

## Acid Strength Distribution and Catalytic Properties of H-ZSM-5: Effect of Deammoniation Conditions of NH<sub>4</sub>-ZSM-5

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Acid strength distribution, catalytic activity in cumene cracking and *o*-xylene isomerization reactions, and the distribution of hydrocarbons formed in methanol and ethanol conversion reactions on H-ZSM-5 zeolites obtained from NH<sub>4</sub>-ZSM-5 under different deammoniation conditions (i.e., by varying temperature, period, atmosphere and heating rate in the deammoniation) have been studied. The catalytic properties of the zeolites are correlated to their acidity. The acid strength distribution, the cracking and isomerization activities, and the distribution of hydrocarbons in the alcohol conversion reactions on the zeolites are affected by the changes in the temperature, period, and atmosphere employed in the deammoniation, the effect produced by the higher deammoniation temperatures (>873 K) being very drastic. The heating rate employed for attaining the deammoniation temperature has no significant effect on either the acidity distribution or the catalytic properties of the zeolite. The conversion of cumene, the xylene isomerization activity, and the extent of aromatization in the alcohol conversion reactions on the zeolites could be very satisfactorily correlated to the number of strong acid sites on which pyridine is adsorbed irreversibly at 673 K.

### INTRODUCTION

Since 1972 when Mobil Oil Corporation introduced (1) a new high-silica zeolite designated as ZSM-5, this zeolite has been gaining more and more importance as a high-potential catalyst in a number of commercially important reactions, such as conversion of methanol (2-4) and ethanol (5-7) to gasoline and aromatics, isomerization of xylenes (8), disproportionation of toluene (9), alkylation of benzene (10, 11) and toluene (12, 13), aromatization of olefins (14, 15), hydrodewaxing of oils (16), etc. These unique catalytic properties of the zeolite are attributed to both its strong acid sites and the three-dimensional system of intersecting channels (17), made up of elliptical straight channels (0.51 × 0.55 nm) and near-circular zig-zag channels (0.54 × 0.5 nm) (18).

ZSM-5 zeolite in its protonated form can be obtained by the thermal decomposition of the NH<sub>4</sub>-exchanged form of the zeolite.

The conditions employed for the deammoniation of NH<sub>4</sub>-ZSM-5 zeolite (temperature, period, atmosphere, and heating rate) are expected to affect the acidity distribution and catalytic properties of H-ZSM-5 zeolite. However, the extent to which the acidic and catalytic properties of H-ZSM-5 are affected by the different deammoniation conditions has not been investigated.

The objective of the present work was to investigate the effect of the deammoniation conditions on the acid strength distribution and catalytic properties of H-ZSM-5 obtained from NH<sub>4</sub>-ZSM-5. The acid strength distribution on the zeolites was measured at near reaction temperatures by the gas chromatographic adsorption/desorption methods (19) involving stepwise thermal desorption (STD) of pyridine and temperature-programmed desorption (TPD) of pyridine under chromatographic conditions. The catalytic activity of the zeolites in the cracking of cumene, isomerization of *o*-xylene, and the conversion of methanol and ethanol to hydrocarbons at 673 K was determined using a pulse micro-

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reactor and the catalytic activity and the acidity of the zeolite are correlated.

#### EXPERIMENTAL

TPA-ZSM-5 (Si/Al = 17.2) was prepared by the method described elsewhere (1). It was heated in air at 813 K for 12 hr to oxidize the organic part and treated with 1 M NH<sub>4</sub>NO<sub>3</sub> solution at 353 K repeatedly. The exchanged zeolite was dried in air at 393 K for 4 hr, powdered, pressed without any binder, and crushed and sieved to get particles of 0.2–0.3 mm size. The unit cell composition of the NH<sub>4</sub>-ZSM-5 was (NH<sub>4</sub>)<sub>5.22</sub>Na<sub>0.06</sub>Al<sub>5.28</sub>Si<sub>90.72</sub>O<sub>192</sub>.

The deammoniation conditions employed for obtaining H-ZSM-5 [I–XIV] are given in Table 1. In order to maintain a particular atmosphere, the gases dried over molecular sieves were passed through the catalyst bed at the flow rate of 10 cm<sup>3</sup> min<sup>-1</sup>. It may be noted that the deammoniation conditions were varied systematically one at a time, keeping the others constant.

The TPA-ZSM-5, NH<sub>4</sub>-ZSM-5, and H-

ZSM-5 [I–V] were analyzed for their crystallinity by the X-ray powder diffraction method using a Holland Philips, PW 1730 X-ray generator with a Ni-filtered Cu K $\alpha$  radiation source and a scintillation counter. The *d*-spacing values for all the zeolites were the same and were found to match exactly with those reported earlier (1, 20). However, an enhancement of the peaks at low angles due to replacement of TPA ions by NH<sub>4</sub><sup>+</sup> ions or protons, and a small decrease in the intensity of the peaks for the zeolites obtained at high deammoniation temperatures were observed.

A Perkin-Elmer Sigma 3B gas chromatograph fitted with a flame ionization detector was used for measuring the acid strength distribution and for analyzing the products of the catalytic reactions on the zeolites.

The acidity distribution of the H-ZSM-5 zeolites, obtained from the NH<sub>4</sub>-ZSM-5 under the different deammoniation conditions, was investigated by the adsorption/desorption of pyridine at catalytically important temperatures and studying the TPD of pyridine under chromatographic condi-

TABLE 1  
Deammoniation Conditions Employed for Obtaining H-ZSM-5 Zeolites from NH<sub>4</sub>-ZSM-5

Zeolite formed	Atmosphere	Deammoniation temperature, $T_{DA}$ (K)	Heating rate, $\beta$ (K · min <sup>-1</sup> )	Deammoniation period $t_{DA}$ (hr)
H-ZSM-5 [I]	Air	673	2.5	12
H-ZSM-5 [II]	Air	773	2.5	12
H-ZSM-5 [III]	Air	873	2.5	12
H-ZSM-5 [IV]	Air	1073	2.5	12
H-ZSM-5 [V]	Air	1223	2.5	12
H-ZSM-5 [VI]	Air	773	2.5	1
H-ZSM-5 [VII]	Air	773	2.5	4
H-ZSM-5 [VIII]	Air	773	2.5	48
H-ZSM-5 [IX]	Nitrogen	773	2.5	12
H-ZSM-5 [X]	Hydrogen	773	2.5	12
H-ZSM-5 [XI]	Vacuum	773	2.5	12
H-ZSM-5 [XII]	Moist nitrogen <sup>a</sup>	773	2.5	12
H-ZSM-5 [XIII]	Air	773	20.0	12
H-ZSM-5 [XIV]	Air	773	Flash <sup>b</sup>	12

<sup>a</sup> Partial pressure of water = 4.5 kPa.

