	4	38	4	43	6	1	2	2
JRC-SIO-5	673	<0.1								
JRC-SIO-7	673	<0.1								
γ -Al ₂ O ₃	673	3.4	33	44	2	17	2	1	1	tr
TiO ₂	673	0.6	31	43	2	13	3	1	3	4
ZrO ₂	673	0.0								
HZSM-5 (12.3) ^c	673	18.8	1	36	28	25	2	2	1	5
HZSM-5 (40.0) ^c	673	6.1	2	35	19	33	3	2	2	4
HZSM-5 (623)	673	18.0	2	33	24	28	2	3	2	6
c	673	0.2								
NaY	673	21.1	1	24	2	55	9	3	5	1
Nb ₂ O ₅ · <i>n</i> H ₂ O	373	6.5	5	52	5	26	5	2	2	3
NiSO ₄ · <i>n</i> H ₂ O	673	54.5	tr	77	3	7	2	1	tr	10 ^e
MgO ^f	873	2.1	100	tr						tr
CaO ^f	873	2.2	95							5

^a α -Pinene, 2 mL; catalyst, 100 mg; reaction time, 3 h. ^b 1, β -pinene; 2, camphene; 3, α -fenchene; 4, limonene; 5, terpinolene; 6, α -terpinene; 7, γ -terpinene; 8, others. ^c Catalyst: 50 mg; reaction temperature, 303 K. ^d Si/Al atomic ratio was 16.1 as a starting material. ^e Tricyclene: 8%. ^f Catalyst: 300 mg as M(OH)₂ (M = Mg, Ca).

especially at a low temperature of 303 K. These results indicate that the effective surface area of MFI type zeolite for α -pinene isomerization is much lower than that of FSM-16. FSM-16 could provide a reaction field for large molecules such as α -pinene. In addition, HZSM-5 of Si/Al = 623 was almost inactive at 303 K and showed low activity even at 353 K, although the Si/Al atomic ratios of the HZSM-5 and FSM-16 were almost the same. The second intriguing point is that the selectivity for formation of α -fenchene was particularly high. It results from restricted transition-state selectivity. Another HZSM-5 of different Si/Al atomic ratio also showed high selectivity for α -fenchene formation. In the small pore of the MFI type zeolite, it is difficult for α -pinene isomerization to bulky transition states to produce terpinolene, α -terpinene, γ -terpinene, and so forth, compared to that of limonene. In contrast, the FAU type zeolite has larger supercages of 13 Å, and this restriction was no longer observed. It was reported that NaY had acid sites, the maximum acid strength of which range from $H_0 = +1.5$ to $+4.0$.³⁵ Although NaY is a very weak acid in nature, its specific surface area was estimated to be 973 m² g⁻¹ by Langmuir plot. The high activity of NaY was due to the large surface area in comparison with other catalysts. Furthermore, over Brønsted acid catalysts, catalytic activity was strongly related to the mobility of protons. From IR experiments, Ward observed the delocalization of protons on HY in the range 473–700 K.³⁶ Baba et al. observed changes of the line width of the ¹H MAS NMR signal of acidic OH groups of HZSM-5 with temperature and found a relation between line widths and catalytic activities.³⁷ They discussed that the mobility of protons depended on temperature and the same amounts of protons would not necessarily exhibit the same activities.

MgO and CaO were also active for α -pinene isomerization. The selectivities for β -pinene formation were almost 100%, while they exhibited low conversion at 353 K (Table 3). The selective isomerization between α -pinene and β -pinene is one of the characteristics of solid base catalyst, and the low conversions were due to the low equilibrium constant of β -pinene to α -pinene.²⁶ Table 4 summarizes isomerization of β -pinene over FSM-16, MgO, and CaO. Over solid base catalysts, only transformation between β -pinene and α -pinene

TABLE 4: Results of β -Pinene Isomerization^a

catalyst	FSM-16	MgO	CaO
pretreatment temperature/K	673	873	873
reaction temperature/K	353	423	423
weight/mg	50	300 ^b	300 ^b
time/h	0.5	3	3
conversion (%)	20.8	3.5	9.3
selectivity (%)			
α -pinene	11	98	99
camphene	27	2	1
limonene	36		
terpinolene	9		
others	17	tr	tr

^a β -Pinene: 2 mL. ^b As M(OH)₂, (M = Mg, Ca).

was electively catalyzed, and formation of other products was negligible. In contrast, the reaction continuously proceeded via α -pinene, and many kinds of secondary products were observed over FSM-16. The result of β -pinene isomerization also strongly suggests that not basic but acidic sites were the main active sites on FSM-16. The lack of basic sites over FSM-16 was supported by the result of but-1-ene isomerization discussed above. In general, solid base catalyzes but-1-ene and the cis/trans ratio of produced but-2-ene is very large.³⁸ In the case of FSM-16, however, that ratio was between 1.4 and 1.7.

