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Alkylations of Benzene, Alkylbenzenes, and Halobenzenes Catalyzed by Protonated Mordenite Pretreated with Chlorofluorocarbons

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The chlorofluorocarbon (CFC) treatment of protonated mordenite (HM) was carried out in a flow reactor under ordinary pressure, usually at 600°C for 10 min using $CClF_3$ as a treatment agent. The mordenite structure was almost completely retained during the CFC treatment. Evidence for dealumination and surface fluorination was observed by XPS examination. Decrease of surface acidity, as seen by NH_3-TPD, accompanied the treatment. The function of HM as a catalyst for alkylations of benzene and alkylated or halobenzenes with methanol was greatly enhanced by the CFC treatment. In particular, the activity maintenance was remarkably improved. Thus, in the alkylations at 300°C under the molar ratios of CH_3OH/Aromatic compound = 1 and W/F = 81.2 (for toluene) or 97.5 (for 1,2,4-trimethylbenzene (TMB)) g h mol^{-1}, the conversions at the initial stage of the run were increased from 27 to 65% (for toluene) and from 12 to 47% (for TMB) by CFC treatment of the HM catalyst. In addition, the conversions of benzene and TMB were well maintained at about 60 and 40%, respectively, throughout the running time of 3 h in the reactions catalyzed by the treated HM, while the conversions of benzene and TMB rapidly decreased and became almost zero within 90 min in the reaction catalyzed by untreated HM.

INTRODUCTION

Synthetic zeolites have proven to be excellent catalysts in the petrochemical industry. However, their catalytic activities are not, in general, well maintained in various reactions, mostly due to deposition of carbonaceous substances, followed by clogging of the channels in the zeolite. Thus, better activity maintenance is essential for more extensive uses of the zeolite catalysts (*1*).

In previous studies on the isomerization of *o*-chlorotoluene (*2*), alkylation of chlorobenzene (*3, 4*), and toluene disproportionation (*5*), the authors have found that chlorofluorocarbon (CFC) treatment of protonated mordenite (HM) is effective for enhancing not only the catalytic activity, but also the activity maintenance. It is desirable then, that the CFC-treated HM be applied in other important reactions as a practical solid acid catalyst. However, details of the surface composition and property, especially the surface acidity, of the CFC-treated HM have not yet been clarified. For further development of the CFC-treated HM as a catalyst, these points must be elucidated.

Hence, in this study, the authors attempted to determine the effect of CFC treatment on the catalytic activities of HM for alkylations of benzene and its derivatives with methanol, considering that the alkylations are especially useful for preparations of important intermediates or raw materials of special polymers. Together with the catalytic activities, the effects of the CFC treatment on the surface compositions and properties of HM were investigated.

EXPERIMENTAL

Reagents and Catalysts

All organic materials except ethylene, propene, and CFCs were special grade reagents supplied from Wako Pure Chemical

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Company and were used without further purification. Olefins, such as ethylene (16.2%, balance N_2) and propene (research grade), and CFCs having a purity of higher than 99% were products of Takachiho Company and Mitsui–Dupont Fluorochemical Company, respectively.

HM, supplied from Toso Company as TSZ-640HOA (SiO_2/Al_2O_3 molar ratio = 19.9), was used as a catalyst after fabrication into granules of 14–20 mesh and heat treatment at 500°C for 3 h.

Treatment with CFC

The CFC treatment of the fabricated HM was carried out in a conventional flow reactor made of quartz (i.d. 15 mm) by passing gaseous CFC at a constant rate of 40 ml min^{-1} after dilution with an equal volume of N_2, through a fixed bed of HM (1 g). Since it has been observed that $CClF_3$ is most suitable as a treatment agent in the activation of HM used as a catalyst for the alkylation of chlorobenzene with methanol (*3*), it was used as the main treatment agent in this study. The treatment was carried out at 600°C for 10 min, unless otherwise noted.

The alkylations were carried out in the reactor used for the CFC treatment at 300°C for 30 min under ordinary pressure, immediately after the CFC treatment. In these reactions, mixtures of aromatic compound and methanol, in an equimolar ratio, were supplied to the reactor together with an equal volume of N_2 carrier, after evaporation in a preheater. The W/F_M (W: Mass of catalyst, g; F_M: Flow rate of feed (benzene + alkylating reagent), mol/h) was kept at the following values:

Aromatics	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	1,2,4-Trimethylbenzene
W/F (g h mol^{-1})	71.7	81.2	89.4	90.3	90.9	97.5

The products were analyzed by gas chromatography using a 3-m column packed with 5% Benton 34 and 5% DIDP on Uniport KA (80–100 mesh).