<sup>b</sup> The NH<sub>4</sub>-ZSM-5 was directly subjected to the deammoniation temperature of 773 K.

tions on the zeolites presaturated with the irreversibly adsorbed pyridine at 673 K. A catalyst column was prepared by packing 0.2 g of the catalyst in a stainless-steel tube (i.d.: 2 mm; o.d.: 3 mm; and length: 15 cm). One end of the column was directly connected to the detector and the other end to the injection block through a 60-cm-long stainless-steel capillary (o.d.: 1.5 mm; i.d.: 0.7 mm), which acted as the preheater. Prior to the measurements, the catalyst was heated at 673 K for 1 hr in the flow of nitrogen.

The initial concentration of pyridine adsorbed reversibly at 673 K was kept the same on all the catalysts in the TPD study. The TPD data for all the zeolites were collected under identical conditions (viz., weight of the zeolite: 0.2 g; N<sub>2</sub> flow rate: 10 cm<sup>3</sup> · min<sup>-1</sup>; initial temperature: 373 K; final temperature 673 K; initial surface concentration of reversibly adsorbed pyridine at 673 K: 0.62 mmol · g<sup>-1</sup>; and linear heating rate: 10 K · min<sup>-1</sup>) by injecting a known amount of pyridine in the catalyst column at 373 K, allowing a period of 1 min to elapse for the redistribution of the base on the catalyst, and starting TPD in the flow of nitrogen.

The STD of pyridine was carried out as follows. The catalyst was saturated with the base at 513 K by injecting a pyridine pulse and the reversibly adsorbed pyridine at this temperature was desorbed in the flow of nitrogen. Pyridine chemisorbed irreversibly at 513 K was desorbed thermally in the flow of nitrogen (10 cm<sup>3</sup> · min<sup>-1</sup>) by heating the catalyst from 513 to 673 K in four steps (each representing a jump of 40 K). The temperature in each step was raised at a linear heating rate of 10 K · min<sup>-1</sup>. After the maximum temperature of the respective step was attained, it was maintained for a period of 1 hr to desorb the base reversibly adsorbed on the catalyst at that temperature. The amount of irreversibly adsorbed pyridine desorbed in a step due to the increase in temperature from  $T_1$  to  $T_2$  is obtained from the relation

$$[q_d]_{T_1}^{T_2} = A_d/[S \cdot W], \quad (1)$$

where  $[q_d]_{T_1}^{T_2}$  is the amount of pyridine desorbed between temperatures  $T_1$  and  $T_2$ ;  $A_d$  is the area under the desorption chromatogram;  $S$  is the detector sensitivity; and  $W$  is the weight of the catalyst. The amount of pyridine irreversibly chemisorbed at different temperatures  $[q_{i(T)}]$  was calculated from the STD data as follows:

$$q_{i(T)} = q_{i(673 \text{ K})} + [q_d]_{T_1}^{673}, \quad (2)$$

where  $q_{i(T)}$  is the amount of pyridine irreversibly adsorbed at temperature  $T$ . The irreversible adsorption at 673 K was determined by the pulse method (21).

The irreversible adsorption in the present study is defined as the amount of base retained by the presaturated catalyst after it was swept with pure nitrogen for a period of 1 hr.

The catalytic activities in the cracking of cumene, the isomerization of *o*-xylene, and in the conversions of methanol and ethanol were measured using a pulse microreactor. The experiments in the pulse microreactor (i.d.: 4 mm) combined with the gas chromatograph were carried out under the following conditions: for cumene cracking and *o*-xylene isomerization: amount of catalyst = 0.05 g; catalyst bed length = 5.0 mm; N<sub>2</sub> flow rate = 780 cm<sup>3</sup> · min<sup>-1</sup>; reaction temperature = 673 K; total pressure = 370 kPa; and pulse size = 0.07 mmol; and for methanol and ethanol conversion reactions: amount of catalyst = 0.1 g; catalyst bed length = 10 mm; N<sub>2</sub> flow rate = 24.5 cm<sup>3</sup> · min<sup>-1</sup>; reaction temperature = 673 K; total pressure = 244 kPa; and pulse size = 0.049 (methanol) and 0.034 (ethanol) mmol. The reaction products of the cracking and isomerization reactions were analyzed using a column of Carbowax 20M (10%) on Chromosorb-W (3 mm × 2 m) at 343 K (carrier N<sub>2</sub> flow rate = 40 cm<sup>3</sup> · min<sup>-1</sup>), while for analyzing the products of the alcohol conversion reactions, a column of Bentone-34 (5%) and dinonyl phthalate (5%) on Chromosorb-W (3 mm × 6.6 m) was used with

the column temperature programmed from 323 to 363 K at the rate of 5 K · min<sup>-1</sup>; the initial and final temperatures were held for 10 and 30 min, respectively.

## RESULTS

### Acidity of H-ZSM-5 Zeolites

In order to ascertain the extent to which the acid strength distribution of H-ZSM-5 zeolite is affected by the different deammoniation conditions employed for its preparation from NH<sub>4</sub>-ZSM-5, the zeolites obtained under different conditions were characterized by the TPD and STD of pyri-

dine at temperatures close to those employed in catalytic reactions and also by studying the model reactions, cracking of cumene and isomerization of *o*-xylene, catalyzed by the protonic acid sites (22). In this paper the acid sites which adsorb pyridine irreversibly at 673 K are considered strong acid sites.