Figure 3 shows NH₃-TPD profiles of FSM-16, SiO₂ gel, and H₂Si₂O₅ pretreated at 673 K. SiO₂ gel and H₂Si₂O₅ exhibited a single peak around at 370 and 360 K, respectively. The profile of FSM-16 shows a peak above 400 K besides a peak at around 355 K; however the peak around at 473 K is not due to strong acid sites.³⁹ It clearly shows that the acid sites of FSM-16 pretreated at 673 K are different from those of the others. This was supported by IR spectra. Figure 4 shows IR spectra of adsorbed pyridine on SiO₂ gel and FSM-16 pretreated at 673 K. Assignment of pyridine adsorption peaks was as follows.⁴⁰ Peaks due to hydrogen-bonded pyridine were 1448 and 1598 cm⁻¹, those due to pyridine adsorbed on Brønsted acid sites were 1546 and 1638 cm⁻¹, and those on Lewis acid sites were 1456 and 1624 cm⁻¹. A peak at 1493 cm⁻¹ was due to pyridine adsorbed on both Brønsted and Lewis acid sites. SiO₂ gel

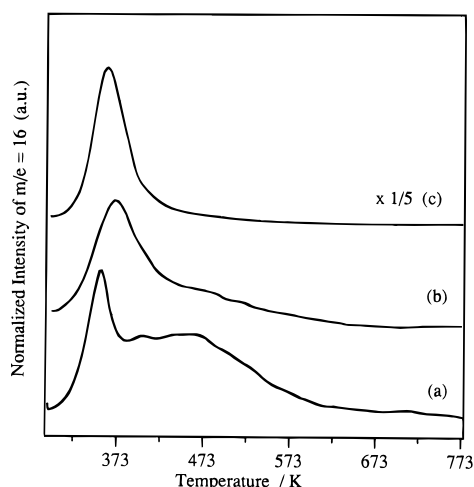


Figure 3. NH_3 -TPD profiles of FSM-16 (a), SiO_2 (b), and $\text{H}_2\text{Si}_2\text{O}_5$ (c) pretreated at 673 K.

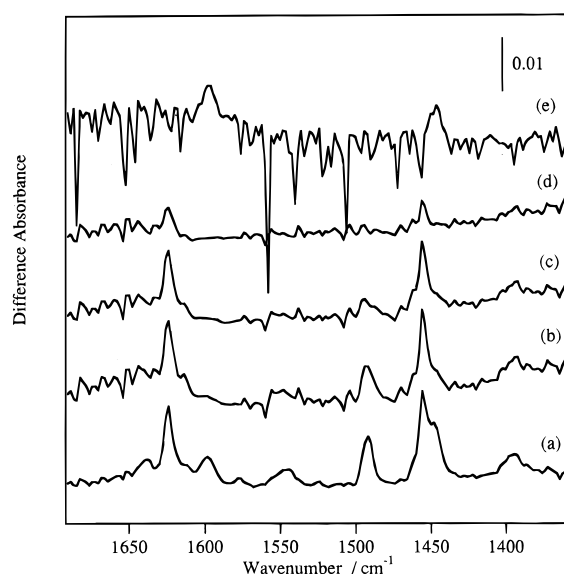


Figure 4. FTIR spectra of adsorbed pyridine at 423 K. FSM-16 (21 mg) evacuated at 423 K (a), 473 K (b), 573 K (c), and 673 K (d) and SiO_2 gel (80 mg) evacuated at 423 K (e).

possessed only hydrogen-bonded sites, whereas FSM-16 possessed both Brønsted and Lewis acid sites besides hydrogen-bonded sites. When FSM-16 adsorbing pyridine was evacuated at 473 K, hydrogen-bonded pyridine and pyridine adsorbed on Brønsted sites were desorbed. Almost all of the pyridine was desorbed at 673 K with increasing evacuation temperature. IR spectra of pyridine adsorbed on Al-containing MCM-41 were measured by many researchers.^{9–11,41} Although Corma et al. observed Brønsted acid sites on MCM-41 of Si/Al = 100,⁹ Jentys et al. observed only Lewis acid sites on the same Si/Al ratio's material.¹¹ Further, Jentys et al. and Mokaya et al.¹⁰ observed only hydrogen-bonded species on pure siliceous MCM-41. While the Si/Al atomic ratio of synthesized FSM-16 was 735, both Lewis and Brønsted acid sites were observed on FSM-16. The spectrum was quite similar to those of Al-MCM-41 (Si/Al = 100). Although we have not compared directly the acidic property between FSM-16 and MCM-41, IR spectra of adsorbed pyridine suggest that the acidic property of FSM-16 is higher than, or at least equal to, those of MCM-41. Zhao et al. performed pyridine TPD of siliceous MCM-41 and observed two desorption peaks in the temperature range 323–523 K.⁴² They claimed that two peaks were due to desorbed pyridine

from hydrogen-bonded SiOH and free SiOH groups, and both activation energies of desorption sites were similar to those of amorphous silica. In fact, the reported pyridine desorption profile for silica gel (Kieselgel 60; Merk NV) was quite similar.⁴³ The pyridine desorption profile for MCM-41 was also quite similar to the NH_3 desorption profile for FSM-16, although it is very difficult to compare with the results of pyridine and NH_3 -TPD experiment. Because the NH_3 -TPD profile for SiO_2 gel was different from that for FSM-16, it could be possible that the property of siliceous MCM-41 is similar to that of FSM-16 demonstrated in the present work.