Surface Area and X-Ray Diffraction

Specific surface area was determined by applying the BET equation to the adsorption isotherm of N_2 at −196°C. X-ray diffraction patterns were measured using Geigerflex D-2 (Rigaku Denki Company) with a Cu$K\alpha$ line for the powdered samples.

XPS Measurement

Surface compositions and bondings were examined by XPS, using the Shimadzu ESCA 750. The contents of various components were calculated from the areas of spectral peaks on the basis of the photoionization cross section at 1245 eV in units of the Cl's cross section, 22,200 barns (1 barn = 10^{-24} cm^{-2}) (*6*).

Acidic Property Measurement

Acidic properties of HM before and after CFC treatment were measured by using NH_3-TPD under the following conditions: evacuation temperature of samples, 500°C; adsorption temperature of NH_3, 100°C; increasing rate of the bed temperature, 20°C per minute.

The Brønsted and Lewis acidities were determined by observing the infrared spectra of pyridine adsorbed on the catalyst surface. The catalyst sample, fabricated into a thin disc by compressing to 400 kg cm^{-2}, was placed in a cell connected to a vacuum apparatus, and the cell was evacuated. After measurement of the background, pyridine (about 5 mm Hg) was introduced and adsorbed for 30 min. Then, excess pyridine

TABLE 1

Results for Alkylations of Benzene and Alkyl- or Halobenzenes with Methanol

Catalyst	Conversion or reactant (%)[a]							
	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	1,2,4-Trimethylbenzene	Chlorobenzene	Fluorobenzene
HM	3.2	12.6	29.1	34.3	31.6	26.4	3.8	1.2
	(0.2)	(1.9)	(1.4)	(0.7)	(3.9)	(1.3)	(0.2)	(0.2)
HM treated	28.3	47.7	63.1	70.8	68.7	66.2	35.3	20.3
with $CClF_3$	(26.8)	(40.6)	(51.5)	(61.5)	(53.3)	(58.2)	(27.2)	(13.7)

[a] The conversions to alkylated products were measured 30 min after beginning the run. The numbers in parentheses are the values observed after a running time of 3 h.

was removed by evacuation at 100°C for 1 h, and the IR spectrum was measured after cooling to room temperature.

MAS-NMR Spectra of ^{29}Si and ^{27}Al

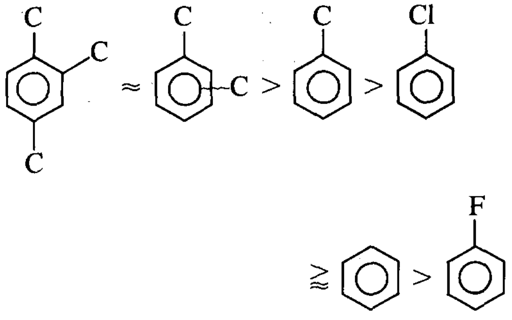
In order to examine the configurations of Si and Al components in HM before and after CFC treatment, ^{29}Si and ^{27}Al MAS-NMR were observed by using the GX-270 FT-NMR apparatus (Nihondenshi) equipped with the solid CP/MAS unit (NM-GSH27MU). Observed frequencies for ^{29}Si and ^{27}Al were 53.7 and 70.4 MHz, respectively.

RESULTS AND DISCUSSION

Alkylations of Benzene and Alkyl- or Halobenzenes

In order to determine the CFC treatment effect on the catalytic activity of HM for alkylations with methanol, the vapor-phase alkylations of benzene, polyalkylbenzenes, and halobenzenes were undertaken. As shown in Table 1, the treatment was effective for enhancement of catalytic activities of HM for all these alkylations. In addition, as is indicated by a comparison of the conversions after a running time of 3 h (denoted by numbers in parentheses) with those at initial stages, the treatment was especially effective for enhancement of the catalytic activity maintenance.

The order of the reactivities of the aromatic compounds over the untreated HM was as follows:



This order seems to be determined, on the whole, by the electron-donating and -withdrawing functions of substituents and their numbers; it remained unaltered for reactions over the CFC-treated HM catalyst.

The compositions of alkylation products are listed in Table 2. The most distinctive feature found for the reaction over the treated HM was the formation of a relatively large amount of pentamethylbenzene. The formation of a large amount of such a bulky compound suggests enlargement of the channels in the HM with the CFC treatment.