*TPD of pyridine under chromatographic conditions.* The TPD chromatograms of pyridine showing the effect of deammoniation temperature [ $T_{DA}$ ] and period [ $t_{DA}$ ] on the strength distribution of weak acid sites, which can adsorb pyridine irreversibly at

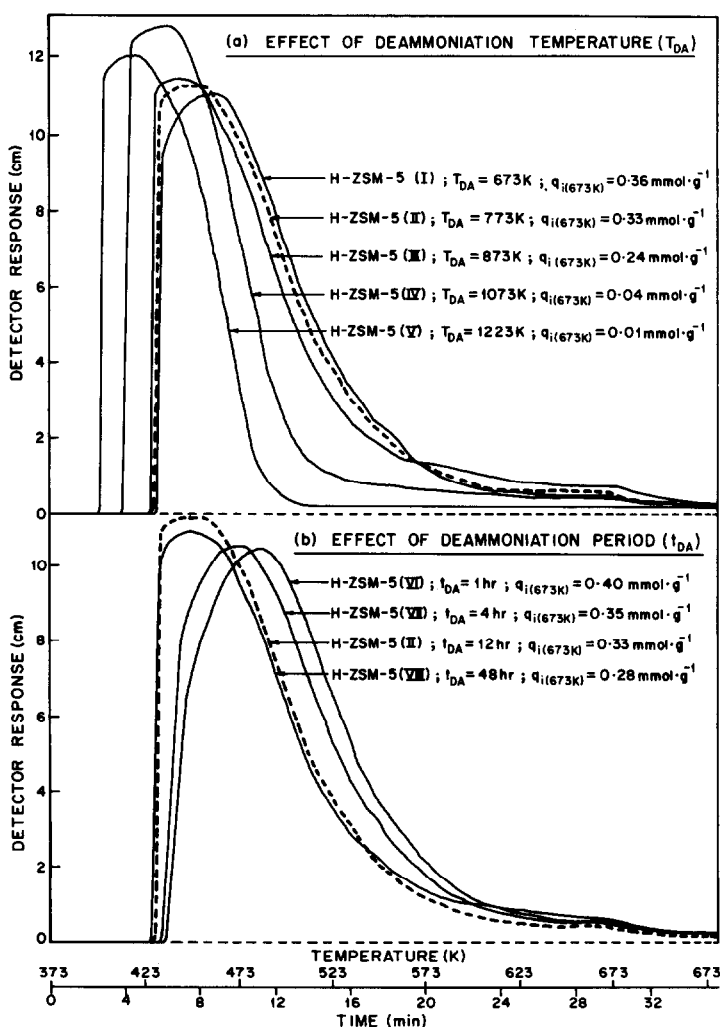


FIG. 1. TPD chromatograms of pyridine on H-ZSM-5 [I–VIII] zeolites.

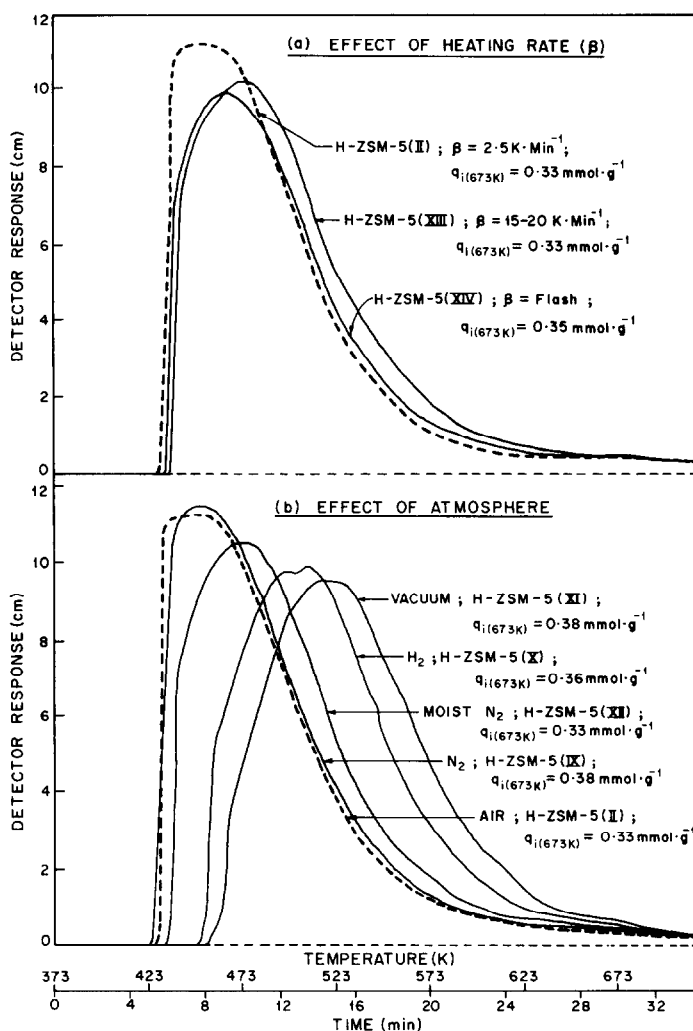


FIG. 2. TPD chromatograms of pyridine on H-ZSM-5 [I, IX-XIV] zeolites.

temperatures below 673 K, are shown in Fig. 1. The TPD chromatograms of pyridine in Fig. 2 show the effect of heating rate [ $\beta$ ] employed for attaining the final deammoniation temperature, and the effect of the atmosphere in which the deammoniation of  $\text{NH}_4$ -ZSM-5 was carried out on the distribution of weak acid sites. It may be noted that all these TPD chromatograms were obtained on the zeolites presaturated with the irreversibly adsorbed pyridine at 673 K at the same initial concentration of reversibly adsorbed pyridine at that temperature. The corresponding values of the irreversible ad-

sorption of pyridine at 673 K,  $q_{i(673\text{K})}$  are given in the figures. In the TPD, the desorption started at a temperature much higher than the boiling point of pyridine, indicating that the base was chemisorbed on the zeolites at the start of TPD.

