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Highly Selective Methylamine Synthesis over Modified Mordenite Catalysts

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Methylamine syntheses from methanol and ammonia on various zeolite catalysts have been studied over a temperature range of 573–673 K at atmospheric pressure. The mordenite catalysts were treated with silicon tetrachloride in sodium form and then ion-exchanged to the acid form; such catalysts have been shown to suppress trimethylamine production almost completely and to generate enhanced yields of dimethylamine and/or monomethylamine. The formation of TMA has been extremely retarded because the pore openings of the catalyst are smaller than TMA molecules. The sorption data of methylamines and IR spectroscopy studies suggest that the more bulky base molecules, such as trimethylamine or pyridine, cannot penetrate into mordenite channels after treatment with silicon tetrachloride. The ^{29}Si- and ^{27}Al-MASNMR studies showed that silicon tetrachloride treatment caused less dealumination of zeolite framework for sodium mordenite than for H mordenite.

INTRODUCTION

Solid acids catalyze the sequential reactions of methanol and ammonia to give monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA); the following equations apply:

$$CH_3OH + NH_3 \rightleftarrows CH_3NH_2 + H_2O \qquad (1)$$

$$CH_3OH + CH_3NH_2 \rightleftarrows (CH_3)_2NH + H_2O \qquad (2)$$

$$CH_3OH + (CH_3)_2NH \rightleftarrows (CH_3)_3N + H_2O. \qquad (3)$$

These reactions generally proceed toward equilibrium, which favors TMA (*1*). At 99.8% conversion of methanol, the equilibrium composition is 15.1% for MMA, 22.8% for DMA, and 62.1% for TMA ($NH_3/CH_3OH = 1.9$) at 623 K (*2*). However, the industrial market demands lower alkylated methylamines, such as MMA and DMA. For the selective synthesis of MMA and DMA, various zeolite catalysts have been proposed to improve the selectivity of MMA and DMA (*1–4*). However, at higher conversions, selectivity for DMA was not high enough. Fukatsu and coworkers (*1*) reported that the partially alkali metal-exchanged mordenite showed a higher selectivity of MMA plus DMA: ca. 80% selectivity at 95% methanol conversion ($NH_3/CH_3OH = 1.9$, 673 K). They also found that suppression of the selectivity of TMA over the mordenite catalyst could be achieved by steam treatment at higher temperatures at the minor expense of slightly lower activity. Weigert proposed that Na mordenite catalysts would show lower selectivity of TMA (*3*). However, the catalytic activity over Na mordenite is lower than that of acid type mordenite. Schannon and co-workers found that the small-pore zeolites, H–RHO, H–ZK5, and chabazite, are not only significantly more active but also have selectivities much greater than those previously reported for these other zeolites (*5–9*). The selectivity of MMA plus DMA

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was ca. 89% at 90% methanol conversion (NH_3/CH_3OH = 1.0, 598 K) (*9*). We found that the mordenite catalyst which was treated with $SiCl_4$ in sodium form and then ion-exchanged to hydrogen form (acidic form) shows higher selectivity and activity for MMA and DMA. The selectivity of MMA plus DMA was ca. 99% at 90% methanol conversion (NH_3/CH_3OH = 1.0, 653 K). In addition, the reaction rate (rate of methanol consumption) of this catalyst was almost equivalent to that of H mordenite.