Another indication of the channel enlargement was the remarkable improvement in the activity maintenance of CFC-treated HM catalyst. Thus, the conversions of benzene and alkylbenzenes were well maintained at a high level throughout the running time of 3 h in the alkylations promoted by the CFC-treated HM (Fig. 1). In contrast to this, the conversions in the reaction over the untreated HM promptly decreased within the first hour, suggesting that the nar-

TABLE 2

Compositions of Products Obtained in the Alkylations with Methanol

Reactant	Composition of product (mol%)[a]											
	Benzene	Toluene	Xylene			Trimethylbenzene			Tetramethylbenzene			Pentamethylbenzene
			o-	*m*-	*p*-	1,3,5-	1,2,4-	1,2,3-	1,2,4,5-	1,2,3,5-	1,2,3,4-	
Benzene	96.4	3.1	0.01	0.03	0.02	0	0	0	0		0	0
	(71.7)	(15.6)	(2.3)	(2.2)	(0.8)	(0.6)	(2.0)	(0.4)	(1.2)		(0.1)	(3.1)
Toluene	14.1	73.6	2.3	5.9	2.6	0.3	0.6	0.1	0		0	0
	(2.4)	(49.9)	(8.2)	(11.0)	(4.7)	(3.2)	(8.6)	(1.4)	(4.1)		(0.5)	(6.0)
o-Xylene	2.8	22.1	10.5	25.4	10.5	6.9	15.0	1.9	3.3		0.4	1.2
	(0.1)	(3.8)	(17.8)	(13.1)	(2.6)	(8.5)	(23.8)	(3.1)	(14.5)		(1.7)	(11.1)
m-Xylene	2.9	22.2	8.6	23.0	9.4	7.2	15.1	1.8	4.7		0.8	4.3
	(0.1)	(3.2)	(5.1)	(17.5)	(4.0)	(9.6)	(23.8)	(3.0)	(18.0)		(2.2)	(13.0)
p-Xylene	3.2	23.2	8.5	23.0	8.5	7.0	15.0	1.9	4.2		0.5	2.7
	(0.2)	(7.0)	(3.5)	(10.6)	(10.5)	(9.4)	(23.5)	(2.9)	(20.0)		(2.1)	(10.2)
1,2,4-Trimethylbenzene	0	0.4	2.5	4.9	1.8	15.9	34.6	4.6	13.6	16.3	3.2	2.1
	(0)	(0.1)	(0.9)	(1.4)	(0.3)	(6.7)	(18.5)	(2.0)	(15.8)	(18.7)	(3.7)	(31.9)

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[a] Product compositions were measured 39 min after beginning the run for the reactions catalyzed by untreated HM. The numbers in parentheses denote the product composition for the reaction catalyzed by the $CClF_3$-treated HM.

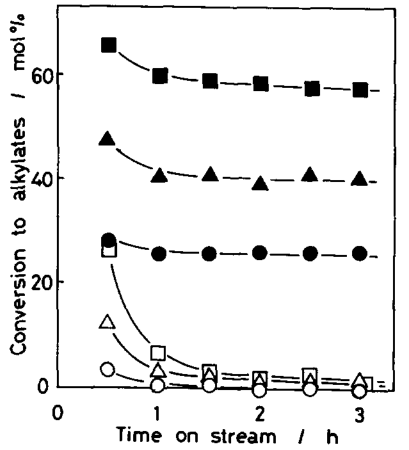


FIG. 1. Maintenance of catalytic activity for alkylation of benzene (○, ●), toluene (△, ▲) or 1,2,4-trimethylbenzene (□, ■) with methanol. ○, ×, □: reactions over HM before treatment; ●, ▲, ■: reactions over HM treated with $CClF_3$ at 600°C for 10 min.

row channels may be readily packed with the large molecules of the products and/or reactants, and finally clogged by the carbonaceous materials formed from the packed compounds.

Concerning the changes of product composition with contact time, *W*/*F*, Fig. 2 shows the results for the alkylation of 1,2,4-trimethylbenzene (TMB). For the reaction over the treated HM, the amount of pentamethylbenzene increased almost linearly to larger than 60% on increasing *W*/*F* to 20 g h mol^{-1}, after which the bulkier compound, hexamethylbenzene, began to form. Thus, the polyalkylated benzene seems to be subsequently formed by increasing the contact time. By contrast, only a small amount of tetramethylbenzene was formed in the reaction over the untreated HM. In such a reaction over untreated HM, most of the untreated methanol was converted to byproducts, especially to olefins which formed some low polymers, covering the active sites and causing deactivation of the HM catalyst. As an indication of the olefin polymerization, the conversion of TMB to alkylated products decreased by increasing the molar ratio of CH_3OH/TMB in the feed, contrary to the result obtained for the reaction over the CFC-treated HM, as shown in Fig. 3. This fact again suggests that the CFC treatment is effective for the modification of HM so as to be catalytically less active for olefin formation from methanol.

