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Amination of 2-Methylpropene over Proton-Exchanged ZSM-5 Zeolite Catalysts

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The reaction between 2-methylpropene and ammonia over various zeolite catalysts having a wide range of silica/alumina ratios from 5.6 to 1340, and over solid acid catalysts ($Cs_xH_{3-x}PW_{12}O_{40}$ (x = 0.15, 0.5), SiO_2–Al_2O_3, and SiO_2–TiO_2) and the solid base MgO was investigated. The significant decrease of activity following substitution of Na^+ for H^+ in H–MFI-40 or by preadsorption of diisopropylamine showed that amination is catalyzed by the acid sites. A similar change in the catalytic activity of H–MFI-40 with the number of Brønsted acid sites at elevated temperatures, as well as the appearance of activities of $Cs_xH_{3-x}PW_{12}O_{40}$ (x = 2.5, 2.85), which has only Brønsted acid sites, indicated amination on the Brønsted acid site. The dependence of conversion into *t*-butylamine, the number of Brønsted acid sites, and the turnover frequencies on the SiO_2/Al_2O_3 ratio suggested that the number and strength of the Brønsted acid sites are the factors controlling the title reaction. Due to the above two factors having the proper values, proton-exchanged ZSM-5 zeolite with a silica/alumina ratio of 81 was the most active for amination among the catalysts tested. © 1994 Academic Press, Inc.

INTRODUCTION

Zeolites can catalyze a wide variety of reactions because of their acidic properties and microporous structures (1). We also reported that hydration (Eq. [1]) (2–4) and ketonization (5–7) of lower alkenes were efficiently catalyzed by proton-exchanged zeolites:

$$R\text{–CH}{=}\text{CH}_2 + \text{H}_2\text{O} \rightarrow R\text{–CH(OH)–CH}_3 \qquad [1]$$

$$R\text{–CH(OH)–CH}_3 + \text{NH}_3 \rightarrow R\text{–CH(NH}_2\text{)–CH}_3 + \text{H}_2\text{O} \qquad [2]$$

$$R\text{–CH}{=}\text{CH}_2 + \text{NH}_3 \rightarrow R\text{–CH(NH}_2\text{)–CH}_3. \qquad [3]$$

Aliphatic amines have been formed by the reaction between the corresponding alcohols and ammonia (Eq. [2]) (8, 9). Since the alcohols are usually obtained through direct or indirect hydration of the alkene with the same carbon number (Eq. [1]), it would be more desirable to synthesize the amine by a direct reaction between the alkene and ammonia (Eq. [3]) (10). Direct amination of ethene to ethylamine has been achieved using alkali metal catalysts in homogeneous systems (11–13). However, these systems provide low yields of higher alkylamines.

Deeba *et al.* also reported that direct amination of ethene or higher alkenes is catalyzed by proton-exchanged Y-type, mordenite, and erionite zeolites at high temperatures and pressures in heterogeneous systems (14–16). The coexistence of water vapor in the ethene-ammonia system increased the catalytic activities of these zeolites (17). Recently, we preliminarily reported that direct amination of 2-methylpropene was most efficiently catalyzed by proton-exchanged ZSM-5 zeolite with a silica/alumina ratio of 50 among various oxide catalysts (18).

In these previous studies, however, little was known of the factors controlling direct amination of 2-methylpropene except for the acidity. Even for the acidity, it is still unclear whether Brønsted or Lewis acid sites are active centers. In the present work, therefore, amination of 2-methylpropene was carried out over zeolite catalysts having a wide range of silica/alumina ratios from 5.6 to 1340, and over solid acid catalysts and the solid base MgO catalyst. We elucidated the primary factors controlling the activity for amination and explained the reason for the high catalytic activity of ZSM-5 zeolite catalysts for amination of 2-methylpropene.

EXPERIMENTAL

Catalysts and reagents. Parent zeolites, ZSM-5 (denoted as MFI) with silica/alumina ratios of 23, 40, and 50, ferrierite (FER), L-type (LTL), offretite/erionite (OFF/ERI), mordenite (MOR), and Y-type (FAU) zeolites were supplied by Tosoh Corporation. ZSM-5 zeolites with silica/alumina ratios of 93 and 1340 were supplied by the Catalysis Society of Japan. The other ZSM-5 zeolites were prepared by hydrothermal crystallization of alkaline reaction mixtures by a method similar to that described in