Contribution of Aluminum to Acidic Property. FSM-16 employed in the present work contains a trace amount of Al (Si/Al = 320, 735), which might be associated with the acid sites. Van Roosmalen et al. reported the catalysis of but-1-ene isomerization over silica gel.⁴³ They concluded that activities of silica gel were directly proportional to the concentration of Al being present as a trace impurity at 600–700 K. In their report, silica gel (Rhône-Progil; Spherosil XOA-400, 361 $\text{m}^2 \text{g}^{-1}$, Si/Al = 100–1000) showed a rate constant of 31 $\text{nmol m}^{-2} \text{s}^{-1}$ at 600 K and $1.1 \times 10^5 \text{ Pa}$ for but-1-ene, whereas in the case of FSM-16, the activity comparable to that reported was exhibited at a low temperature of 323 K and a low pressure of $4.7 \times 10^3 \text{ Pa}$ for but-1-ene. Furthermore, we confirmed that the amorphous silica prepared from the same water glass was inactive. West et al. reported that many reactions catalyzed by silica gel took place at impurity sites.⁴⁵ They observed improvement of activity more than 100 times for hex-1-ene isomerization over $\text{Al}(\text{NO}_3)_3$ added to silica gel (120 ppm as Al) than the original silica gel. However, the original silica gel (Davison Grade 59 or Grade 70) contains 0.1% Al_2O_3 , 0.01% Fe_2O_3 , 0.02% TiO_2 , 0.07% CaO , 0.06% Na_2O , and 0.03% ZrO_2 , and the rate of hex-1-ene isomerization was reported to be 0.2 $\text{mmol h}^{-1} \text{g}^{-1}$ at 373 K.⁴⁵ This value was about 60 times smaller than the rate of but-1-ene isomerization over FSM-16 at 323 K. Although it is hard to compare them, we should suppose that the acidity of FSM-16 is much higher than that of silica gel containing 0.1% Al_2O_3 .

In the case of ZSM-5, it was reported that catalytic activities of many reactions were directly proportional to the concentration of Al and the proportional relations were applicable down to 10 ppm.⁴⁶ The reported reactions were propylene polymerization,⁴⁷ *n*-hexane cracking,^{48–50} hex-1-ene isomerizations,⁴⁹ and so forth. However, all reactions were performed over 700 K. On the other hand, isomerization of but-1-ene and α -pinene proceeds over FSM-16 even at 323 K. There have been no reports that butene isomerization proceeds at ambient temperature on silica including such a trace amount of impurity at measurable rates. In α -pinene isomerization, activities of FSM-16 whose Si/Al atomic ratio was 320 and 735 were almost the same. We emphasize again that the acidity of FSM-16 exhibited by the present sample is not due to Al impurity.

Dehydroxylation. As shown in Figure 1 and Table 2, FSM-16 pretreated at 673 K showed maximum catalytic activity. The activity was drastically reduced when FSM-16 was pretreated at higher than 873 K. Sintering or the change of surface property is thought to be the reason for deactivation. The possibility that sintering causes deactivation can be excluded from the result of BET measurements. Therefore, the change of surface property should be the main reason for deactivation. Dehydration and condensation of SiOH groups should relate closely to the change of specific property.

Figure 5 shows a thermogravimetric analysis and H_2O -TPD profile of FSM-16. The weight loss completely corresponded

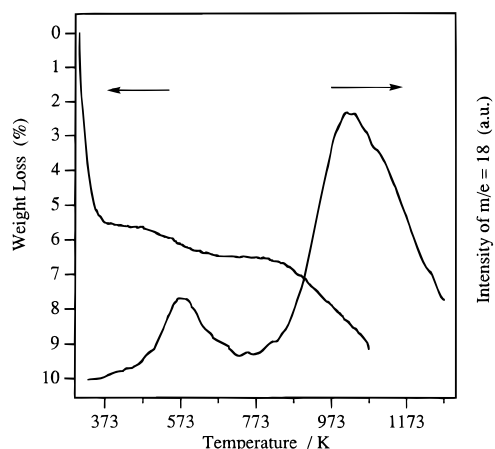


Figure 5. Thermogravimetric analysis and H₂O-TPD profile of FSM-16. Prior to TPD measurement, 20 mg of FSM-16 was evacuated at 373 K for 1 h.