Effect of CFC Treatment on Structure of HM

Figure 4 shows the XRD patterns of HM before and after the CFC treatment at 450 and 600°C. The HM structure was almost completely retained even after treatment at as high a temperature as 600°C. However, further pattern details indicate that the

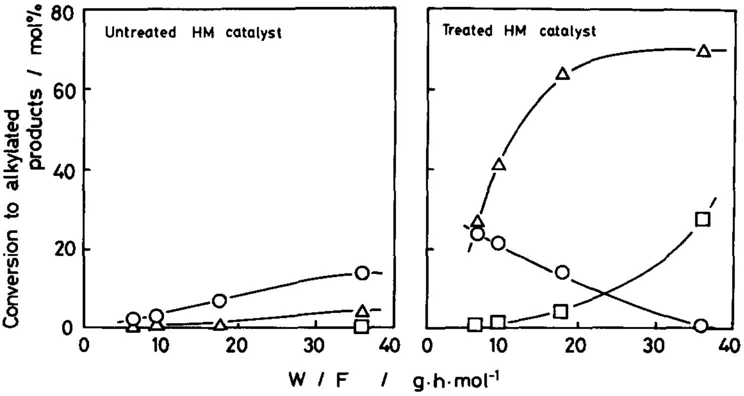


FIG. 2. Effect of *W*/*F* on conversion of 1,2,4-trimethylbenzene to polymethylbenzene. Alkylation products, ○: tetramethylbenzene; △: pentamethylbenzene; □: hexamethylbenzene.

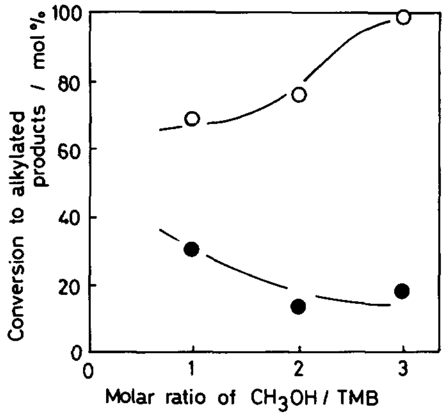


FIG. 3. Effect of molar ratio (CH$_3$OH/TMB) on conversion of TMB to alkylated products. Reactions were carried out at 300°C over HM before (●) and after (○) treatment with CClF$_3$. The conversions were measured after a running time of 30 min.

peaks at higher diffraction angles were weakened by elevating the treatment temperature, and parameters of the unit cell determined by $K\alpha$ line ($19° < 2\theta < 32°$) was changed from (a = 17.97 Å, b = 20.07 Å, c = 7.39 Å) to (a = 18.01 Å, b = 20.15 Å, c = 7.43 Å) by the CFC treatment at 600°C. This change in XRD patterns seems to be related to the enlargement of channels due to elimination of Al or (Al + Si) components as volatile halides, e.g. $AlCl_3$ (bp = 180.2°C), SiF_4 (−94.8°C), $SiClF_3$ (−70.0°C), $SiCl_2F_2$ (31.8°C), $SiCl_3F$ (12.2°C), or $SiCl_4$ (56.8°C). In fact, the peak at 24.8 Å, assignable to ($\alpha + \gamma$) AlF_3 was found in the pattern for HM treated at 450°C and became more distinct as the treatment temperature was raised to 600°C. The crystalline AlF_3 may be formed by aggregation of eliminated $AlCl_3$ on the HM surface, followed by the halogen-exchange reaction with $CClF_3$. A part of the crystalline AlF_3, however, was possibly formed directly by exchange of O atoms bonded to Al atoms with F atoms in the treatment agent, since it has been ascertained that CF_4 is also effective for the surface fluorination of HM carried out at higher temperatures (*5*).

In spite of the eliminations of Al or (Al + Si) atoms in the bulk, the surface area of HM was well maintained during the CFC treatment at 450°C. Although it decreased to some extent on increasing the treatment temperature up to 550°C, no further decrease was found even at a treatment temperature of 650°C (Table 3).

Surface Compositions of HM before and after CFC Treatment

The changes in surface composition during the CFC treatment are shown in Table 3. A fairly large amount of fluorine was introduced into the HM surface; by contrast, little or no chlorine was introduced. Since the bond strength of C–Cl (360 kJ mol^{-1} (*7*)) is far less than that of C–F (490 kJ mol^{-1} (*8*)), chlorides of silicon and aluminum are considered to be formed at first. Part of the chlorides might be removed from the surface as soon as they are formed. The remaining chlorides, however, might be converted to Al- and Si-fluorides, since fluorides of aluminum and silicon are much more thermodynamically stable than the respective chlorides.