EXPERIMENTAL

Preparation of catalysts. Zeolites (JRC-Z) and silica–alumina (JRC-SAL-2, Si/Al = 5.3) samples were supplied by the Catalysis Society of Japan (JRC: Japan Reference Catalysts). Three different types of zeolites were studied: H–Y (JRC-Z-HY5.6, Si/Al = 2.8), H–M (H mordenite: JRC-HM10, Si/Al = 5; JRC-HM20, Si/Al = 10), and H–ZSM5 (JRC-Z5-25H, Si/Al = 12.5). Some Na–M samples (Na mordenite: JRC-M10, Si/Al = 5 and JRC-M20, Si/Al = 10) were treated with $SiCl_4$ at 973 K for 3 h, followed by washing with boiling distilled water and drying at 373 K, and were then calcined at 773 K (Na–SC–M). For the treatment with $SiCl_4$, granular type of zeolite samples (4 g) were packed in the quartz tubular reactor. Then 10 kPa of $SiCl_4$ vapor with N_2 carrier gas was introduced into the reactor. The flow rate of the mixture gas was 150 cm^3 min^{-1}. Acid-type mordenites, after treatment with $SiCl_4$ (H–SC–M), were prepared by ion exchange of the Na form (Na–SC–M) with an aqueous solution of NH_4NO_3; ion-exchanged samples were dried at 373 K for 24 h and then calcined in the furnace at a constant temperature increase rate (1 K min^{-1}) from 373 to 773 K and kept at 773 K for 5 h. For the reference, H–M (JRC-HM20, Si/Al = 10) was also treated with $SiCl_4$ (SC–H–M), followed by washing with boiling water, drying at 373 K, and calcining at 773 K.

Catalytic reactions. Methylamine (MA) synthesis from CH_3OH and NH_3 was carried out at 573 to 673 K by using a flowing reaction system under atmospheric pressure with a mixture of NH_3, CH_3OH, and N_2 in the ratio of 1/1/31. The flow rate of the mixture gas was 100 cm^3 min^{-1}. Prior to the reaction, the catalyst (50–500 mg) was calcined at 773 K under O_2 flow for 2 h. The reaction products were analyzed by a gas chromatograph (TCD) which was equipped with a 4.6-m column of PEG-400 (25%) + KOH (2.5%) on acid-washed Chromosorb W at 358 K (*3*). The activities and selectivities were calculated in carbon base from the chromatograms.

Adsorption measurements. Chemisorption measurements of base molecules, CH_3OH, and CH_3OCH_3 were performed under vacuum conditions. A McBain type of quartz spiral spring was hung down to the sample basket. The catalyst was evacuated at 773 K for 2 h. After evacuation, 0.7 kPa of base molecules (MMA, DMA, TMA, NH_3, and C_5H_5N) were admitted at 373 K for several hours until adsorption had equilibriated, then evacuated at 373 K for 12 h. The amount of chemisorption of base molecules was determined by the change in length of the spring, which was equipped with a displacement meter (Type 2U, Shinko Electronic). Adsorptions of CH_3OH and of CH_3OCH_3 were also studied. In such experiments, the adsorption and desorption temperature was 300 K.

IR spectroscopy. A vacuum-tight IR cell with KBr windows was designed to fit an infrared spectrometer (270-30, Hitachi) and to be attached to a vacuum system (10^{-4} Pa). The calcined aliquots of the zeolites were pressed into platelets having a thickness of about 10 mg cm^{-2}. These were mounted on a Pyrex rack which positioned them between the KBr windows (optical path length: 5 mm) of a vacuum-tight spectroscopic cell. The cell was arranged that the zeolite wafer could be lowered into slots between the optical windows, and withdrawn upward by the action of a magnet into the heated portion for the pretreatment and adsorption of NH_3 and C_5H_5N. After evacuation at 773 K for 1h, the zeolite sample was cooled to 423 K before adsorption of the base molecules to be studied. Finally, the zeolite sample and its rack assembly were moved back between the KBr windows for spectroscopic investigation. IR spectra were obtained at room temperature.

XPS and MASNMR spectroscopy and XRF analysis. For the determination of surface Si/Al atomic ratio, x-ray photoelectron spectroscopy (XPS) measurements of the zeolite samples before or after treatment with $SiCl_4$ on an XPS spectrometer (SSX-100, Surface Science Laboratory) with a monochromatic Al*Kα* radiation (1486.6 eV). For the determination of the framework Si/Al atomic ratio of the zeolite sample, the MASNMR was employed for zeolite samples after they had been hydrated in a desiccator with a saturated aqueous solution of NH_4Cl at room temperature for 24 h in order to minimize the line width of ^{27}Al-MASNMR spectra. The MASNMR spectra were obtained at 53.7 MHz for ^{29}Si and 70.4 MHz for ^{27}Al on a Fourier transform pulsed NMR spectrometer (JNM-GX270, JEOL) which was equipped with a CP/MAS unit (NM-GSH27MU JEOL). All NMR spectra combined with magic angle spinning (MAS) spectra were measured with proton decoupling during data acquisition. Cross polarization (CP) was not employed, since the protons of zeolite samples do not attach directly to ^{29}Si and ^{27}Al nuclei. Then 8 K data points were collected with 700 to 1300 scans accumulated per spectrum. The chemical shifts are calibrated by TMS and $Al(H_2O)_6^{3+}$ for ^{29}Si- and ^{27}Al-MASNMR measurements, respectively. In order to determine the bulk Si/Al atomic ratio of zeolite, X-ray fluorescence analyses (SXF-1200, Shimadu: Rh target, 40 kV, 70 mA) have been employed. For the measurement, the sample was pressed into platelets.