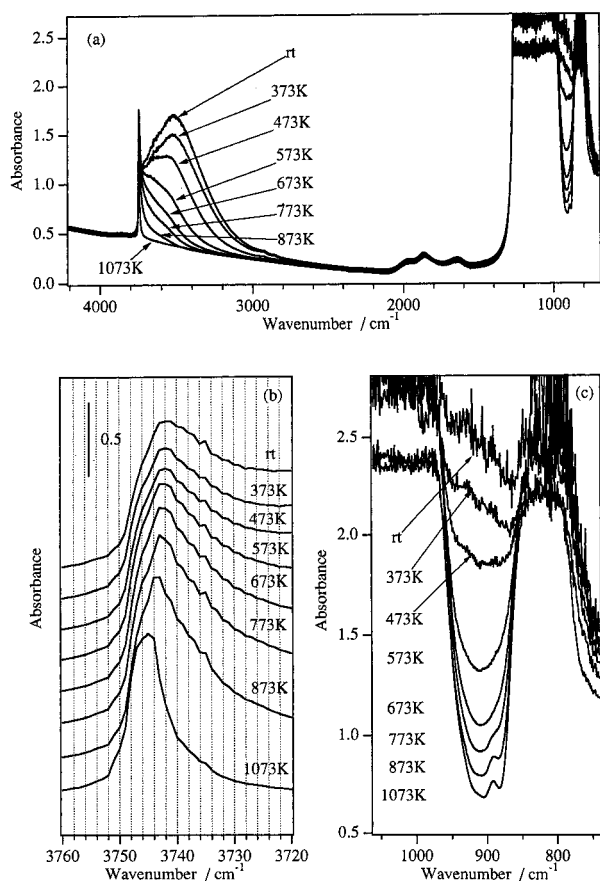


Figure 6. FTIR spectra of FSM-16 evacuated at various temperatures.

to desorption of H₂O. Since large part of physisorbed H₂O was eliminated below 373 K, a TPD experiment was performed after preevacuation at 373 K for 1 h. Because FSM-16 was once calcined at 823 K in a synthesis step, the signal intensity of $m/e = 18$ below 773 K was small. Dehydroxylation continuously proceeded over 773 K. A large quantity of H₂O evolution over 773 K was due to dehydroxylation of a silanol group to form a siloxane bridge,⁵¹ and catalytic activities were drastically lowered in this region.

IR spectra of FSM-16 showed similar behavior, as shown in Figure 6. With increasing evacuation temperature, a very broad band at around 3500 cm⁻¹ gradually decreased and a new window at around 900 cm⁻¹ appeared. The band at around 3500 cm⁻¹ is due to strongly hydrogen bonded silanol groups. Figure

6b shows spectra of isolated silanol groups. In the case where the evacuation temperature was below 773 K, positions of the peak maximum were 3742 cm⁻¹. As evacuation temperature increases, the peak position was shifted to higher frequency. When FSM-16 was evacuated at 1073 K, the peak position was finally reached at 3745 cm⁻¹. Morrow et al. reported that observed bands of isolated silanol groups were a combination of two species.⁵² One was truly isolated silanol ($\nu(\text{SiO}-\text{H})$ of species I: 3750 cm⁻¹), and the other was weakly perturbed vicinal pairs of silanols ($\nu(\text{SiO}-\text{H})$ of species II: 3740 cm⁻¹). Morrow et al. also reported that fumed silica and precipitated silica have different peak frequencies and bandwidths of isolated silanol because different preparation methods caused the ratio of the two isolated silanols to differ. If the concentration of weakly perturbed vicinal pairs of silanol is high, the peak position should be near 3740 cm⁻¹. On the contrary, if the concentration of truly isolated silanol is high, the peak position should be near 3750 cm⁻¹. From the band position of FSM-16, we conclude that isolated silanol groups on FSM-16 are rich in species II (weakly perturbed vicinal pairs of silanol). Ishikawa et al. observed a silanol band at 3740 cm⁻¹ over FSM-16 and estimated the surface concentration.⁵³ The wavenumber also indicates that almost all the silanol groups are weakly perturbed, although their concentration was lower than that of ordinary silica gel. Over siliceous MCM-41, the band due to isolated silanol groups was confirmed at 3738 cm⁻¹ which was also close to the band of species II.⁴²