The comparison of the TPD chromatograms in Figs. 1 and 2 shows that the strength distribution of the weak acid sites (which can adsorb pyridine irreversibly at  $<673\text{K}$ ) is affected by the change in the deammoniation conditions. The TPD curves shift more and more toward the lower energy region and become narrower

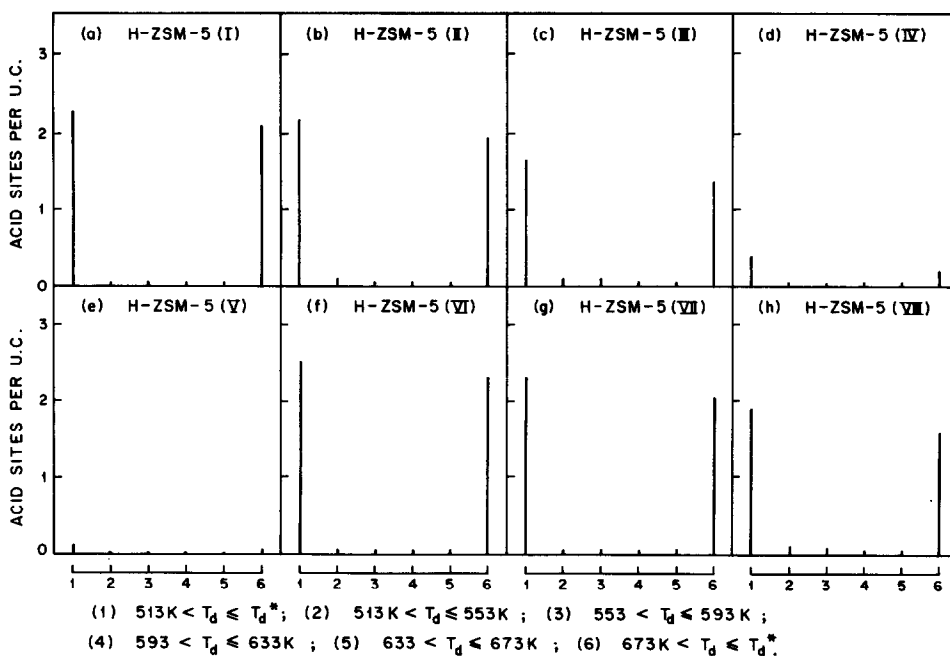


FIG. 3. Acid strength distribution of H-ZSM-5 [I-VIII] zeolites obtained from NH<sub>4</sub>-ZSM-5 under different deammoniation conditions.

with the increase in the temperature and the period of deammoniation; and with the change in the atmosphere, the shift is in the following order: vacuum > H<sub>2</sub> > moist N<sub>2</sub> > N<sub>2</sub> > air.

*STD of pyridine.* The acid strength distributions of H-ZSM-5 [I-XIV] zeolites [prepared under the different deammoniation conditions (Table 1)], obtained from the STD data, are shown in Figs. 3 and 4. The first column in each of the acidity distributions for the different zeolites shown in the figures represents the number of acid sites having acid strength of  $513\text{ K} < T_d \leq T_d^*$  (expressed in terms of desorption temperatures) present in the zeolite, while the other columns show the strength distribution of the total acid sites. The number of sites with acid strengths  $513\text{ K} < T_d \leq T_d^*$  and  $673\text{ K} < T_d \leq T_d^*$  were determined from the amount of pyridine adsorbed irreversibly at 513 and 673 K, respectively, while the sites of acid strength  $T_1 < T_d \leq T_2$  were obtained from the amount of pyridine, which was initially adsorbed irreversibly at  $T_1$ , subse-

quently desorbed when the temperature was increased from  $T_1$  to  $T_2$ .

In the determination of acid sites from the amount of adsorbed or desorbed pyridine, it is assumed that one acid site is involved in the adsorption of one pyridine molecule. The strength of the acid site is expressed in terms of the desorption temperature of pyridine,  $T_d$ , which lies in the range of temperature in which the irreversibly adsorbed pyridine gets desorbed.  $T_d^*$  is the maximum acid strength possessed by the site and corresponds to the temperature at which the pyridine adsorbed irreversibly on the strongest site is desorbed.

The temperature dependence of the irreversible adsorption of pyridine on H-ZSM-5 [I-XIV] zeolites, showing the effects of the various deammoniation conditions on the irreversible adsorption, is shown in Fig. 5. In all the cases the quantity of irreversibly adsorbed base decreases almost linearly with the adsorption temperature.

Figures 3-5 show that both the total acid sites (measured in terms of quantity of pyri-

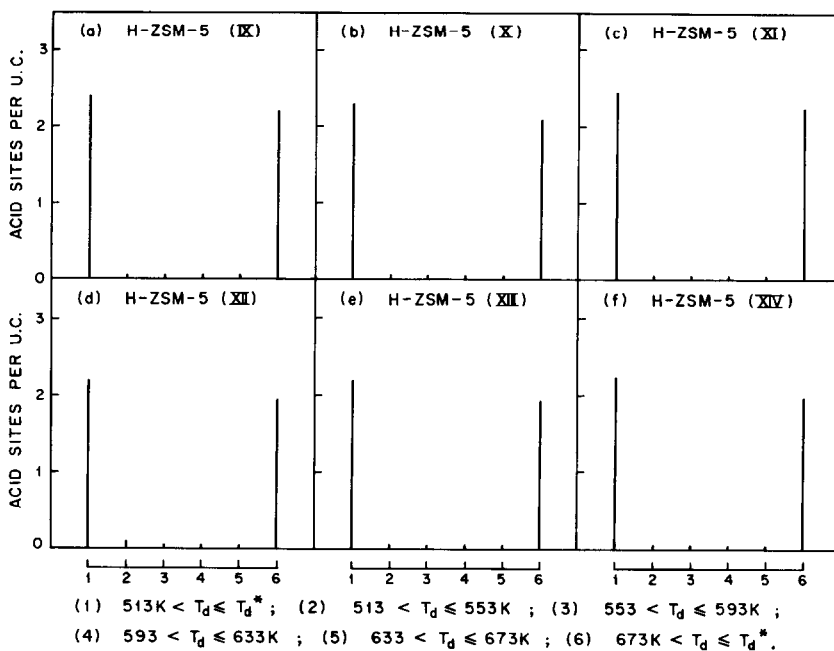


FIG. 4. Acid strength distribution of H-ZSM-5 [IX-XIV] zeolites obtained from  $\text{NH}_4$ -ZSM-5 under different deammoniation conditions.

dine irreversibly adsorbed at 513 K) and the strong acid sites (measured in terms of the quantity of pyridine irreversibly adsorbed at 673 K) decrease with the increase in the deammoniation temperature and period, and also with the change in the atmosphere. This decrease is in the following order: vacuum >  $\text{N}_2$  >  $\text{H}_2$  > moist  $\text{N}_2$  > air. However, the heating rate at which the final deammoniation temperature (773 K) is attained has no significant effect on the acidity distribution of the zeolite. When H-ZSM-5 [IV] (obtained by deammoniation at 1073 K) was rehydrated by passing water vapors over the zeolite at 773 K for 8 hr, the amount of pyridine adsorbed irreversibly on the rehydrated zeolite was found to be 0.025, 0.017, 0.011, 0.008, and 0.006  $\text{mmol} \cdot \text{g}^{-1}$  at 513, 553, 593, 633, and 673 K, respectively.