RESULTS AND DISCUSSION

Catalytic activity and selectivity for methylamine synthesis. Acid types of zeolite catalysts tested in this work include faujasite (H–Y), mordenite (H–M, H–SC–M, and Na–SC–M), and ZSM5 (H–ZSM5). Amorphous SiO_2–Al_2O_3 (JRC-SAL-2) was also tested for this reaction. The catalytic activities and selectivities over the various zeolite catalysts are summarized in Table 1. The selectivities of each MA and DME were obtained above 90% conversion of methanol. On H–Y and SiO_2–Al_2O_3 catalysts, the initial rate of reaction on the basis of methanol consumption is higher than on the other zeolite catalysts, but the selectivities of TMA and DME are rather high; the selectivity is about 45–53% for TMA and 11–27% for DME. The higher catalytic activity may be due to a higher concentration of aluminum sites (lower Si/Al ratios), which gives higher numbers of acidic sties. Therefore, the reaction rate on H–ZSM5 is lower than that of H–Y and H–M. In addition, the acid type of zeolite catalysts shows higher activity for the reaction than the Na form of zeolites. On Na–SC–M (Na mordenite treated with $SiCl_4$), the activity is about one or two orders of magnitude lower than on H zeolites. However, the selectivities for TMA and DME are extremely retarded in comparison with the catalysts without treatment with $SiCl_4$. When Na–SC–M is ion-exchanged to a protonic form (H–SC–M), the catalytic activity is enhanced to a value similar to that of H–M, and selectivities of MMA and DMA are also enhanced. The formation of TMA and DME on H–SC–M is almost negligible up to 100% of methanol conversion. In addition, no deactivation has been observed over the whole range of reaction conditions. Even though the treatments with $SiCl_4$ over Na mordenite are effective for the improvements of the selectivities of MMA and DMA, SC–H–M (H–M treated with $SiCl_4$) shows lower selectivities for MMA and DMA. This may be due to the dealumination from the framework of H–M, which will be described in the next section. For industrial applications, a higher partial pressure of NH_3 has been required in order to minimize the selectivity of TMA (*2*) and to achieve a higher conversion level of methanol. The

TABLE 1

Catalytic Activities and Selectivities for Methylamine Synthesis on Various Acid-type Zeolites

Catalyst	Si/Al[a]	Reaction rate[b] 10^{-2} mol g^{-1} h^{-1}	Selectivity[c]/%			
			DME	MMA	DMA	TMA
H-Y	2.8	15.6	10.7	13.8	22.8	52.7
SiO_2-Al_2O_3	5.3	16.5	27.1	17.8	10.6	44.5
H-M	9.7	4.45	20.6	21.1	20.4	37.8
H-ZSM5	12.5	3.00	18.7	8.9	17.5	54.9
Na-SC-M	10.3	0.121	3.8	38.4	56.8	1.0
H-SC-M	10.5	3.88	0.7	33.1	64.8	1.4
SC-H-M	21.1	8.62	48.4	9.4	12.5	29.8

[a] Si/Al atomic ratio was determined by x-ray fluorescence analysis.

[b] Initial rate of methanol consumption at 653 K (NH_3/CH_3OH = 1.0, P_{MeOH} = 2.8 kPa).