The fluorine concentration increased with increasing treatment temperature and at-

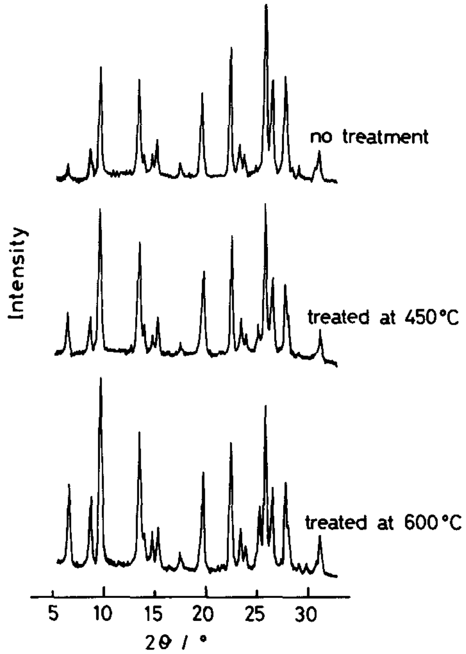


FIG. 4. X-ray diffraction patterns.

TABLE 3

Specific Surface Areas and Surface Compositions of HM before and after CFC Treatment

Treatment temperature (°C)	Specific surface area ($m^2 g^{-1}$)	Surface composition (atom.%)				
		Si	Al	O	F	Cl
Before treatment	356	31.3	3.7	65.0	0	0
450	354	32.6	2.4	59.2	5.8	trace
500	—	28.5	2.8	59.2	8.7	0
550	318	31.4	2.7	60.2	5.7	0
600	317	35.1	2.5	57.9	4.5	trace
650	323	36.9	2.9	57.5	2.7	trace

tained a maximum at 500°C. The decrease at high temperatures, especially at 650°C, is ascribable to hydrolysis of the fluoride by neighboring OH groups or H_2O formed from the OH groups, since aluminum fluoride may readily react with steam at higher temperatures (*9*).

Regarding the behaviors of surface components during the CFC treatment, changes of peak positions in the XPS spectra with treatment temperatures are shown in Table 4. The peak position due to Al2*p* was shifted from 74.9 eV, which is close to the value for Al_2O_3 (74.3 eV (*10*), to 75.5 eV by treatment at 450°C; then it was further shifted to 77.8 eV, coinciding with the value for AlF_3 (*10*), by increasing the treatment temperature to 500°C. In addition, the peak due to F1*s* for the samples treated at 450 and 500°C was found at around 688 eV, close to that for AlF_3 (687.3 eV (*11*)). These facts may further substantiate the formation of AlF_3 on the HM surface treated with CFC, which was presented on the basis of XRD data (Fig. 4).

The peak position due to Al2*p*, which was shifted once to the higher binding energy side by the treatment at temperatures lower than 600°C, returned to the value found for untreated HM with the treatment at a high temperature, 600°C. The change of the peak position may result from the reaction of AlF_3 with H_2O or OH groups forming Al_2O_3, as was previously noted.

Configurations of Al and Si Atoms in HM before and after CFC Treatment

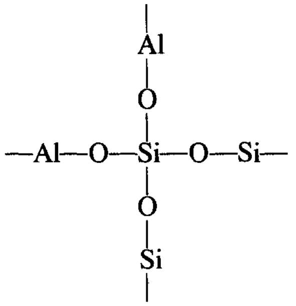
Figure 5 shows the results of ^{29}Si MAS-NMR for HM before and after treatments at temperatures ranging from 450 to 650°C. It has been found that the peak position of ^{29}Si changes with the number of neighboring Si atoms as given below (*12*):

TABLE 4

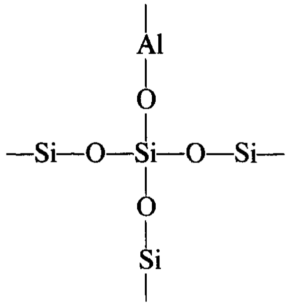
Peak Positions of Surface Components of HM before and after CFC Treatment

Treatment temperature (°C)	Peak position (eV)[a]			
	Si2*p*	Al2*p*	O1*s*	F1*s*
Before treatment	103.1	74.9	532.8	—
450	103.3	75.5	532.9	687.0
500	103.8	77.8	533.5	687.7
600	104.1	77.2	533.5	697.7
650	103.8	74.7	533.2	697.6

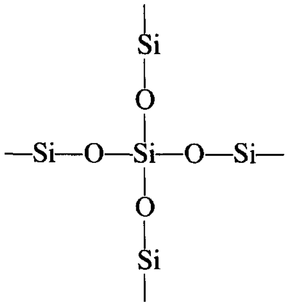
[a] Binding energies were measured by assuming the C1'*s* value of the contaminant carbon as 285 eV.