#### Catalytic Activity in Cumene Cracking and *o*-Xylene Isomerization

The variation in the catalytic activity (measured in terms of the fractional conver-

sion [ $x$ ] of cumene and *o*-xylene in the cracking and isomerization reactions, respectively) at 673 K and the number of strong acid sites with the deammoniation temperature [ $T_{\text{DA}}$ ] and period [ $t_{\text{DA}}$ ] is shown in Fig. 6. The catalytic activity for the two reactions at 673 K on the zeolites obtained by the deammoniation in different atmospheres and at different heating rates [ $\beta$ ] is given in Table 2.

Figure 6 reveals that the activity of the catalyst in both the cracking and isomerization reactions decreases with the increase in the temperature and period of deammoniation. The conversion data in Table 2 indicate that (a) the effect of the nature of the atmosphere on the catalytic activity for both the reactions is only slight, the activity being in the following order: Vacuum >  $\text{N}_2$  > air >  $\text{H}_2$  > moist  $\text{N}_2$  and (b) the effect of heating rate on the catalytic activity is not significant.

The dependence of the conversion of cumene and *o*-xylene in the cracking and isomerization reactions, respectively, on

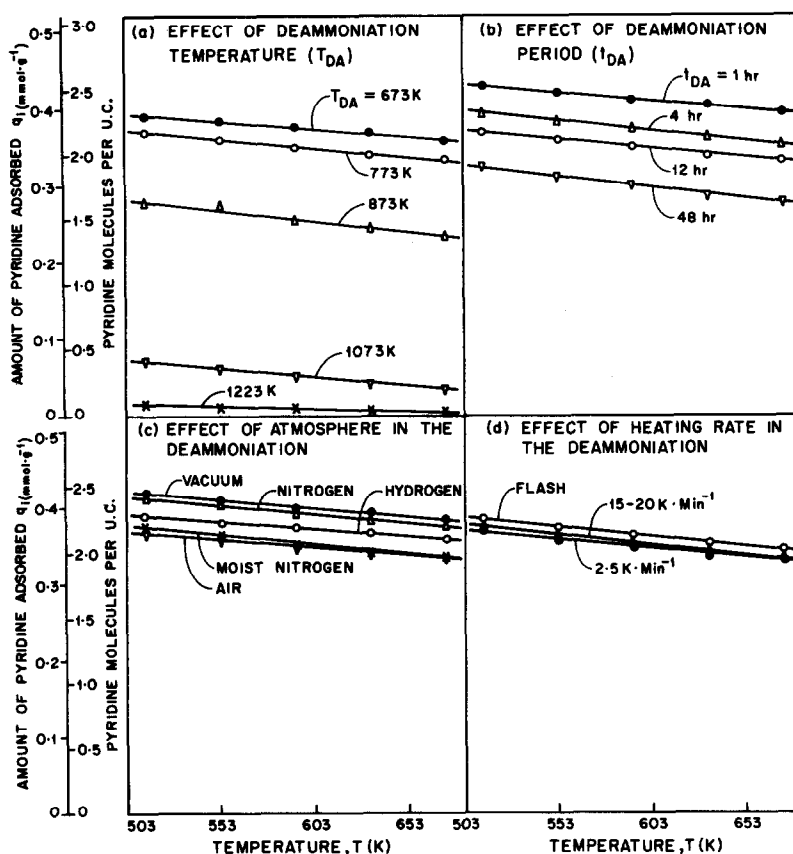


FIG. 5. Variation of irreversible adsorption of pyridine on H-ZSM-5 [I-XIV] zeolites (obtained from NH<sub>4</sub>-ZSM-5 under different deammoniation conditions) with temperature.

TABLE 2

Activity of H-ZSM-5 Zeolites, Obtained by Deammoniation in Different Atmospheres, under Vacuum, and Using Different Heating Rates, in Cracking of Cumene and Isomerization of *o*-Xylene

Deammoniation condition	Zeolite	Fractional conversion [x]	
		Cumene <i>o</i> -Xylene	
<b>Atmosphere</b>			
Air	H-ZSM-5 [II]	0.786	0.148
Nitrogen	H-ZSM-5 [IX]	0.809	0.150
Hydrogen	H-ZSM-5 [X]	0.769	0.147
Vacuum	H-ZSM-5 [XI]	0.813	0.159
Moist nitrogen	H-ZSM-5 [XII]	0.718	0.136
<b>Heating rate [β]</b>			
2.5 K · min <sup>-1</sup>	H-ZSM-5 [III]	0.786	0.148
15-20 K · min <sup>-1</sup>	H-ZSM-5 [XIII]	0.784	0.154
Flash	H-ZSM-5 [XIV]	0.787	0.144

the number of strong acid sites on the zeolite is shown in Fig. 7. The data on the H · Na-ZSM-5 zeolites having the same Si/Al ratio as that of the zeolite used in the present investigation but with different degrees of H<sup>+</sup> exchange (23) are also included in the figure.

In the case of *o*-xylene isomerization, the conversion increases linearly with the number of strong acid sites.

#### Methanol and Ethanol Conversion Reactions

Distribution of the hydrocarbons in the products of the reaction of methanol on H-ZSM-5 [I-XIV] at 673 K in a pulse micro-reactor is given in Tables 3 and 4; while that of the reaction of ethanol on the zeolites is given in Tables 5 and 6. In both the reac-