When FSM-16 was evacuated at above 773 K, weakly perturbed vicinal pairs of silanol (species II) were selectively dehydroxylated to form truly isolated silanol (species I). The blue shift of the isolated silanol band on FSM-16 was due to a change of their ratio. These phenomena were more clearly shown in difference spectra, as shown in Figure 7. Below 673 K, broad bands of strongly hydrogen bonded silanol groups were mainly weakened. The difference spectrum between 573 and 673 K has the largest band area. It corresponded to the first peak of the H₂O-TPD profile and a gravimetric decrease (Figure 5). Above 773 K, the position of the weakened band was shifted to higher frequency. The most typical case was the difference spectra between 873 and 1073 K. The positions of weakened and strengthened peaks were 3741 and 3748 cm⁻¹, respectively. In this region, elimination of silanol groups occurred. We observed a new band generation at around 892 cm⁻¹ in accordance with blue shift of isolated silanol bands (Figure 6c). Morrow et al. observed generation of new two bands at 908 and 888 cm⁻¹ on fumed silica. New bands appeared when silica was evacuated at temperatures higher than 873 K, and these intensities reached a maximum at 1473 K.⁵⁴⁻⁵⁶ They assigned these peaks to a reactive strained siloxane bridge formed by condensation of isolated silanol groups. Further, Bunker et al. assigned them to an edge-shared silicate tetrahedral ring.⁵⁷ In the second derivative of the IR spectrum, a trace peak and a distinct peak were observed on FSM-16 at 912 and 892 cm⁻¹, respectively. IR behavior exhibited by FSM-16 resembles that previously reported on fumed silica, although the new band on FSM-16 was almost single. The IR result suggests that weakly perturbed vicinal pairs of silanols on FSM-16 condensed to produce siloxane bridges, similar to those on fumed silica and silica gel.⁵¹ Therefore the dehydroxylation of surface silanol groups of FSM-16 was responsible for the deactivation. The temperature of 673 K is the point where catalytic activity of FSM-16 decreased. Matsumura et al. reported that silica gel pretreated above 1000 K was active for selective ethanol dehydrogenation and the active site was an active siloxane bridge

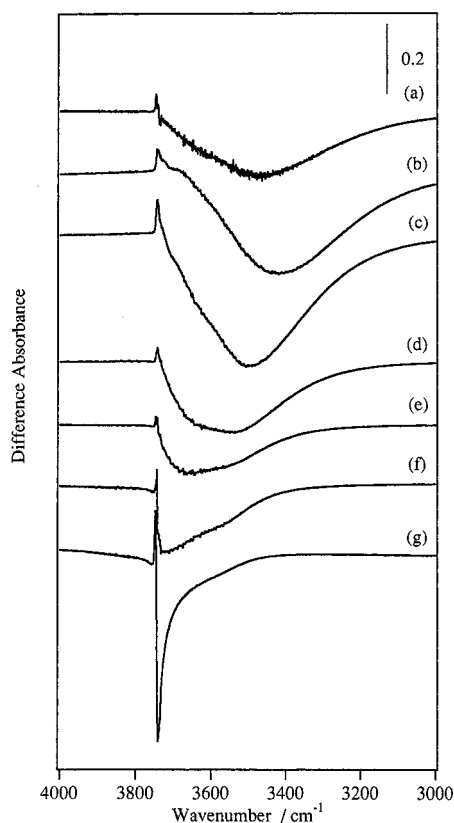


Figure 7. Difference IR spectra of FSM-16 evacuated at various temperatures: between 373 K and room temperature (a), 473 and 573 K (b), 573 and 673 K (c), 673 and 773 K (d), 773 and 873 K (e), and 873 and 1073 K (f).

formed by the dehydration of silanol groups.^{58,59} In contrast, the siloxane bridge on FSM-16 did not concern the isomerization because no increase in activity was observed for FSM-16 evacuated at higher temperatures. The isolated silanol band observed on FSM-16 was only one and the wavenumber was around 3742 cm^{-1} , so-called neutral. We conclude that the active sites were surface silanol groups of species II themselves and/or silanol-related sites, although they were not so-called acidic silanol bands around 3600 cm^{-1} . This presumably results from the synthesis method and the crystal structure of FSM-16, on which the silanol groups were supposed to be regularly arrayed. There are very few reports in which neutral silanol groups are active sites for any reactions. Sato et al. claimed that Beckmann rearrangement of cyclohexanone oxime was catalyzed by neutral silanol groups, whose wavenumber was 3740 cm^{-1} , on the external surface of highly siliceous MFI type zeolites.⁶⁰ Although they did not discuss the silanol groups in detail, we suspect that the silanol groups should be weakly perturbed vicinal pairs.

Regeneration of Acid Sites. In the previous section, we mentioned that catalytic activity of the highest FSM-16 was exhibited by pretreatment at 673 K and deactivation was due to dehydroxylation of silanol groups. To examine whether silanol groups of FSM-16 participate in acidic property or not, we prepared calcined and rehydrated FSM-16. If only silanol groups were the active sites, rehydrated FSM-16 should exhibit the same activity as fresh catalyst. Table 5 summarizes results of α -pinene isomerization over variously treated FSM-16. Pretreatments were performed at 673 K in all cases. The catalyst noted simply as FSM-16 in Table 5 was the fresh catalyst, which was the same catalyst as listed in Table 2. FSM-16 calcined at 1173 K (FSM-1173) was less active than the fresh catalyst, but

TABLE 5: Change of the Activity of α -Pinene Isomerization over FSM-16^a

catalyst	pretreatment temp/K	conversion (%)	selectivity ^b (%)							
			1	2	3	4	5	6	7	8
FSM-16	673	44.6	tr	40	4	43	9	2	2	tr
FSM-1173	673	8.8	1	36	4	46	8	2	2	1
FSM-1173H	673	48.1	tr	42	4	43	7	2	1	1
FSM-1373H	673	<0.1								

^a α -Pinene: 2 mL. Catalyst: 50 mg. Reaction temperature: 303 K. Reaction time: 0.5 h. ^b 1, β -pinene; 2, camphene; 3, α -fenchene; 4, limonene; 5, terpinolene; 6, α -terpinene; 7, γ -terpinene; 8, others.