(a)

-100 ppm


(b)

-105 ppm


(c)

-111 ppm.

With increasing treatment temperature, peaks (a) and (b) gradually decreased, and almost disappeared at 650°C, and peak (c) assignable to Si surrounded by four Si atoms, Si(4Si) or Si(0Al), split more distinctly, and three sharp peaks appeared at 650°C. Apparently the new peaks are assignable to a new surface structure formed by the CFC treatment, such as $(SiO)_3SiF$ and $(SiO)_2(SiF)_2$. However, such a splitting has been observed also in the spectra of the commercial mordenite (Norton, Na^+-Zeolon, with a bulk elemental analysis SiO_2/Al_2O_3 of 10 (*13*)) after repeated treatments with nitric acid and steam. Further, a similar splitting has been found also in the spectra of well-defined silicalite and ZSM-5 samples, where up to nine different peaks assignable to Si(0Al) may be observed (*14*). Consequently, the splitting may not be simply or directly related to the formation of the new structure containing F atoms. At the present stage of this study, it is accepted that the new peaks are assignable to the Si(0Al) groups being present on different sites, which are crystallographically nonequivalent with the original Si(0Al), although further details must be made clear in the near future.

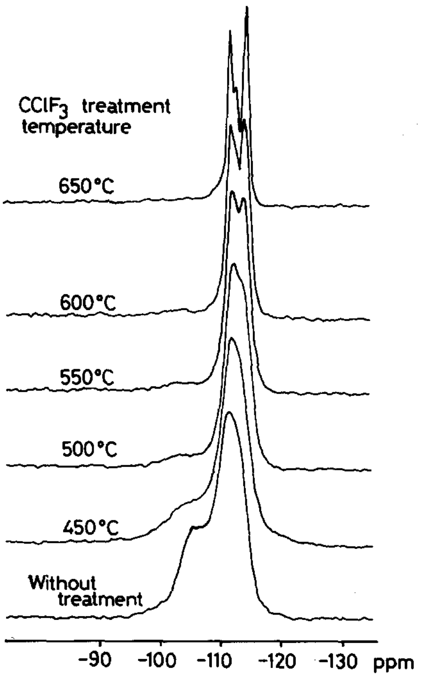


FIG. 5. ^{29}Si MAS-NMR spectra.

Then, the results of ^{27}Al MAS-NMR are presented in Fig. 6. Two peaks were found at 53 ppm and at around 0 ppm for HM before the CFC treatment. The former is assignable to Al atoms constituting the zeolite lattice, and the latter, to the interstitial Al atoms or Al atoms in the channel (*15*). The lattice Al atoms were found to be removed by treatment at a relatively lower temperature such as 450°C and further decreased on increasing the treatment temperature to 600°C. The results were in good accord with previous ^{29}Si MAS-NMR studies. While the interstitial Al atoms appeared

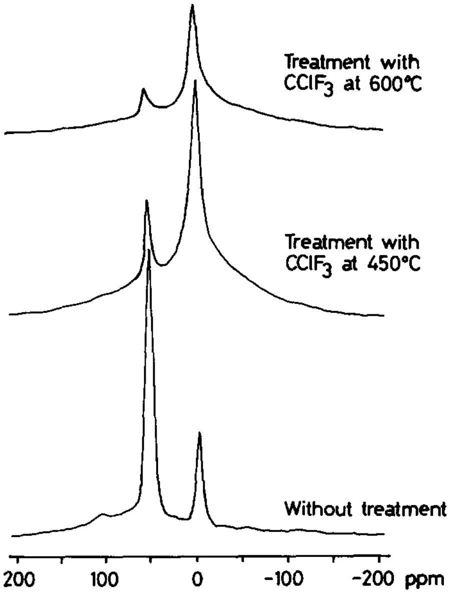


FIG. 6. ^{27}Al MAS-NMR spectra.

to be increased by the treatment at 450°C, the increase may result from the removal of the lattice ions, possibly as $AlCl_3$ and deposition as AlF_3, taking place inside the channel. Most of the deposited AlF_3 was considered to be amorphous because only a slight amount of crystalline AlF_3 was found in the XRD pattern (Fig. 4), especially for the sample treated at a lower temperature, 450°C. Nevertheless, a fairly large amount of fluorine was introduced in HM by the CFC treatment as shown in Table 3. The amorphous AlF_3 should be unstable and so, easily removable through hydrolysis and partly through sublimation at higher temperatures.

Change in Surface Acidity Due to CFC Treatment

As shown by NH_3-TPD (Fig. 7), both the strong and weak acid sites on HM were significantly decreased by the CFC treatment at 450°C. They were further decreased by elevating the treatment temperature, and they almost disappeared at 650°C.