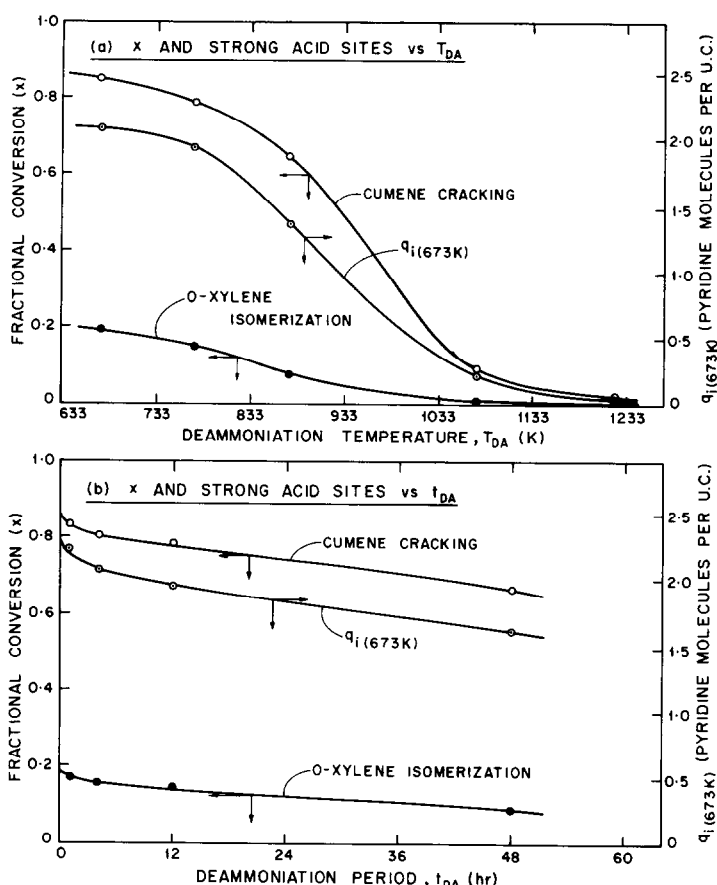


FIG. 6. Variation of the conversion of cumene and *o*-xylene and irreversible adsorption of pyridine molecules at 673 K [ $q_i(673\text{ K})$ ] with the deammoniation temperature and period on the H-ZSM-5 zeolites.

tions, the concentrations of aliphatics (olefins and saturated hydrocarbons) increase with the deammoniation temperature, the increase being very significant above 873 K (Tables 3 and 5), while the concentrations of most of the aromatics (viz., benzene, toluene, xylenes, and  $C_{9+}$  aromatics) decrease (Tables 3 and 5).

Figure 8 shows the effect of the deammoniation temperature on the distribution of aromatics produced in the alcohol conversion reactions. It can also be noted that the change in the deammoniation temperature from 673 to 873 K causes no significant effect on the distribution of aromatic hydrocarbons formed in the two reactions. However, a very significant effect on the

distribution is observed above the deammoniation temperature of 873 K.

The effect of the deammoniation temperature on the distribution of xylene isomers is shown in Fig. 9. In both the reactions the distribution is not affected up to the deammoniation temperature of 873 K, but above this temperature the ratios of *p*- to *o*-xylene and *p*- to *m*-xylene increase exponentially with increase in deammoniation temperature.

The concentration of *p*-ethyl toluene in ethyl toluenes formed in both the reactions (Tables 3 and 5) increases very sharply when the deammoniation temperature is increased above 873 K.

The total integration counts for the chro-

TABLE 3

Product Distribution in the Reaction of Methanol on H-ZSM-5 [I-VIII] Obtained from NH<sub>4</sub>-ZSM-5 under Different Deammoniation Conditions

Conversion (%):	H-ZSM-5							
	I	II	III	IV	V	VI	VII	VIII
	100	100	100	100	100	100	100	100
	Concentration of hydrocarbons (wt%)							
Aliphatics	72.06	72.21	77.18	92.64	99.34	72.10	72.56	79.17
Benzene	2.97	2.90	2.18	0.20	0.00	2.91	2.89	1.70
Toluene	10.57	10.38	8.68	1.32	0.10	10.40	10.31	7.07
Ethyl benzene	0.31	0.33	0.32	0.49	0.04	0.31	0.31	0.29
<i>p</i> -Xylene	2.53	2.53	2.27	1.89	0.33	2.55	2.48	2.02
<i>m</i> -Xylene	5.69	5.73	4.72	0.90	0.03	5.79	5.76	4.41
<i>o</i> -Xylene	2.61	2.63	2.13	0.21	0.00	2.61	2.58	2.27
[Total xylenes]	[10.83]	[10.89]	[9.12]	[3.00]	[0.36]	[10.95]	[10.82]	[8.70]
<i>p</i> -Ethyl toluene	0.18	0.16	0.16	0.74	0.11	0.25	0.14	0.13
<i>m</i> -Ethyl toluene	0.41	0.42	0.40	0.44	0.00	0.35	0.28	0.30
<i>o</i> -Ethyl toluene	0.12	0.19	0.13	0.00	0.00	0.10	0.13	0.06
Trimethyl benzenes and other aromatics	2.55	2.52	1.83	1.17	0.05	2.63	2.56	2.58
[Total C <sub>9+</sub> aromatics]	[3.26]	[3.29]	[2.52]	[2.33]	[0.16]	[3.33]	[3.11]	[3.07]
Total	100	100	100	100	100	100	100	100

TABLE 4

Product Distribution in the Reaction of Methanol on H-ZSM-5 [IX-XIV] Obtained from NH<sub>4</sub>-ZSM-5 under Different Deammoniation Conditions

Conversion (%):	H-ZSM-5					
	IX	X	XI	XII	XIII	XIV
	100	100	100	100	100	100
	Concentration of hydrocarbons (wt%)					
Aliphatics	73.22	75.10	72.13	75.16	72.66	72.72
Benzene	2.72	2.29	2.93	2.15	2.73	2.77
Toluene	10.04	9.22	10.25	9.21	10.22	10.34
Ethyl benzene	0.34	0.39	0.27	0.30	0.31	0.31
<i>p</i> -Xylene	2.47	2.35	2.54	2.34	2.51	2.48
<i>m</i> -Xylene	5.66	5.57	5.72	5.44	5.75	5.70
<i>o</i> -Xylene	2.37	2.17	2.58	2.38	2.58	2.56
[Total xylenes]	[10.50]	[10.09]	[10.84]	[10.16]	[10.84]	[10.74]
<i>p</i> -Ethyl toluenes	0.14	0.16	0.13	0.20	0.14	0.13
<i>m</i> -Ethyl toluenes	0.32	0.38	0.39	0.44	0.34	0.32
<i>o</i> -Ethyl toluenes	0.17	0.04	0.17	0.17	0.23	0.18
Trimethyl benzenes and other aromatics	2.55	2.33	2.89	2.21	2.53	2.49
[Total C <sub>9+</sub> aromatics]	[3.18]	[2.91]	[3.58]	[3.02]	[3.24]	[3.12]
Total	100	100	100	100	100	100

TABLE 5

Product Distribution in the Reaction of Ethanol on H-ZSM-5 [I-VIII] Obtained from NH<sub>4</sub>-ZSM-5 under Different Deammoniation Conditions