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TABLE 1

Chemical Compositions and Textural Properties of the Zeolite Catalysts Used

No.	Catalyst	Chemical composition[a]	SiO_2/Al_2O_3 ratio[a]	Surface area ($m^2 \cdot g^{-1}$)	Pore volume $/cm^3 \cdot g^{-1}$	Acidity ($mmol \cdot g^{-1}$) Total[b]	Acidity ($mmol \cdot g^{-1}$) B/L[c]
1	H–MFI-1340	$H_{0.1}Al_{0.1}Si_{95.9}O_{192} \cdot 6.2H_2O$	1340			Trace	
2	H–MFI-129	$H_{1.5}Al_{1.5}Si_{94.5}O_{192} \cdot nH_2O$	129	339	0.190		
3	H–MFI-113	$H_{1.7}Al_{1.7}Si_{94.3}O_{192} \cdot nH_2O$	113	384	0.216		
4	H–MFI-93	$H_{2.0}Al_{2.0}Si_{94.0}O_{192} \cdot 16H_2O$	92.5	372		0.11	2.3
5	H–MFI-81	$H_{2.3}Al_{2.3}Si_{93.7}O_{192} \cdot nH_2O$	81.0	349	0.202	0.12	2.7
6	H–MFI-50	$H_{3.7}Al_{3.7}Si_{92.3}O_{192} \cdot 16H_2O$	49.8 (51.2)[d]	430	0.216	0.22	
7	H–MFI-40	$H_{4.5}Al_{4.5}Si_{91.5}O_{192} \cdot 16H_2O$	40.4 (40.7)	356	0.136	0.35	2.0
8	H–MFI-23	$H_{7.5}Na_{0.1}Al_{7.6}Si_{88.4}O_{192} \cdot 16H_2O$	23.3 (25.0)	360		0.28	2.1
9	Na–MFI-23	$Na_{7.6}Al_{7.6}Si_{88.4}O_{192} \cdot 16H_2O$	23.3 (25.0)	368	0.269	0	
10	H–MOR-19	$H_{4.6}Al_{4.6}Si_{43.4}O_{96} \cdot 24H_2O$	18.9 (19.0)			1.23	3.1
11	H–MOR-15	$H_{5.5}Na_{0.1}Al_{5.6}Si_{42.4}O_{96} \cdot 24H_2O$	15.0 (15.6)	519	0.254	1.20	4.0
12	Na–MOR-15	$Na_{5.6}Al_{5.6}Si_{42.4}O_{96} \cdot 24H_2O$	15.0			0	
13	H–FAU-40	$H_{23.8}Na_{0.2}Al_{24.0}Si_{168.0}O_{384} \cdot 240H_2O$	14.0 (40.0)				
14	H–FAU-12	$H_{48.1}Na_{0.5}Al_{48.6}Si_{143.4}O_{384} \cdot 240H_2O$	5.9 (12.0)				
15	H–FAU-6	$H_{36.4}Na_{14.1}Al_{50.5}Si_{141.5}O_{384} \cdot 240H_2O$	5.6	650		0.57	2.5
16	Na–FAU-6	$Na_{50.5}Al_{50.5}Si_{141.5}O_{384} \cdot 240H_2O$	5.6			0	
17	H–FER-17	$H_{3.6}K_{0.2}Al_{3.8}Si_{32.2}O_{72} \cdot 18H_2O$	16.8	289	0.349	1.14	
18	H–OFF/ERI-8		7.7	417	0.542		
19	H–LTL-6	$H_{8.5}K_{0.5}Al_{9.0}Si_{27.0}O_{72} \cdot 22H_2O$	6.0 (6.6)	432	0.253		

[a] Determined by atomic absorption spectroscopy.

[b] Obtained from the profiles of temperature-programmed desorption of ammonia; see text. Cited in part from Ref. (2).

[c] The ratios of the amounts of Brønsted acid sites to those of Lewis acid sites were obtained by the IR spectroscopy of pyridine adsorbed.

[d] Obtained by ^{29}Si MAS NMR.

Mobil's patent (19). Ultrastable Y-type zeolites were prepared by steaming. MgO ($H_- \leq 18.4$ (20)) was obtained from the Catalysis Society of Japan. SiO_2–Al_2O_3 and SiO_2–TiO_2 were commercially obtained from Catalysts & Chemicals Ind. Co. and Fuji-Davison Chemicals, respectively. $Cs_xH_{3-x}PW_{12}O_{40}$ (x = 2.5, 2.85, 3.15) catalysts were prepared according to Ref. (21).

Each proton-exchanged zeolite was prepared by ion-exchange in NH_4NO_3 solution and calcination at 773–813 K for 2–4 h (2–4). The amounts of Al, Si, and Na or K in each zeolite were determined by atomic absorption spectroscopy after the zeolite samples were dissolved in a hydrogen fluoride solution, and silica/alumina ratios in the zeolite framework were determined by ^{29}Si MASNMR as described previously (6, 7). The catalysts were abbreviated as H–MFI-81 (cation–zeolite structure-silica/alumina ratio). The exchange level of protons in each zeolite was approximately 100%, except for H–FAU-6. The BET surface area and pore-size distribution were measured by means of N_2 adsorption using an Autosorb-1 (Yuasa Ionics. Co., Ltd.). The chemical compositions and the textural and acid properties of the zeolite and the other oxide catalysts are summarized in Tables 1 and 2, respectively.

The SiO_2/Al_2O_3 ratios obtained by atomic absorption spectroscopy agreed well with those obtained by ^{29}Si MASNMR in the case of H–MFI, H–MOR, and H–LTL zeolites (Table 1), showing that there is no extraframework aluminum ion on these zeolites and that little dealumination occurred during the preparation. Therefore, the latter discussion would not be affected by the extra-

TABLE 2

Textural Properties of the Other Oxide Catalysts

No.	Catalyst	Surface area ($m^2 \cdot g^{-1}$)	Acidity[a] ($mmol \cdot g^{-1}$) Brønsted	Acidity[a] ($mmol \cdot g^{-1}$) Lewis
20	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	140	0.03[b]	0[b]
21	$Cs_{2.85}H_{0.15}PW_{12}O_{40}$	160	0.01	0
22	$Cs_{3.15}PW_{12}O_{40}$	130	0	0
23	SiO_2–Al_2O_3 (SiO_2/Al_2O_3 = 4.2)	511	0.04	0.16
24	SiO_2–TiO_2 (SiO_2/TiO_2 = 9.7)	269		
25	Al_2O_3	170	0[c]	0.19[c]
26	MgO	17	0	0

[a] Measured by IR spectroscopy of pyridine adsorbed.

[b] Hibi, T., Takahashi, K., Okuhara, T., Misono, M., and Yoneda, Y., *Appl. Catal.* **24**, 69 (1986).