In order to understand the change of acidic character of HM due to the CFC treatment, IR spectra of HM before and after pyridine adsorption were recorded. As shown by a comparison of spectra for pyridine adsorbed on the treated HM (Fig. 8(B)) with those on untreated HM (Fig. 8(A)), both the peak at 1540 cm^{-1}, assignable to Brønsted acid sites, and that at 1450 cm^{-1}, assignable to Lewis acid sites, were weakened by the CFC treatment. In particular, weakening of the Brønsted acid sites appeared more remarkable compared to that of the Lewis acid sites. Most alkylations were reported to be promoted by the Brønsted acid sites (*16*). Then, it was expected that the catalytic activity for the alkylation would be decreased by the treatment. Nevertheless, the catalytic activity for the alkylation was enhanced, as shown previously in Figs. 1 and 2. This discrepancy should suggest that the efficiency or so-called turnover frequency of these active sites on the HM surface may be enhanced by the CFC treatment.

In general, desorptions or removals of reaction products, being highly polar or less volatile, are assumed to be performed less readily, especially in the reaction over an acidic catalyst of zeolytic structure. Thus, desorptions of the products may control the

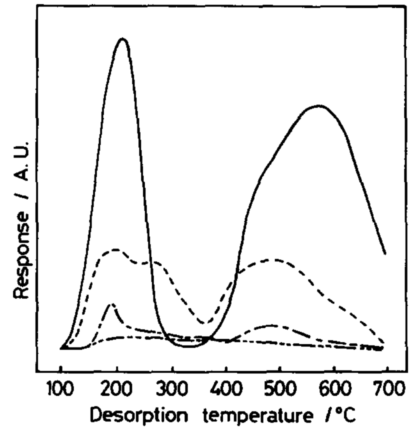


FIG. 7. NH_3-TPD spectra of HM before and after treatment with $CClF_3$. ——: before treatment; ----: after treatment at 450°C; ——: after treatment at 600°C; – ·· –: after treatment at 650°C.

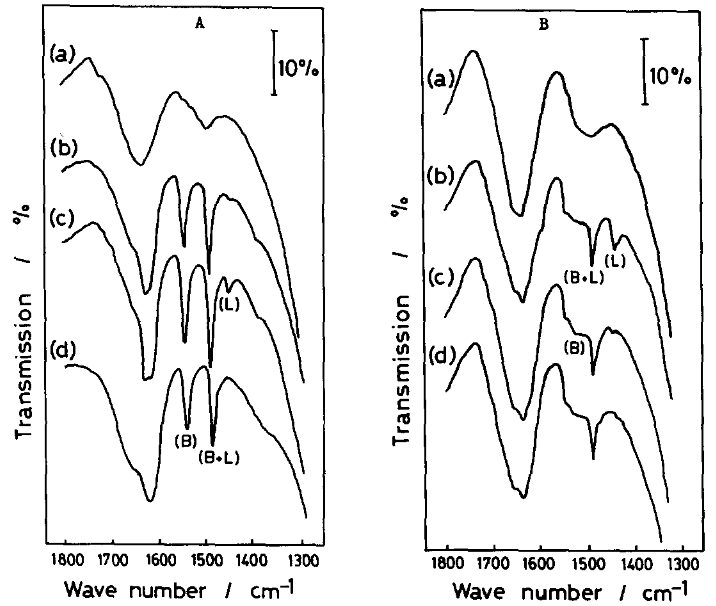


FIG. 8. IR spectra of pyridine adsorbed on HM before (A) and after (B) treatment with $CClF_3$ at 600°C. (a): background; (b) exposed to pyridine vapor followed by evacuation at 100°C; (c) subsequent evacuation at 300°C; (d) exposed to H_2O vapor followed by evacuation at room temperature.

apparent catalytic activity for the alkylations studied here, in which the reaction product is highly polar (H_2O) or less volatile (polyalkylbenzenes).

We have found that SiO_2 (*17*) and Al_2O_3 surface became hydro- and lipophobic by the CFC treatment. Such a change should contribute to promoting desorption of the reaction products, resulting in enhancement of the utility of active sites on HM. In addition, the enlargement of channel size due to elimination of Al (and perhaps also Si) component is probably effective for removal of reaction products.

Changes in Adsorptive Activities for Various Gases

The changes of surface properties due to the CFC treatment were examined by adsorptions of various gases on HM before and after the treatment. As Fig. 9 shows, the adsorptive activities of HM for polar gases such as water and methanol were decreased somewhat by the treatment. In particular, the HM surface turned out to be remarkably hydrophobic with the treatment. This change should be advantageous for desorption of the product, water, resulting in an enhancement of the availability of active sites on HM as described previously.