[c] Selectivity was obtained at above 90% conversion of methanol.

reaction rate was increased with increasing partial pressure of NH_3. In Table 1, however, the catalytic activities were almost identical on either H-SC-M or H-M, and the selectivities of methylamines are different. From the separate experiments, we studied the catalytic activities and selectivities at different partial pressure of NH_3 (NH_3/CH_3OH = 0.25-2.0). On H-SC-M, the major product was DMA regardless of NH_3 pressure, and the selectivities of DME and TMA were much smaller than those on H-M. On the other hand, over H-M catalyst, DME and TMA were the major products at lower partial pressures of NH_3, and the selectivity of TMA was still high even at higher partial pressures of NH_3.

Even though the reaction rate was lower on Na-SC-M than on H zeolite catalysts, the time course of methylamine synthesis has been studied at 675 K. Only this experiment used the conventional closed recirculating system (230 cm^3). A hundred milligrams of catalyst was packed in the Pyrex tubular reactor. Prior to the reaction, the catalyst was treated with 40 kPa of O_2 and evacuated at 723 K. Then 10.6 kPa of CH_3OH and 21.3 kPa of NH_3 were introduced to the reaction system. The reaction products were analyzed by an on-line gas chromatograph which was the same system as the flowing reaction system. As shown in Fig. 1, the initial product of reaction was MMA, and formation of DMA followed. However, formations of TMA and of DME are almost negligible over the whole range of reaction. When the catalyst was changed from Na-SC-M to H-SC-M, the reaction rate on H-SC-M was enhanced about one order of magnitude, and the selectivities of methylamines were quite the same as the results in Fig. 1. After complete consump-

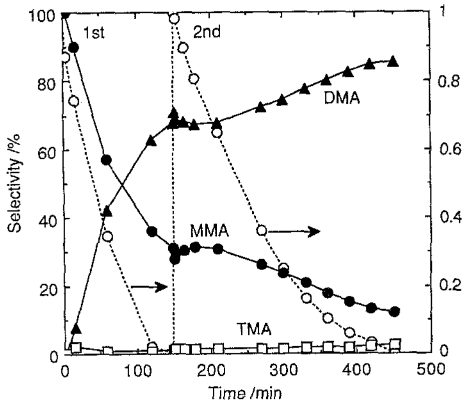

FIG. 1. Time courses of methylamine synthesis on Na-SC-M at 675 K: P_{CH_3OH} = 10.6 kPa, P_{NH_3} = 21.3 kPa, Reaction temperature = 675 K, $1 - x$ = the remaining mole fraction of methanol in the reaction system.

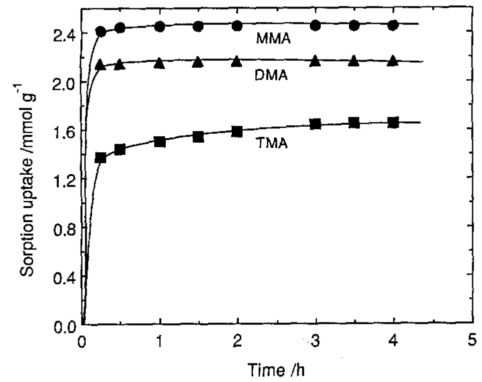

FIG. 2. Sorption profiles of methylamines over H–M (Si/Al = 9.7) as a function of exposure time at 373 K: P_{MA} = 1.3 kPa.

tion of CH_3OH (after ca. 2.5 h), the same amount of CH_3OH was readmitted to the reaction system, and then the reaction was followed. The rate of CH_3OH consumption became slower than the first reaction, since the reaction rates obeyed good first-order kinetics with respect to the partial pressure of NH_3. It is quite interesting that during the second reaction, formation of TMA is also negligible even after complete consumption of CH_3OH. Finally, the selectivity of DMA reached about 90%.