[c] Take, J., *Shokubai* **22**, 123 (1980).

framework aluminum ion. The SiO_2/Al_2O_3 ratios of two kinds of ultrastable Y-type zeolites (H–FAU) were 5.9 and 14 by atomic absorption spectroscopy and 12 and 40 by ^{29}Si MASNMR. Clearly, the difference is due to dealumination and therefore the latter values are used hereafter for the abbreviation of the zeolites.

The total amounts of acidic sites on zeolites were obtained from the profiles of temperature-programmed desorption (TPD) of ammonia (2). In the TPD spectra two desorption peaks of NH_3 (α and β) were observed and the desorption peak at higher temperature (β peak) was concluded to be related to the acidic sites (2, 4). Therefore, the amounts of β-NH_3 are shown in Table 1.

Powder X-ray diffraction patterns were recorded on a powder X-ray diffractometer (Materials Analysis and Characterization, MXP^3) by using Cu $K\alpha$ radiation.

$NaNO_3$ and NH_4NO_3 were analytical grade reagents and used without further purification. Diisopropylamine and pyridine were used after the dehydration with Molecular Sieve 5A and 3A, respectively.

Reaction. The reaction of 2-methylpropene with ammonia in the presence or absence of water vapor was carried out in a conventional flow reactor at 423–673 K at atmospheric pressure using 0.5–1.0 g catalysts. Before the experimental run the catalysts were treated in an N_2 stream (20 $cm^3 \cdot min^{-1}$) at 573–973 K for 1 h, except for $Cs_xH_{3-x}PW_{12}O_{40}$ (x = 2.5–3.15) samples, which were used without the treatment because of thermal instability. The standard treatment temperature in N_2 was 773 K unless otherwise stated. The flow rates of 2-methylpropene, ammonia, and water vapor were 1.7–10.0, 5.0–16.0, and 0–0.90 $cm^3 \cdot min^{-1}$, respectively. Total flow rate was 7.5–21.0 $cm^3 \cdot min^{-1}$.

The path between the outlet of the reactor and the inlet of the sampler was heated at ca. 353 K to suppress the adsorption of gases on the wall. The reactants and products were sampled by use of an on-line stainless-steel sampler kept at ca. 353 K and analyzed by FID gas chromatography (Shimadzu GC-8A) on Porapack-Q (for alkenes and ammonia), Amipack-141 (for amines, alcohols, and alkenes), PEG-1000 (for dimerization and oligomerization products), and Sebaconitrile (for isomerization products) columns. It was confirmed for H–MFI that the carbon and nitrogen balances were more than 99%.

Infrared spectra. All self-supporting disks of H–MFI-40 (7–20 mg, 2 cm in diameter) were prepared by pressing powder under a pressure of 300 $kg \cdot cm^{-2}$ for 30 min, and the IR spectra were recorded at 298 K with an IR-810 spectrometer (Japan Spectroscopic Co., Ltd.).

At first the IR technique was applied to find adsorbed species on the catalyst during the reaction. After the H–MFI-40 sample was treated in an N_2 stream at 773 K for 1 h or was used for amination, it was pressed into a disk. Then it was transferred into an *in situ* IR cell (309 cm^3) in an N_2 atmosphere and the IR spectra were measured without further treatment.

The adsorption of *t*-butylamine, the product, was also measured. After a disk of H–MFI-40 was evacuated in an *in situ* IR cell at 773 K for 1 h, it was exposed to *t*-butylamine vapor (ca. 5 mmHg) at 473 K for 2 h and evacuated at the same temperature for 1 h. Subsequently, the IR spectra were recorded at 298 K.

Second, the ratio of the number of Brønsted acid sites to that of Lewis acid sites on H–MFI-40 was studied by the pyridine adsorption method. After an H–MFI-40 disk was evacuated in an *in situ* IR cell at 423–973 K for 1 h, it was exposed to pyridine vapor (ca. 10 mmHg) at 423 K for 2 h and evacuated at the same temperature for 1 h. The IR spectra were recorded at 298 K. In a similar way, the acidic properties of H–MFI-93, –81, and –23, H–MOR-15 and -19, $Cs_{2.85}H_{0.15}PW_{12}O_{40}$, and SIO_2–Al_2O_3 were measured. The IR bands at 1545 and 1455 cm^{-1} assigned to the pyridinium ion and coordinatively bound pyridine, respectively, were used to determine the relative concentrations of Brønsted and Lewis acid sites. Due to the difficulty in measuring the weak IR absorption bands of pyridine adsorbed on high-silica zeolites, this method could only be applied to the zeolites with SiO_2/Al_2O_3 ratios of 93 or less.

RESULTS AND DISCUSSION

Reaction. The conversion into *t*-butylamine from 2-methylpropene and ammonia on H–MFI-40 at 473 K increased with time, and an approximately steady formation of *t*-butylamine was attained after 2 h. Increases of the conversions with time similar to those on H–MFI-40 were observed for the other catalysts. The selectivity to *t*-butylamine was more than 95% under the present conditions. Little oligomerization and isomerization products were observed, and the selectivity to each product was less than 1%. The carbon balance was more than 99%, confirming no formation of the other products and the high selectivity to amine. This is in good agreement with the report that the selectivity to *t*-butylamine was more than 99% on H–FAU and H–MOR zeolites, oligomerization of 2-methylpropene was not observed below 553 K at ammonia/2-methylpropene molar ratio of 2, and that at lower ratios (≤ 1) acid-catalyzed polymerization was observed (16).