On the other hand, the adsorbed amount of nonpolar compounds such as benzene and carbon tetrachloride increased with the treatment, as shown in Fig. 10. The results support the foregoing view that the HM channels might be enlarged by the treatment. Therefore, the decrease in the adsorptive activity for polar compounds (shown in Fig. 9) must result from the change of not the structure, but the surface property itself. Thus, it can be deduced that the polarity of the HM surface due to oxygen atoms or partial ions and hydroxyl groups was greatly diminished by replacement of these atoms and groups with fluorine atoms in CFC molecules, resulting in a decrease in the affinity to polar compounds such as water and methanol.

Such a modification of the HM surface

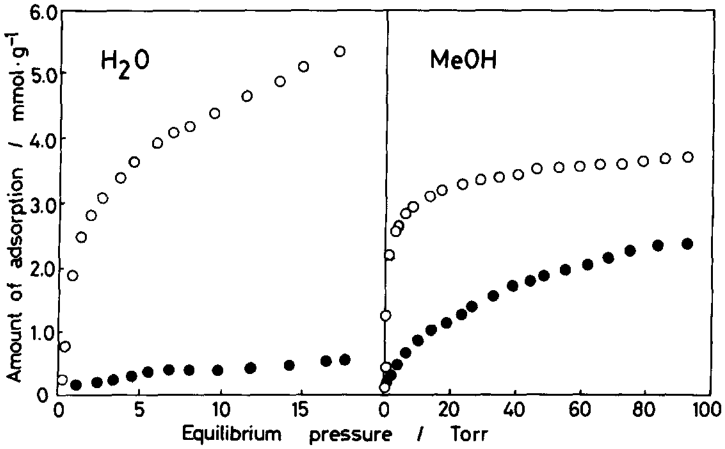


FIG. 9. Adsorption isotherms for H_2O and methanol on HM before (○) and after (●) $CClF_3$ treatment. Samples (0.5 g) fabricated to particles (14–20 mesh) were evacuated at 500°C for 1 h, followed by cooling to 50°C, and were in contadt with H_2O or CH_3OH vapor under various pressure at 50°C. The adsorbed amounts were measured by an ordinary gravimetric method.

property due to surface fluorination is considered to be related to the elimination of excessively strong acid sites promoting olefin formation from methanol and may contribute to the improved activity maintenance of HM together with the enlargement of channel size.

CONCLUSION

In this study, it has been found that the availability of H mordenite as a catalyst for alkylations of benzene, alkylbenzenes, and halobenzenes are remarkably enhanced by the CFC treatment.

There are at least two reasons for the enhancement of the availability. The first one is related to the modification of surface properties, such as surface acidity and adsorptive activity of the zeolite, due to the CFC treatment. Namely, the treatment is effective for the removal of the excessively strong acid sites on the surface which may promote various side reactions, including low polymerization and carbonization tak-

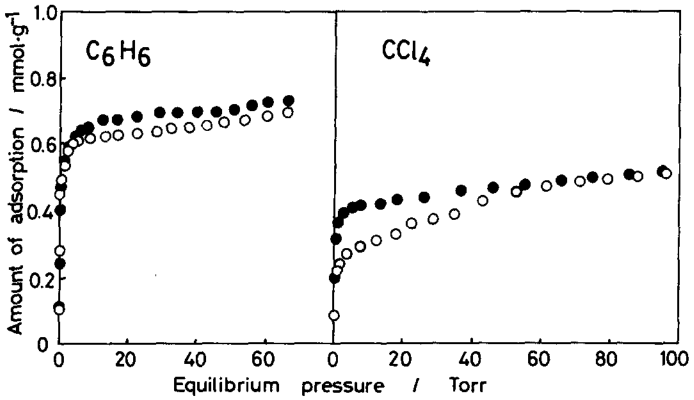


FIG. 10. Adsorption isotherms for benzene and CCl_4 on HM before (○) and after (●) $CClF_3$ treatment. The procedures were similar to those shown in Fig. 9.

ing place on the active sites. The treatment is consequently useful for the improvements of the selectivity for the alkylation and the catalytic activity maintenance. At the same time, the surface is changed to be hydro- and lipophobic by the treatment. Such a change may contribute to the promotion of the desorption or removal of the products such as H_2O and alkylated compounds, resulting in the enhancement of the frequency for the use of active sites on the zeolite.

The second one is concerned with the enlargement of the channel-size resulting from the dealumination. Such an enlargement should be effective for the active migrations of reactants and products. As well as the enhancement of the desorptive activity due to the change of surface property described above, the enlargement should be effective for increasing the frequency of the use of active sites, resulting in the increase in the apparent catalytic activity shown by the increase in the conversion of the reactant.

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