Adsorption of base molecules on catalysts. Adsorption uptake of methylamines, pyridine, CH_3OH, and CH_3OCH_3 (DME) on the catalysts has been measured by using the vacuum balance. After evacuation at 773 K, the sample was exposed to 1.3 kPa of base molecules at 373 K, or to 1.3 kPa of CH_3OH or DME at 300 K. Sorption uptake was determined by the weight increase of the sample as a function of exposure time. Figure 2 shows the sorption uptake of methylamines on H–M. MMA and DMA are quickly saturated, while TMA needs a longer time to reach equilibrium on H–M. On the other hand, in Fig. 3, adsorption of TMA on H–SC–M is completely retarded, only MMA is quickly saturated, and DMA requires a longer time to be saturated. Sorption profiles on H–SC–M are totally different from the profiles on H–M, since the results suggest that TMA cannot penetrate into the pore channels of H–SC–M, and the size of the pore openings of H–SC–M can be estimated to be similar to the kinetic diameter of DMA (0.49 nm).

After becoming equilibriated with 1.3 kPa of base molecules, CH_3OH, or DME, the sample was evacuated at the same temperature of adsorption for 12 h. Chemisorption uptake was determined by the weight increase of the sample from the weight prior to the adsorption. Table 2 summarizes chemisorption uptake of base molecules, CH_3OH, and DME on various catalysts. For the adsorption of base molecules, the acidic type of catalysts generally show higher chemisorption uptake than on sodium–zeolite (Na–M, Na–SC–M). After treatment of Na–M by $SiCl_4$ (Na–SC–M) and the ion exchange to hydrogen type (H–SC–M), the uptake of TMA or pyridine is extremely retarded. The kinetic diameter of pyridine (0.55–0.60 nm) is quite similar to that of TMA (0.61 nm) (*1*). The results suggest that the diffusion of bulkier base molecules such as TMA into mordenite channels can be especially limited over Na–SC–M and H–SC–M. These results would correlate the higher selectivities of MMA and DMA on these catalysts. When H–M is treated with $SiCl_4$ (SC–H–M), the adsorption uptake of TMA and pyridine are not lower than

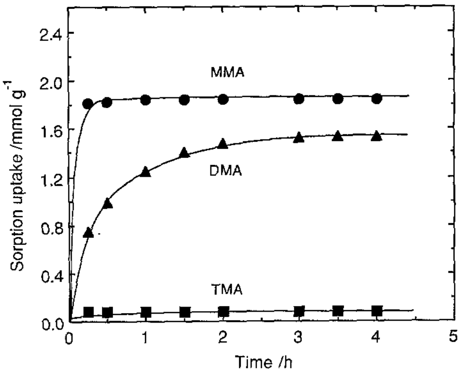

FIG. 3. Sorption profiles of methylamines over H–SC–M (Si/Al = 10.5) as a function of exposure time at 373 K: P_{MA} = 1.3 kPa.

TABLE 2

Adsorption of Base Molecules, Methanol, and Dimethylether over Mordenites

Catalyst	Chemisorption uptake/mmol g^{-1}						
	MMA[a]	DMA[a]	TMA[a]	Pyridine[a]	NH_3[a]	CH_3OH[b]	DME[b]
SiO_2–Al_2O_3	1.20	0.75	0.54	0.49	1.03	1.52	0.40
Na–M[c]	0.47	0.50	0.50	0.82	0.50	1.12	0.81
H–M[d]	1.47	1.37	1.19	1.05	1.83	1.51	1.18
Na–SC–M[d]	0.54	0.50	0.05	0.04	0.68	1.25	0.25
H–SC–M[d]	1.03	0.91	0.05	0.04	1.30	1.36	0.54
SC–H–M[d]	0.42	0.35	0.12	0.20	0.68	0.66	0.24

[a] Sample was exposed to 1.3 kPa of base molecules at 373 K and then evacuated at 373 K.

[b] Sample was exposed to 1.3 kPa of MeOH or DME at 300 K and then evacuated at 300 K.

[c] Si/Ai atomic ratio = 9.8.

[d] All Si/Al atomic ratios are the same as in Table 1.

Na–SC–M and H–SC–M. This is may be due to some destruction of the zeolite framework by the dealumination with $SiCl_4$.