The color of the zeolites and the other oxides after their use as catalysts was only slightly grayish, showing that little coke was formed. No deterioration of each zeolite catalyst was observed at 473 K even after 30 h of continuous service, and no change in XRD patterns between the fresh and used catalysts was observed. In addition, the difference in the BET surface area or pore volume be-

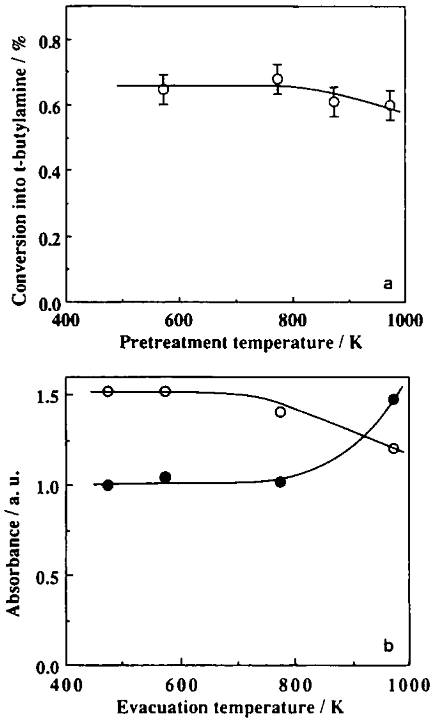

FIG. 1. Effects of the pretreatment temperature on the conversion into *t*-butylamine over H–MFI-40 and on the relative integrated intensities of the IR bands of pyridine adsorbed on H–MFI-40. (a) Effect of the pretreatment temperature on the conversion into *t*-butylamine over H–MFI-40; 2-methylpropene, 4.0 $cm^3 \cdot min^{-1}$; ammonia, 16.0 $cm^3 \cdot min^{-1}$; catalyst weight, 1.0 g; reaction temperature, 473 K. (b) Effect of the pretreatment temperature on the relative integrated intensities of the IR bands of pyridine adsorbed on H–MFI-40. ○, 1545 cm^{-1}; ●, 1455 cm^{-1}.

tween fresh and used samples was small; the BET surface area and pore volume of the fresh H–MFI-50 zeolite catalyst were 430 $m^2 \cdot g^{-1}$ and 0.216 $cm^3 \cdot g^{-1}$, respectively, and those after use were 440 $m^2 \cdot g^{-1}$ and 0.186 $cm^3 \cdot g^{-1}$, respectively.

The amount of *t*-butylamine formed per number of Al atoms or Brønsted acid sites after a 30-h reaction on H–MFI-40 was greater than 2, showing that the reaction is catalytic. The initial small value (0.14% at 0.67 h) of the conversion into *t*-butylamine is probably due to the adsorption of the basic *t*-butylamine on the acidic sites of the catalysts, as discussed later in this section. Hereafter, the catalytic activity is evaluated by conversion into *t*-butylamine after ca. 6 h.

Conversion of 2-methylpropene to *t*-butylamine was only 0.34% at 473 K on H–MFI-40. It is probably due to the equilibrium limitation between the starting materials (2-methylpropene and ammonia) and the product (*t*-butylamine). Equilibrium conversion at 473 K is ca. 3%. It was confirmed for H–MFI-40 that conversion was proportional to contact time (weight of catlayst/total flow rate); for example, the conversions were 0, 0.34, 0.38, and 0.68% at the contact times of 0, 1.5, 2.0, and 3.0 $g \cdot s \cdot cm^{-3}$, respectively, where the error limit calculated was ±0.05%.

When water vapor was added to the reactant gases of 2-methylpropene and ammonia, the activity of each zeolite changed little and selectivity to *t*-butylamine slightly decreased to 87–97% from 95–100% due to the formation of 2-methyl-2-propanol. Thus, the addition of water vapor did not improve the catalytic properties. The fact is in contrast to the increase in activity of amination of ethene by the addition of water vapor (17), and suggests that no water (or 2-methyl-2-propanol) is involved in the reaction for amination or that a trace amount of water works catalytically in the reaction.

The pretreatment temperature dependence of the conversions into *t*-butylamine on H–MFI-40 is shown in Fig. 1a. The conversion was constant in the range 473–773 K and then slightly decreased above 773 K. The reason for the decline above 773 K is presumably attributed to a decrease in the concentration of Brønsted acid sites as discussed in the next section.

The temperature dependence of conversion into *t*-butylamine on H–MFI-40 is shown in Fig. 2 as an example. At first conversion increased with the reaction temperature as in usual catalysis. The maximum conversion was observed at 473 K. Above 473 K conversion became close to the equilibrium conversion (22) indicated by the broken line in Fig. 2 and decreased with it, showing that the decrease at higher temperatures is attributable to the reduction in equilibrium conversion into *t*-butylamine. For all the catalysts used, maximum conversion was observed around 473 K. The reaction between 2-methylpropene and ammonia was hereafter carried out at 473 K after pretreatment at 773 K.

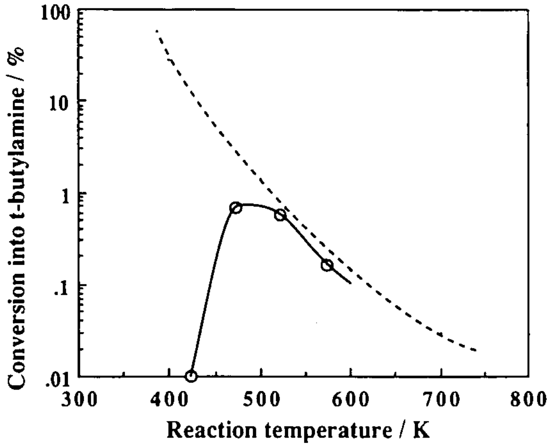

FIG. 2. Temperature dependence of the conversion into *t*-butylamine over H–MFI-40. 2-Methylpropene, 4.0 $cm^3 \cdot min^{-1}$; ammonia, 16.0 $cm^3 \cdot min^{-1}$; catalyst weight, 1.0 g. The broken line corresponds to the equilibrium conversion.