Conversion (%):	H-ZSM-5							
	I	II	III	IV	V	VI	VII	VIII
	100	100	100	100	100	100	100	100
	Conversion of hydrocarbons (wt%)							
Aliphatics	68.81	69.64	72.92	93.71	96.06	69.21	69.40	73.18
Benzene	4.33	4.22	3.65	0.35	0.15	4.28	4.20	3.55
Toluene	13.68	13.33	11.94	1.33	0.79	13.54	13.50	12.01
Ethyl benzene	0.73	0.71	0.74	0.56	0.38	0.71	0.69	0.79
<i>p</i> -Xylene	2.27	2.22	2.01	1.04	1.30	2.23	2.12	1.98
<i>m</i> -Xylene	5.14	5.02	4.58	0.92	0.23	5.12	5.03	4.30
<i>o</i> -Xylene	2.35	2.30	2.02	0.61	0.08	2.30	2.22	1.91
[Total xylenes]	[9.76]	[9.54]	[8.61]	[2.57]	[1.61]	[9.65]	[9.37]	[8.19]
<i>p</i> -Ethyl toluene	0.29	0.29	0.21	0.51	0.68	0.27	0.28	0.28
<i>m</i> -Ethyl toluene	0.64	0.60	0.60	0.41	0.03	0.61	0.63	0.67
<i>o</i> -Ethyl toluene	0.15	0.19	0.11	0.00	0.00	0.15	0.18	0.15
Trimethyl benzenes and other aromatics	1.61	1.48	1.22	0.56	0.30	1.58	1.75	1.18
[Total C <sub>9+</sub> aromatics]	[2.69]	[2.56]	[2.14]	[1.48]	[1.01]	[2.61]	[2.84]	[2.28]
Total	100	100	100	100	100	100	100	100

TABLE 6

Product Distribution in the Reaction of Ethanol on H-ZSM-5 [IX-XIV] Obtained from NH<sub>4</sub>-ZSM-5 under Different Deammoniation Conditions

Conversion (%):	H-ZSM-5					
	IX	X	XI	XII	XIII	XIV
	100	100	100	100	100	100
	Concentration of hydrocarbons (wt%)					
Aliphatics	70.00	71.91	69.13	72.88	69.91	70.44
Benzene	4.02	3.82	4.26	3.68	4.25	4.18
Toluene	13.03	12.30	13.62	12.12	13.35	13.01
Ethyl benzene	0.80	0.97	0.68	0.71	0.67	0.65
<i>p</i> -Xylene	2.24	2.13	2.28	2.00	2.16	2.19
<i>m</i> -Xylene	5.01	4.66	5.06	4.54	4.95	4.90
<i>o</i> -Xylene	2.34	1.83	2.39	1.83	2.21	2.23
[Total xylenes]	[9.59]	[8.62]	[9.73]	[8.37]	[9.32]	[9.32]
<i>p</i> -Ethyl toluene	0.31	0.29	0.26	0.26	0.26	0.26
<i>m</i> -Ethyl toluene	0.63	0.70	0.59	0.61	0.60	0.59
<i>o</i> -Ethyl toluene	0.19	0.18	0.19	0.15	0.17	0.17
Trimethyl benzenes and other aromatics	1.43	1.21	1.54	1.22	1.47	1.38
[Total C <sub>9+</sub> aromatics]	[2.56]	[2.38]	[2.58]	[2.24]	[2.50]	[2.40]
Total	100	100	100	100	100	100

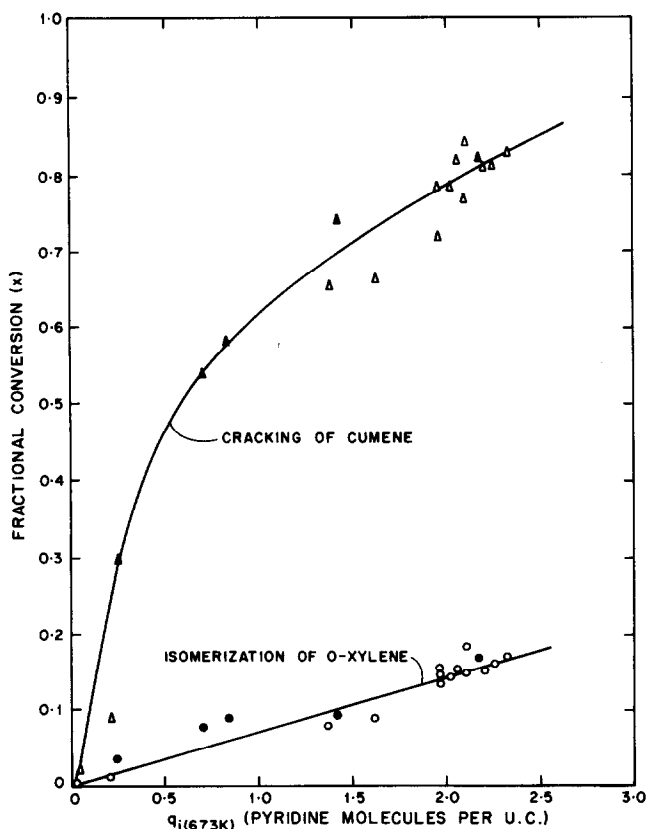


FIG. 7. Variation of the conversion of cumene and *o*-xylene at 673 K with the corresponding irreversible adsorption of pyridine molecules at 673 K [ $q_{i(673K)}$ ] on the H-ZSM-5 zeolites.  $\blacktriangle$ ,  $\bullet$ —Represent data on H-ZSM-5 zeolites obtained from  $\text{NH}_4\text{-ZSM-5}$  zeolites having different degrees of  $\text{NH}_4^+$  exchange under identical deammoniation conditions.

matograms of the hydrocarbons produced in the two reactions on the zeolites obtained at deammoniation temperatures up to 873 K were more or less the same. However, the corresponding integration counts for the hydrocarbons formed on the zeolites obtained at the deammoniation temperatures of 1073 and 1223 K were fewer by about 8 and 40%, respectively, for the reaction of methanol and by about 20 and 30%, respectively, for the reaction of ethanol than those observed in the former case. This fact indicates that in both the reactions, certain amounts of hydrocarbons are retained on the zeolite obtained at higher deammoniation temperatures (above 873 K).