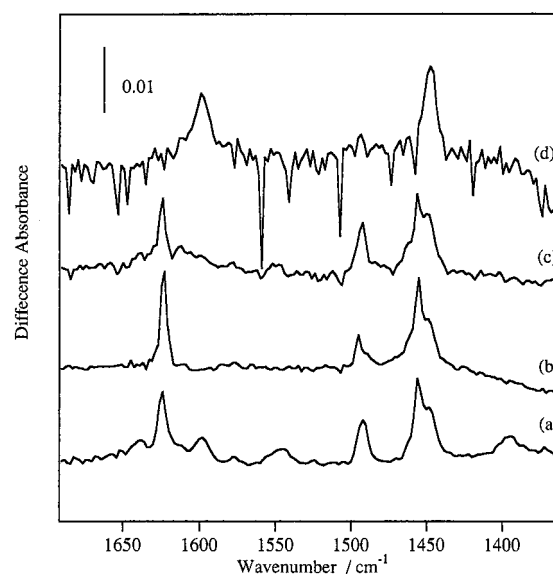


Figure 8. FTIR spectra of adsorbed pyridine at 423 K: fresh FSM-16 (21 mg) (a), FSM-1073pre (20 mg) (b), FSM-1173H (30 mg) (c), and FSM-1373H (80 mg) (d).

the activity was slightly higher than that pretreated at 1073 K. As expected, the activity of the less active catalyst was completely restored by hydration of the catalyst at 353 K followed by calcination at 773 K (FSM-1173H). The selectivity was not changed. These results indicate that hydration to restore silanol groups on FSM-16 regenerates acidic sites. The reason FSM-1173 was more active than FSM-16 pretreated at 1073 K was explained as follows. By moisture in atmospheric air, partial rehydration proceeded on FSM-1173 during the storage. Rehydrated FSM-16 having been calcined at 1373 K (FSM-1373H) did not catalyze isomerization of α -pinene, in contrast to the result of FSM-1173H. This indicates that FSM-1373H no longer had the same properties as fresh FSM-16. The reason for the difference of catalytic activity between FSM-1173H and FSM-1373H is considered as follows. The possible first reason may be that the active elements such as Al and Ti on FSM-16 were lost during various treatments. The first reason can be excluded because no change of elemental composition was found (Table 1). The second is the fundamental structural change of FSM-16. This is only sintering.

To investigate the difference of acidic properties more in detail, IR spectra of adsorbed pyridine were recorded. Figure 8 shows those of four typical variously treated FSM-16. The four catalysts are the fresh one, FSM-16 pretreated at 1073 K (FSM-1073pre), FSM-1173H, and FSM-1373H. Brønsted pyridine was observed on the fresh FSM-16, while not on FSM-1073pre. Although as many Lewis acid sites existed on the surface as on fresh FSM-16, FSM-1073pre was inactive for

but-1-ene and α -pinene isomerization. The band at around 1492 cm^{-1} was assigned to overlapping 19a bands of both Lewis and Brønsted pyridine. The intensity ratio of the band at 1492 cm^{-1} to a 19b band of Lewis pyridine at 1456 cm^{-1} was quite different from fresh FSM-16 and FSM-1073pre. The ratio of Lewis and Brønsted acid sites ($[L]/[B]$ ratio) can be calculated from the band area of adsorbed pyridine at 1455 and 1492 cm^{-1} .⁶³ The calculated $[L]/[B]$ ratio of fresh FSM-16 was 2.6, and that of FSM-1073pre was 5.6. This suggests that the fraction of Brønsted sites was decreased by pretreatment at 1073 K. The majority of acid sites were Lewis acid, however, Lewis acid sites are inactive for the catalysis of the isomerization of α -pinene and but-1-ene. The IR spectrum of adsorbed pyridine on FSM-1173H was quite similar to that on fresh FSM-16, and the $[L]/[B]$ ratio of FSM-1173H was 2.6. This is in good accordance with the results of the catalysis. In other words, the surface property of FSM-1173H was the same as that of fresh FSM-16. On the other hand, FSM-1373H was quite different. Only hydrogen-bonded pyridine was observed in the IR spectrum of adsorbed pyridine on FSM-1373H, and it was quite similar to that of SiO_2 gel (Figure 4). This strongly suggests that FSM-1373H was fundamentally different from that of fresh FSM-16 and FSM-1173H. From the results of catalytic activities and IR spectra, we conclude that the surface property of FSM-1373H is similar to that of ordinary silica gel rather than that of FSM-16.