TABLE 3

Catalytic Activities of Various Catalysts for the Amination of 2-Methylpropene into *t*-Butylamine at 473 K[a]

Catalyst	Conv. into *t*-butylamine[b] (%)	Selectivity to *t*-butylamine[c] (%)
H–MFI-81	1.73	99
H–MFI-93	1.18	99
H–MFI-113	0.90	98
H–MFI-50	0.85	99
H–MFI-129	0.80	99
H–MFI-40	0.68	99
H–MFI-23	0.62	99
H–MOR-19	0.53	99
H–MOR-15	0.42	99
H–FAU-40	0.22	95
H–LTL-6	0.11	99
H–FAU-12	0.06	99
H–OFF/ERI-8	0.05	98
H–MFI-1340	0.04	99
H–FAU-6	0.04	99
H–FER-17	0.02	99
Na–MFI-40	0.01	99
Na–FAU-6	0.01	99
Na–MOR-15	0	—
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.17	89[d]
$Cs_{2.85}H_{0.15}PW_{12}O_{40}$	0.15	84[d]
SiO_2–Al_2O_3	0.08	98
SiO_2–TiO_2	0.03	100
Al_2O_3	0.01	99
$Cs_{3.15}PW_{12}O_{40}$	0	—
MgO	0	—

[a] 2-Methylpropene, 4.0 $cm^3 \cdot min^{-1}$; ammonia, 16.0 $cm^3 \cdot min^{-1}$; catalyst weight, 1.0 g.

[b] Mol *t*-butylamine formed/mol 2-methylpropene introduced.

[c] Mol *t*-butylamine formed/total mol of products.

[d] Although the G.C. peak was observed at about the retention time of 9 min on the Amipack-141 column (*t*-butylamine, 6.6 min), this could not be identified. In this case, the selectivity was calculated on the assumption that the molar sensitivity of the unidentified product was the same as that of *t*-butylamine.

The activities of various catalysts at 473 K are summarized in Table 3. H–MFI-81, on which the conversion reached ca. 60% of the equilibrium conversion, showed the highest activity among the zeolite catalysts, solid acid catalysts ($Cs_xH_{3-x}PW_{12}O_{40}$ (x = 2.5–3.15), SiO_2–Al_2O_3, SiO_2–TiO_2), and solid base MgO. *t*-Butylamine was the major product: the selectivities to *t*-butylamine and to oligomerization and isomerization products were more than 84% and less than 16%, respectively, under the present conditions.

Figure 3 shows the effect of preadsorption of diisopropylamine on the catalytic activity of H–MFI-40. Without the preadsorption, the steady state reaction was attained within 2 h (○, Fig. 3). The preadsorption of diisopropylamine greatly decreased the initial conversion into *t*-butylamine as shown in Fig. 3 (●). The conversion was gradually increased with time and gradual desorption of diisopropylamine was observed (▲, Fig. 3). These phenomena are consistent with the reports that *t*-butylamine is more basic than diisopropylamine in the gas phase (23) and that the higher the gas-phase proton affinity is, the higher the affinity for acidic sites on the zeolite is (22). The great decrease of the initial conversion into *t*-butylamine by preadsorption of diisopropylamine supports that the amination is catalyzed by acidic sites.

The pressure dependencies were measured at 473 K for H–MFI-40, in the range of the partial pressures of 2-methylpropene, 0.11–0.96 atm, and ammonia, 0.04–0.89 atm, and are summarized in Eq. [4]. A similar equation was observed for H–MFI-50. The respective dependencies on the partial pressures of the reactants indicate that ammonia adsorbs strongly and 2-methylpropene weakly:

$$-d[C_4H_8]/dt = k\,P_{C_4H_8}^{0.8\pm0.1}P_{NH_3}^{0\pm0.1}. \qquad [4]$$

The IR spectra of H–MFI-40 after the use in the catalytic run were measured. Curve (a) in Fig. 4 is the spectrum of H–MFI-40 itself after the treatment in N_2 at 773 K for 1 h. After the reaction was carried out between 2-methylpropene (4 $cm^3 \cdot min^{-1}$) and ammonia (16 $cm^3 \cdot min^{-1}$) on H–MFI-40, five bands were observed in the range 1600–1300 cm^{-1}; 1500, 1473, 1409, and 1384 cm^{-1} (due to C–H deformation bands of CH_3 and CH_2 (24)) with a shoulder at 1440 cm^{-1} (Curve (b)). Curve (c) shows the IR spectrum of *t*-butylamine adsorbed on H–MFI-40 preevacuated at 773 K for 2 h. The spectrum was similar to that of curve (b) except for the absence of the band at 1440 cm^{-1}. It was confirmed in a separate experiment

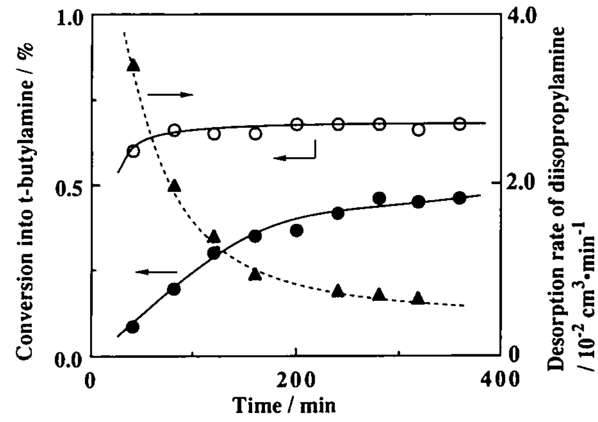

FIG. 3. Effect of diisopropylamine preadsorption on the conversion into *t*-butylamine. Catalyst, H–MFI-40. Reaction conditions of the amination were the same as those in Table 3. ● and ○, conversions into *t*-butylamine with and without preadsorption of diisopropylamine, respectively; ▲, desorption rate of diisopropylamine.