On the catalysts without treatment by $SiCl_4$, the selectivity of DME for methylamine syntheses (see Table 1) shows a rather higher value than that on Na–SC–M and H–SC–M. In addition, the selectivity of DME on SC–H–M is much higher than on other catalysts. The formation of DME on the catalysts during the reaction may be generated on weaker acidic sites, which are located on the outer surfaces of zeolites or on the pore surfaces inside the zeolite channels. The sorption uptakes of DME at 300 K on various solid acids as a function of exposure time are shown in Fig. 4. Only on H–SC–M does adsorption of DME require a longer time to be saturated by the treatments with $SiCl_4$ due to the smaller pore openings. This result, together with the results of IR spectroscopy, can explain the lower selectivity of TMA and DME on H–SC–M.

Very recently, Corbin and co-workers reported chemical modification of surfaces for improved selectivity to dimethylamine in synthesis from methanol and ammonia (*10*). The relative contributions of external and intracrystalline acidic sites of small pore H–RHO zeolite for the reaction have been studied. The H–RHO zeolites typically contain chabazite and pollucite impurities. Nonselective surface reactions which produce predominantly TMA can be eliminated by covering the external acidic sites with trimethylphosphite. In this study, similar behavior of the effect of surface treatments by $SiCl_4$ over mordenites has been observed.

For acidic types of mordenites, either zeolite pore size or the internal and external acidic sites are significantly affected by the treatment with $SiCl_4$. The OH stretching vi-

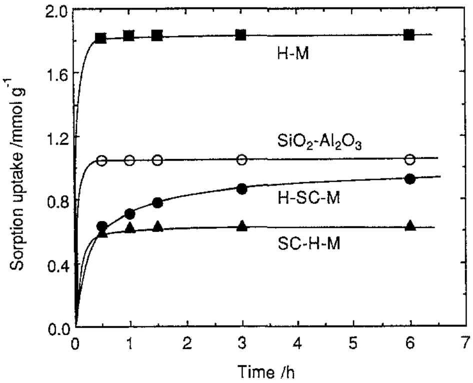

FIG. 4. Sorption profiles of dimethylether (DME, P_{DME} = 1.3 kPa) over several solid acids as a function of exposure time at 300 K: H–M (Si/Al = 9.7), SiO_2–Al_2O_3 (Si/Al = 5.3), H–SC–M (Si/Al = 10.5), SC–H–M (Si/Al = 21.1).

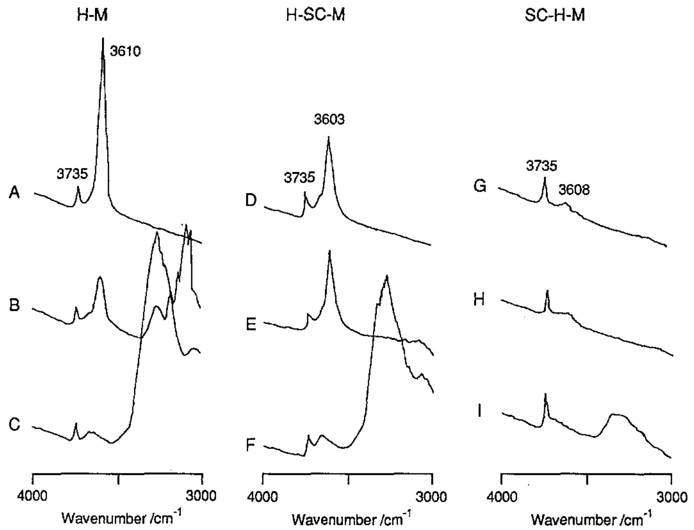

FIG. 5. IR spectra of OH stretching region of H–M (Si/Al = 9.7), H–SC–M (Si/Al = 10.5), and SC–H–M (Si/Al = 21.2): (A, D, G); after evacuation at 773 K, (B, E, H); pyridine adsorbed and evacuated at 473 K, (C, F, I); NH_3 adsorbed and evacuated at room temperature.