To clarify the difference of each structure, we measured the XRD pattern of these samples. Figure 9 shows those of variously treated FSM-16 listed in Table 5. The XRD pattern of fresh FSM-16 exhibited four peaks and the primary d spacing was 38 \AA . This profile is identical with that reported previously.³⁰ All peaks observed on FSM-1173 were shifted to higher degree. This was due to shrinkage of the lattice, and the shrunk primary d spacing was 32 \AA . FSM-1173 and FSM-1173H still kept the structure of FSM-16, although the fourth peak disappeared. The result of XRD measurements shows that a series of rehydration procedures scarcely influenced the structure of FSM-1173. In the case of FSM-16 calcined at 1373 K, peaks below 10 degrees completely disappeared and no peaks were observed in all regions. This clearly shows that FSM-1373H became amorphous. From XRD results, we conclude that acidic properties appeared on only the crystal FSM-16. This result strongly suggests that the active site of FSM-16 was not due to impurity.

Over FAU type zeolites, Severino et al. reported that the change of the $[L]/[B]$ ratio around 1.0 caused an abrupt change of selectivity to camphene in α -pinene isomerization.⁶⁴ They concluded that the reaction rate catalyzed by Brønsted sites was higher than that by Lewis sites and that Lewis sites preferentially catalyzed to produce bicyclic products such as camphene. In the case of FSM-16, selectivity for camphene was independent of pretreatment temperature. Further, low-temperature-treated niobic acid, known to be a typical Brønsted acid, gave a high selectivity for camphene. The suggestion by Severino et al. was not applicable to our experiments. The majority of acid sites on FSM-16 were Lewis sites, but Lewis sites did not participate in the catalysis of both but-1-ene and α -pinene isomerization. Therefore, we concluded that Brønsted acid sites were active sites for both reactions and that the sites were weakly perturbed vicinal pairs of silanol groups (species II).

Survey of Catalyst Property. It was reported that reversible dehydroxylation of silanols occurred below 673 K and irreversible dehydroxylation of isolated silanols occurred above 923 K.⁵¹ On the other hand, silanol groups of FSM-1173 were

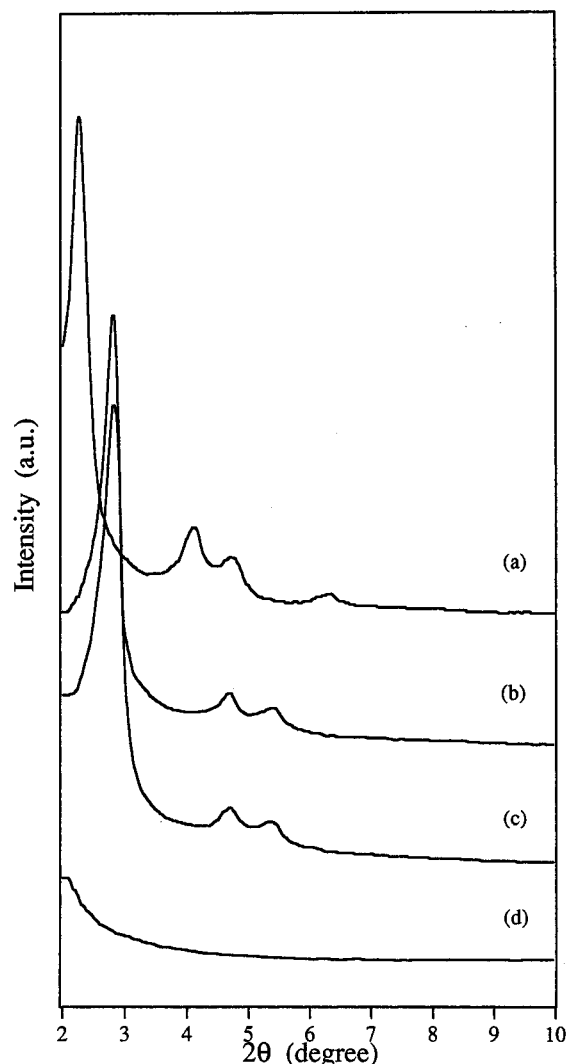


Figure 9. Cu K α XRD patterns of fresh FSM-16 (a), FSM-1173 (b), FSM-1173H (c), and FSM-1373 (d).

completely restored by rehydration procedures. This was supported by results of α -pinene isomerization, as shown in Table 5. The difference between our experiments and reported results was due to rehydration processes. The rehydration has been attempted at ambient temperature with 100% relative humidity,^{61,62} whereas FSM-16 was rehydrated in water at 353 K. To investigate the property of catalysts further, we measured the maximum of acid strength of catalysts by Hammett indicators. Table 6 summarizes maximum acid strength and BET specific surface area. Once SiO_2 gel (BET specific surface area was $650\text{ m}^2\text{ g}^{-1}$) was calcined at 1173 K, the surface area was reduced to $445\text{ m}^2\text{ g}^{-1}$. Even if calcined silica gel was rehydrated in water at 353 K, complete regeneration of silanol groups was impossible because of its sintering. In contrast, the surface area of FSM-1173 was maintained at $965\text{ m}^2\text{ g}^{-1}$. FSM-16 was stable at temperatures up to 1273 K and possessed high surface area even for a rehydrated sample calcined at 1173 K (Table 6). The rigid structure of FSM-16 made it possible to complete reversible dehydroxylation of isolated silanols.