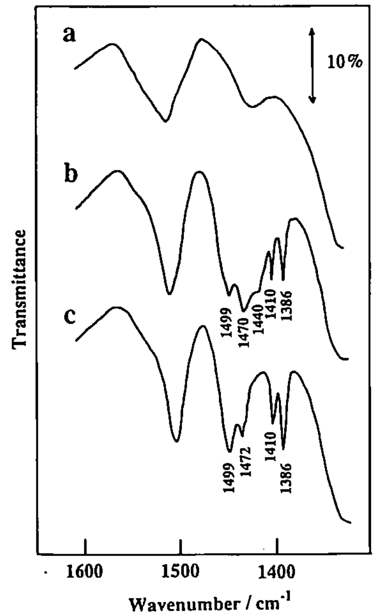

FIG. 4. IR spectra of H–MFI-40 and *t*-butylamine adsorbed on H–MFI-40. Curve (a), the spectrum of H–MFI-40 itself after the sample was treated in N_2 at 773 K for 1 h; curve (b), the spectrum of H–MFI-40 after the reaction was carried out in the same conditions as those in Table 3; curve (c), the spectrum after the adsorption of *t*-butylamine.

that the 1440-cm^{-1} band is attributable to δNH_4^+. No bands due to 2-methylpropene were observed in Curve (b). It follows that during amination on H–MFI-40, *t*-butylamine and ammonia were the main adsorbates and 2-methylpropene was weakly adsorbed.

Factors controlling catalytic activity. We investigate how the catalytic activities can be recognized by Brønsted or Lewis acidity. Figure 1b shows the changes in the number of Brønsted and Lewis acid sites of H–MFI-40 with evacuation (pretreatment) temperature. The number of Brønsted and Lewis acid sites changed little in the range 473–773 K. The ratio of the number of Brønsted acid sites to that of Lewis acid sites was 2.0 by using the ratio 1.3 of the extinction coefficient of the band at 1545 to that at 1445 cm^{-1} (25). The number of Brønsted acid sites decreased somewhat above 773 K, while that of Lewis acid sites increased somewhat above 773 K, due to the interconversion of Brønsted to Lewis acid sites. A fair correlation was observed above 473 K for H-MFI-40 between the number of Brønsted acid sites (O in Fig. 1b) and the catalytic activity (O in Fig. 1a), which supports the notion that direct amination of 2-methylpropene is catalyzed by the Brønsted acidity. The fact that $Cs_xH_{3-x}PW_{12}O_{40}$ (x = 2.5, 2.85) heteropoly compounds having only Brønsted acid sites showed activity for amination, while Al_2O_3 having only Lewis acid sites showed little activity also supports the above idea.

Figure 5 shows the correlation between the activity of the various catalysts and the number of Brønsted acid sites. Conversion increased with the number of Brønsted acid sites, reached a maximum for H–MFI-81, and then decreased. The increase was consistent with the idea that Brønsted acid sites are the active centers. The decrease shows that amination is not a simple function of the number of Brønsted acid sites and is probably due to the lower acid strength as investigated in the later part.

The correlation between SiO_2/Al_2O_3 ratio and conversion into *t*-butylamine is shown in Fig. 6a. In the range of silica/alumina ratios 23–81, conversion for H–MFI zeolites monotonically increased. The increase of conversion with SiO_2/Al_2O_3 ratios up to 40 was also observed for FAU zeolites. Further increase in the silica/alumina ratios of H–MFI zeolites decreased the conversions. A similar dependence of the catalytic activities on the SiO_2/Al_2O_3 ratios was reported for the hydrolysis of ethyl acetate on H–MFI zeolites in aqueous solution (27).

All the rates could not be expressed by the one line as shown in Fig. 6a: The conversion on H–MFI-40 was different from that of H–FAU-40, though the SiO_2/Al_2O_3 ratios were the same. The difference of conversion between H–MOR-15 and H–FER-17, for which the SiO_2/Al_2O_3 ratios were very close, was also observed. Such different dependencies of conversion on the SiO_2/Al_2O_3 ratios could be explained by the number and strength of the Brønsted acid sites as described below.

Figure 6b shows the correlation between the number of Brønsted acid sites and the SiO_2/Al_2O_3 ratios. The number of Brønsted acid sites increased with the SiO_2/Al_2O_3 ratios, reached a maximum at 15, and then decreased. Conversion into *t*-butylamine increased with the increment of the SiO_2/Al_2O_3 ratios from 6 (no. 15) to 15 (no. 11), as shown in Fig. 6a. Such a similar increase was

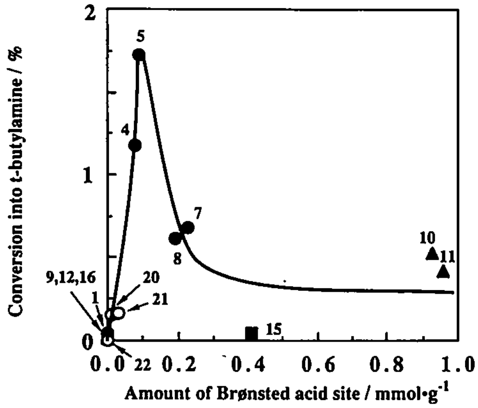

FIG. 5. Correlation between the conversions into *t*-butylamine and the amounts of Brønsted acid sites. ●, MFI; ▲, MOR; ■, FAU; O, $Cs_xH_{3-x}PW_{12}O_{40}$. The sample numbers attached indicate the same catalysts as those in Tables 1 and 2.