brations of acid type mordenites after evacuation at 773 K are shown in Fig. 5. Two types of OH groups are observed at wavenumbers from 3800 to 3500 cm^{-1}. Terminal Si–OH groups at the outer surface of zeolite (*11, 12*) give a band at 3735 cm^{-1}. Those terminal Si–OH groups showed very weak chemical interactions between pyridine or NH_3. The acidic OH bands whose intensities reduced or disappeared after adsorption of base molecules give bands of 3610 cm^{-1}. At the expense of those acidic OH bands of H–M (Fig. 5A), NH stretching bands built up at 3500 to 3000 cm^{-1} region. After adsorption of pyridine on H–M, about 25% of the acidic OH band at 3610 cm^{-1} still remained even after adsorption at room temperature (Fig. 5B), When NH_3 is introduced to H–M, the acidic OH band almost vanished (Fig. 5C). We conclude that about 25% of acidic OH groups in mordenite are located in smaller channels, which cannot be accessed by bulkier base molecules (pyridine), and the rest are in main channels or on outer surfaces. However, the acidic OH band in H–SC–M (Fig. 5E) does not interact with pyridine, but does interact with NH_3 (Fig. 5F). The results can be explained as due to the lower selectivities of TMA and DME on H–SC–M. The adsorption and IR results suggest that the more bulky base molecules, such as pyridine or TMA, cannot penetrate into or diffuse out of the mordenite channels after treatment with $SiCl_4$. The results from IR experiments are in good agreement with the results of adsorption measurements. In addition, these results suggest that pyridine cannot absorb on the outer surfaces of H–SC–M. On the other hand, the acidic OH band of SC–H–M does not exist in the OH stretching region (Fig. 5G). This may be due to the dealumination from the zeolite framework by the treatment with $SiCl_4$ at higher temperatures. The protonic sites in the mordenite channels may act as catalytic sites for dealumination. In addition, both pyridine and NH_3 interact slightly or not at all with SC–H–M.

Al sites of mordenite before or after treatment with $SiCl_4$. In order to elucidate higher values of activity and selectivity of methylamine synthesis from CH_3OH and NH_3 over mordenite catalysts, which are treated with $SiCl_4$ in sodium form and then ion ex-

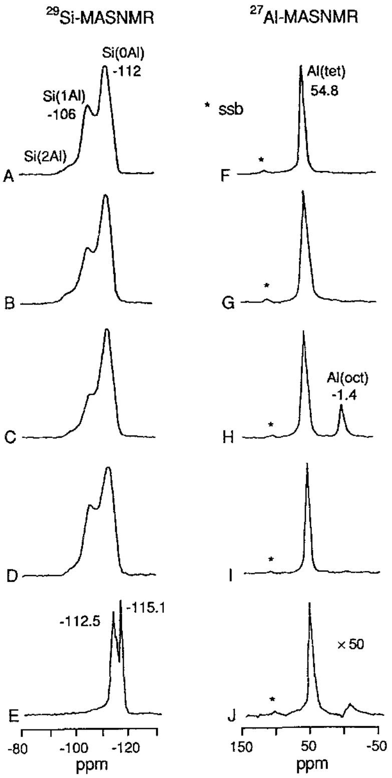

FIG. 6. ^{29}Si- and ^{27}Al-MASNMR spectra of mordenites before or after treatments with $SiCl_4$: (A, F) Na–M (Si/Al = 9.0); (B, G) Na–SC–M (Si/Al = 9.1); (C, H) H–SC–M (Si/Al = 11.4); (D, I) H–M (Si/Al = 9.3); (E, J) SC–H–M (Si/Al = 58.0). Si/Al atomic ratios were determined by ^{29}Si-MASNMR.