FSM-16 pretreated at 673 and 1073 K exhibited medium acid strength of $H_0 = -3.0$. This value is almost the same as those for $\text{SiO}_2\text{-MgO}$ ^{65,66} and $\text{NiSO}_4 \cdot n\text{H}_2\text{O}$,⁶⁷ but much weaker than that of $\text{SiO}_2\text{-Al}_2\text{O}_3$, which is stronger than $H_0 = -8.2$.^{65,66} FSM-16, with Si/Al atomic ratios of both 735 and 320, showed the same value of maximum acid strength. The maximum acid

TABLE 6: Maximum Acid Strength and BET Specific Surface Area

catalyst	pretreatment temp/K	surface area/ m ² g ⁻¹	<i>H</i> ₀ max
FSM-16	473		-3.0 ^c
	673	1078	-3.0
	873	1045	
	1073	1026	-3.0
	1273	815	-5.6
FSM-16 ^a	673	965	-3.0
FSM-1173H	673	874	-3.0
FSM-1373H	673	37	-3.0 ^c
FSM-16 ^b	673	960	-3.0
SiO ₂	673	650	+4.8
	1073	490	+3.0
H ₂ Si ₂ O ₅	673	144	+3.0 ^c

^a Calcined in a dry air stream at 1173 K for 2 h. ^b Supplied by Toyota Central R & D Labs., Inc. (lot no. NG78-550). ^c Hammet indicator was faintly colored.

strengths of SiO₂ gel were much weaker than those for FSM-16. Werner et al. reported that crystalline silicates have much stronger acid sites than those of silica gel. For example, H₂-Si₂O₅ and H₂Si₁₄O₂₉·5H₂O exhibited a maximum acid strength of *H*₀ = +2.3 to +3.3 and -5 to -3, respectively.⁶⁸ They discussed that the high acidity resulted from regular and extended hydrogen-bonding systems including the surface water molecules. The maximum acid strength of synthesized H₂Si₂O₅ was the same as the reported value of *H*₀ = +3.0, although calcined H₂Si₂O₅ became amorphous. From elemental analysis, the Al concentration of H₂Si₂O₅ was estimated to be only 80 ppm (Table 1); however, its maximum acid strength of *H*₀ = +3.0 was higher than that of SiO₂ gel of +4.8. These results show that almost pure siliceous materials have the possibility to exhibit acidic properties. Thus, we conclude that but-1-ene and α-pinene isomerizations were catalyzed by Brønsted acid sites with an acidic strength of *H*₀ < +3.0. In the case of FSM-16, the selectivity of α-pinene isomerization and the maximum acid strength were independent of the pretreatment temperature. This result indicates that the change of catalytic activity of FSM-16 does not depend on the change of the acid strength but on the number of acid sites. IR and H₂O desorption experiments showed that active sites on FSM-16 were blocked by hydrogen-bonded adsorbed water when FSM-16 was pretreated at below 673 K. This was supported by the result that addition of water to pretreated FSM-16 drastically lowered catalytic activity. Although FSM-16 pretreated at 1273 K showed the maximum acid strength of *H*₀ = -5.6, the number of the strongest acid sites was quite small because no change of selectivity for α-pinene isomerization was observed and activities for α-pinene and but-1-ene isomerization were quite low. Although FSM-1373H was amorphous, it still possessed a small number of acid sites whose *H*₀ max was -3.0. As shown in Table 5, the activities of FSM-1373H and fresh FSM-16 were different from each other by over 400 times. On the other hand, the BET specific surface area of FSM-1373H was about 3% of the fresh one. The reduction of catalytic activity was far from that of the surface area. Therefore, the possibility that sintering was the main reason for deactivation is excluded. The structure of FSM-16 is indispensable to acidic property, although the mechanism of generation of acid sites is not clear. This is supported by the fact that FSM-16, having become amorphous, could not regenerate the acidic property by the rehydration process.

We suppose that the structure of FSM-16 is indispensable to acidic property, especially to its thin wall and regularly arrayed silanol groups.

Conclusion

FSM-16 catalyzes but-1-ene isomerization at 323 K and α-pinene isomerization at 303 K in the liquid phase. Catalytic activity of FSM-16 was dependent upon pretreatment temperatures and showed a maximum at 673 K. The activity of FSM-16 calcined at higher than 773 K was much reduced, but it could be restored by rehydration procedures as long as the samples maintained the crystal structure. The active sites were weakly perturbed silanol groups and a trace amount of Al of FSM-16 did not affect acidic property. Maximum acid strength was invariably *H*₀ = -3.0, independent of pretreatment temperatures. These properties are related to the regular structure of FSM-16.

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