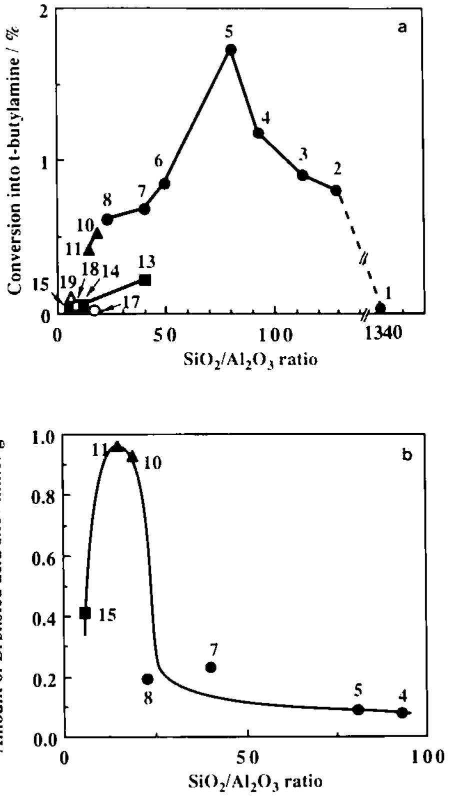

FIG. 6. Correlations between the SiO_2/Al_2O_3 ratios and the conversions into *t*-butylamine or the amounts of Brønsted acid sites. (a) Correlation between the SiO_2/Al_2O_3 ratios and the conversions into *t*-butylamine. (b) Correlation between the SiO_2/Al_2O_3 ratios and the amounts of Brønsted acid sites. ●, H-MFI; ▲, H-MOR; ■, H-FAU; ○, H-FER; △, H-LTL; □, H-OFF/ERI. For the sample numbers attached, see Table 1.

consistent with the idea that Brønsted acid sites are the active centers. However, the SiO_2/Al_2O_3 ratios at the maxima in Figs. 6a and 6b were 81 and 15, respectively, and quite different. This also shows that amination is not a simple function of the number of Brønsted acid sites.

Figure 7 shows the correlation between the turnover frequencies per Brønsted acid site and the SiO_2/Al_2O_3 ratios of the zeolites. The turnover frequencies can be expressed by one line and they increase with the increment of the SiO_2/Al_2O_3 ratios up to 93. Therefore, the difference of the SiO_2/Al_2O_3 ratios at the maxima between Figs. 6a and 6b or the decrease of conversion above the number of Brønsted acid sites of 0.09 mmol · g^{-1} in Fig. 5 is probably due to the change of the turnover frequencies. On the basis of the report that the acid strength increases with increasing SiO_2/Al_2O_3 ratios (28), the increase of the turnover frequencies in Fig. 7 is probably due to the increment of the acid strength. Thus, not only the number of Brønsted acid sites but also the acid strength are important factors for the present reaction, as has been usually interpreted in the cracking of alkanes (29). Due to the above two factors having the proper values, H-MFI-81 is the most active for the reaction to directly form *t*-butylamine among the catalysts tested.

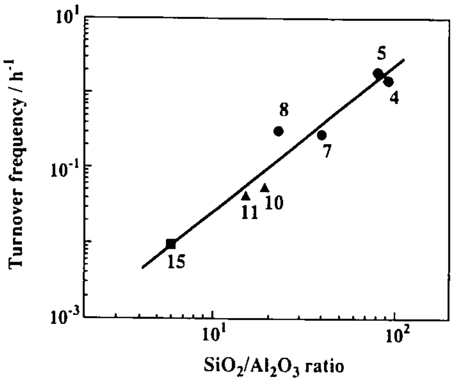

FIG. 7. Correlations between the SiO_2/Al_2O_3 ratios the turnover frequencies. Turnover frequencies, amounts of *t*-butylamine formed per 1 h/amounts of Brønsted acid sites. ●, H-MFI; ▲, H-MOR; ■, H-FAU. For the sample numbers attached, see Table 1.

Finally, it should be noted (Fig. 8) that a linear correlation has been recognized between the activities of the respective zeolites for amination and liquid-phase hydration (3) of 2-methylpropene. The latter reaction is suggested to be controlled by the Brønsted acidity (26). The correlation can be understood by the following two ideas. The first is that direct amination of 2-methylpropene is controlled by the Brønsted acidity, as described above. The second is the idea that 2-methyl-2-propanol, which is formed by the reaction between 2-methylpropene and a trace amount of water molecule (Eq. [1]), is an interme-

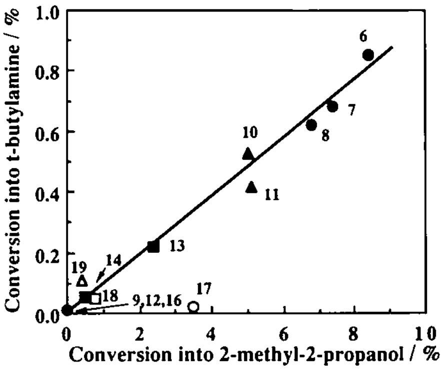

FIG. 8. Correlation between the activities of various proton-exchanged zeolite catalysts for amination and hydration of 2-methylpropene. Reaction conditions of the amination were the same as those in Table 3. The activities for the hydration were cited from Ref. (3). ●, H- or Na-MFI; ▲, H-MOR; ■, H-FAU; ○, H-FER; △, H-LTL; □, H-OFF/ERI. The numbers indicate the same catalysts as those in Table 1.

diate in amination. Further investigations should be carried out to clarify the reaction mechanism.