changed to acidic form (H–SC–M), high-resolution solid state magic angle spinning nmr (MASNMR) for mordenite samples has been studied. The results are shown in Fig. 6. In framework aluminosilicates, there are five possibilities, described by the formula Si(nAl), where n = 0, 1, 2, 3, or 4. These five basic units of Si(nAl) express the fact that each silicon atom is linked, via oxygens, to n aluminium neighbors (*13*). The ^{29}Si-MAZSNMR spectra of Na–M, Na–SC–M, H–SC–M, H–M (Fig. 6A–6D) show three different resonance peaks, which represent three kinds of Si tetrahedra attached to different numbers of adjacent Al tetrahedra: Si(2Al), Si(1Al), and Si(0Al). The distribution of Si(nAl) before treatment with $SiCl_4$ (Fig. 6A) is similar to that after treatment with $SiCl_4$ (Fig. 6B). However, the spectrum of SC–H–M (H–M was treated with $SiCl_4$ at 973 K) in Fig. 6E shows only Si(0Al). Such a result suggests that almost all aluminun sites in the framework are removed by $SiCl_4$. The spectrum is composed of at least three different resonance lines at −112.5 to −111.1 ppm from TMS. In this case, there are three different distortions among Si(0Al) tetrahedra in the framework. The ^{27}Al-MASNMR spectra of Na–M and of Na–SC–M in Fig. 6F, 6G give one sharp resonance peak at 59 ppm from $Al(H_2O)_6^{3+}$, which is assigned to tetrahedral framework sites occupied by the aluminum. ^{27}Al-MASNMR also shows directly that six-coordinated aluminum (Al-octahedra) builds up at the expense of the four-coordinated aluminum in the framework at −1.4 ppm, when the Na–SC–M sample is ion exchanged to protonic form (H–SC–M), which is shown in Fig. 6H. If we can minimize the formation of six-coordinated aluminum sites during the ion exchange procedures, we may be able to obtain a more highly active and more selective catalyst for methylamine synthesis. Even if ^{29}Si-MASNMR spectra of SC–H–M show only Si(0Al) (Fig. 6E), very small numbers of aluminum sites are observed in ^{27}Al-MASNMR spectrum (Fig. 6J).

Si/Al ratios of mordenite samples before or after treatment with $SiCl_4$ are summarized in Table 3. Si/Al atomic ratios were determined by x-ray fluorescence analysis (bulk composition of mordenite), by ^{29}Si-MASNMR (framework composition of mordenite), and by x-ray photoelectron spectroscopy (surface composition of mordenite). In Na–M, Si/Al ratios in bulk, framework, and surface show almost similar numbers that represent very uniform distributions in parent mordenite samples. When Na–M was treated with $SiCl_4$ at 973 K (Na–SC–M), only the values of the surface are enhanced due to the deposition of silicious materials on the surfaces. However, no detectable dealumination from the mor-

TABLE 3

Si/Al Ratios of Mordenites before and after Treatment with $SiCl_4$

	Si/Al atomic ratio		
	Bulk[a] $(Si/Al)_{xrf}$	Framework[b] $(Si/Al)_{nmr}$	Surface[c] $(Si/Al)_{xps}$
Na–M	10.0	9.0	10.8
Na–SC–M	10.3	9.1	15.1
H–SC–M	10.5	11.4	13.8
H–M	9.7	9.3	10.5
SC–H–M	21.1	58.0	∞

[a] Values were determined by x-ray fluorescesnce analysis.

[b] Values were determined by ^{29}Si-MASNMR.

[c] Values were determined by x-ray photoelectron spectroscopy.

denite framework has been observed. Such results suggest that only very small amounts of SiO_2 are deposited on the external surfaces of Na–M. In addition, when Na–SC–M was ion-exchanged to protonic form, some dealumination occurred, and the values of Si/Al in surface were also higher than the values in bulk or framework. On the other hand, when H–M was treated with $SiCl_4$ at 973 K, serious dealumination occurred. We conclude that protonic sites of H–M may act as catalytic sites for dealumination from the framework. SiO_2 coatings on the external surfaces of mordenites in sodium form and then ion-exchanged to acidic form are very effective in increasing DMA and MMA and in decreasing TMA and DME selectivities in synthesis from methanol and ammonia.

CONCLUSIONS

Methylamine syntheses from methanol and ammonia on various zeolite catalysts have been studied. The mordenite catalyst (H–SC–M), which was pretreated with $SiCl_4$ at 973 K in Na form and then ion-exchanged to protonic form by aqueous solution of NH_4NO_3, showed higher catalytic activities and higher selectivities of MMA and DMA. Over this catalyst, dealumination in the framework does not occur significantly over Na–M after treatment with $SiCl_4$, but does occur slightly during ion-exchange procedures. The formation of TMA over H–SC–M has been extremely retarded because the pore openings of the catalyst are smaller than TMA molecules. In addition, no deactivation of the catalyst has been observed over the whole range of reaction conditions.

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