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REFERENCES

1. Ono, Y., *Catal. Rev.-Sci. Eng.* **34,** 179 (1992); Rabo, J. A., and Gajda, G. J., *Catal. Rev.-Sci. Eng.* **31,** 385 (1989–1990); Misono, M., and Nojiri, N., *Appl. Catal.* **64,** 1 (1990).
2. Iwamoto, M., Tajima, M., and Kagawa, S., *J. Catal.* **101,** 195 (1986).
3. Iwamoto, M., Yahiro, H., Mori, H., and Takasu, I., *in* "Catalytic Science and Technology" (S. Yoshida, N. Takezawa, and T. Ono, Eds.), Vol. 1, p. 415. Kodansha, Tokyo, 1991.
4. Mori, H., Mizuno, N., Shirouzu, T., Kagawa, S., and Iwamoto, M., *Bull. Chem. Soc. Jpn.* **64,** 2681 (1991).
5. Mori, H., Ueno, H., Mizuno, N., Yahiro, H., and Iwamoto, M., *Chem. Lett.*, 2289 (1990).
6. Mori, H., Mizuno, N., Tajima, M., Kagawa, S., and Iwamoto, M., *Catal. Lett.* **10,** 35 (1991).
7. Mizuno, N., Mori, H., Tajima, M., Kagawa, S., Ueno, H., Yahiro, H., and Iwamoto, M., *J. Mol. Catal.* **80,** 229 (1993).
8. Schweizer, A. E., Fowlkes, R. L., McMakin, J. H., and Whyte, T. E., *in* "Encyclopedia of Chemical and Technology" (H. F. Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, Eds.), Vol. 2, p. 272. Wiley, New York, 1978.
9. Corbin, D. R., Keane, M., Jr., Abrams, L., Farlee, R. D., Bierstedt, P. E., and Bein, T., *J. Catal.* **124,** 268 (1990); Keane, M., Jr., Somnichsen, G. C., Abrams, L., Corbin, D. R., Gier, T. E., and Shannon, R. D., *Appl. Catal.* **32,** 361 (1987); Segawa, K., and Tachibana, H., *J. Catal.* **131,** 482 (1991).
10. Roth, J. F., *Stud. Surf. Sci. Catal.* **54,** 3 (1990).
11. Pez, G. P., U. S. Patent 4,302,603 (1981).
12. Howk, B. W., Little, E. L., Scott, S. L., and Whitman, G. M., *J. Am. Chem. Soc.* **76,** 1899 (1954).
13. Gagné, M. R. Stern, C. L., and Marks, T. J., *J. Am. Chem. Soc.* **114,** 275 (1992) and Refs. (6–9) therein.
14. Deeba, M., Ford, M. E., and Johnson, T. A., *J. Chem. Soc. Chem. Commun.*, 562 (1987).
15. Deeba, M., Ford, M. E., and Johnson, T. A., *in* "Catalysis" (J. W. Ward, Ed.), p. 221. Elsevier, Amsterdam, 1987; *in* "Catalysis of Organic Reactions" (D. W. Blackburn, Ed.), p. 241. Dekker, New York, 1990.
16. Deeba, M., and Ford, M. E., *J. Org. Chem.* **53,** 4594 (1988).
17. Tabata, M., Masters Thesis, Miyazaki University, 1991.
18. Tabata, M., Mizuno, N., and Iwamoto, M., *Chem. Lett.*, 1027 (1991).
19. British Patent 1972, 1,402,981.
20. Sakata, Y., Katsube, H., Tsuchiya, S., Kawashita, T., and Imamura, H., *in* "Meeting of Catalysis Society of Japan, 3F19, Nagasaki, 1989."
21. Tatematsu, S., Hibi, T., Okuhara, T., and Misono, M., *Chem. Lett.*, 865 (1984).
22. Stull, D. R., Westrum, E. F., Jr., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds." Wiley, New York, 1967.
23. Aue, D. H., and Bowers, M. T., *in* "Gas Phase Ion Chemistry" (M. T. Bowers Ed.), Vol. 2, p. 2. Academic Press, New York, 1979.
24. Take, J., Yamaguchi, T., Miyamoto, K., Ohyama, H., and Misono, M., *Stud. Surf. Sci. Catal.* **28,** 495 (1986).
25. Emeis, C. A., *J. Catal.* **141,** 347 (1993).
26. Tanabe, K., Misono, M., Ono, Y., and Hattori, H., "New Solid Acids and Bases," p. 252. Kodansha–Elsevier, Tokyo–Amsterdam, 1989.
27. Namba, S., Hosonuma, N., and Yashima, T., *J. Catal.* **72,** 16 (1981).
28. Jacobs, P. A., Mortier, W. J., and Uyterhoeven, J. B., *J. Inorg. Nucl. Chem.* **40,** 1919 (1978); Mortier, W. J., and Geerlings, P., *J. Phys. Chem.* **84,** 1982 (1980).
29. Wang, I., Chen, T. J., Chao, K. J., and Tsai, T. C., *J. Catal.* **60,** 140 (1979); Kikuchi, E., Nakano, H., Shimomura, K., and Morita, Y., *Sekiyu Gakkaishi* **28,** 210 (1985).