From the distribution of hydrocarbon

products on H-ZSM-5 [II, VI-VIII] in the reaction of methanol (Table 3) and ethanol (Table 5), it can be noted that the distribution of the products in both the reactions is not affected significantly by the variation in the deammoniation period from 1 to 12 hr. However, when the deammoniation period is increased from 12 to 48 hr, the concentration of aliphatic hydrocarbons increases from 72.2 to 79.2% and from 69.6 to 73.2% in the reactions of methanol and ethanol, respectively.

Figure 10 shows the effect of the deammoniation period on the distribution of aromatic hydrocarbons formed in the reaction of methanol and ethanol on H-ZSM-5 zeolite.

The ratios of xylene isomers (Tables 3

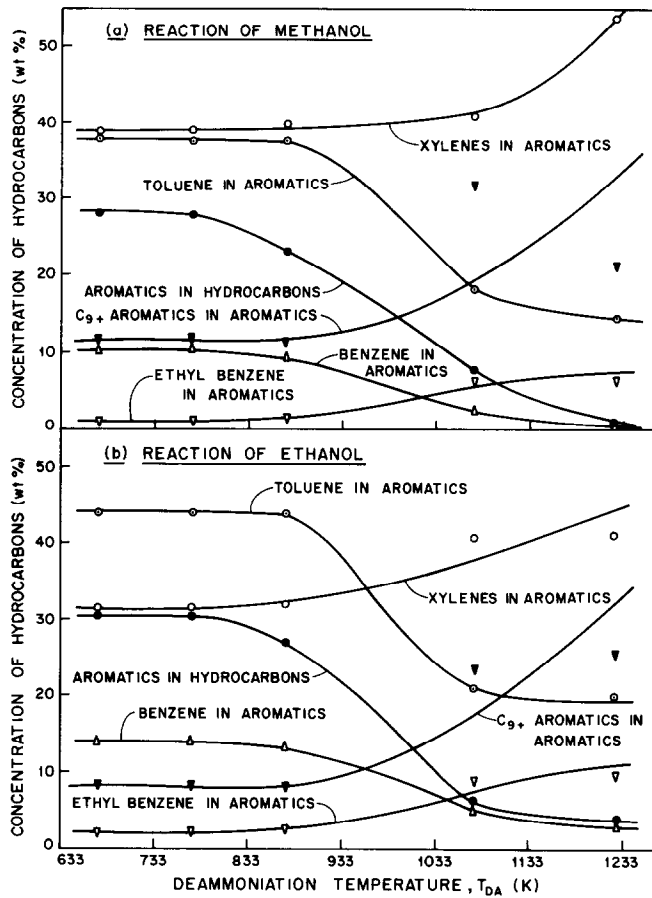


FIG. 8. Dependence of the distribution of aromatics formed in the reactions of methanol and ethanol on deammoniation temperature [ $T_{DA}$ ] of  $NH_4$ -ZSM-5.

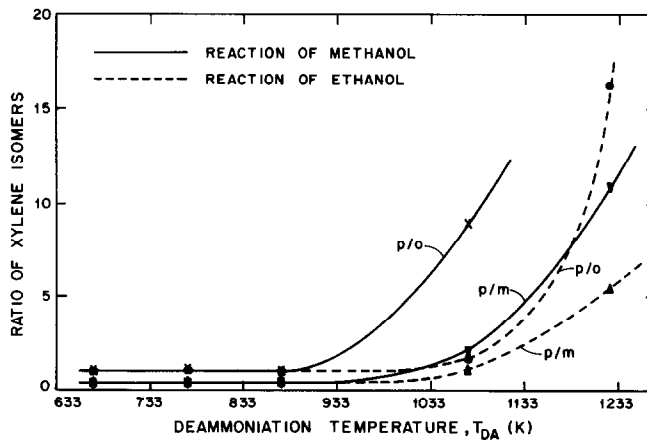


FIG. 9. Dependence of the ratios of xylene isomers formed in the reactions of methanol and ethanol on deammoniation temperature [ $T_{DA}$ ] of  $NH_4$ -ZSM-5.

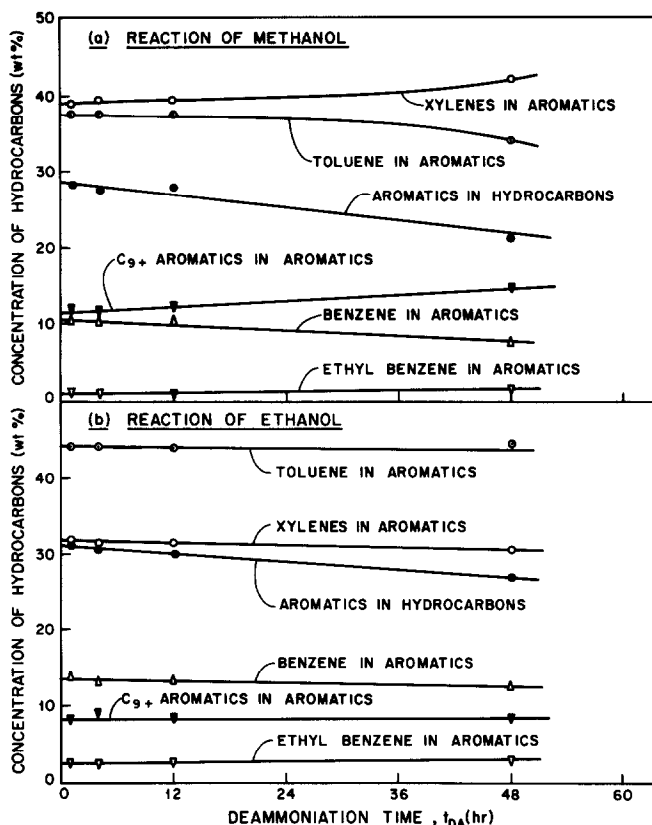


FIG. 10. Dependence of the distribution of aromatics formed in the reactions of methanol and ethanol on deammoniation time [ $t_{DA}$ ] of  $\text{NH}_4$ -ZSM-5.

and 5) and the distribution of aromatic hydrocarbons (Fig. 10) formed in both the reactions were affected to only a small extent when the deammoniation period was varied from 1 to 48 hr. The data on H-ZSM-5 [II, IX-XII] (Tables 3-6) obtained in the different atmospheres show that the concentration of aromatics in the hydrocarbons formed in both the alcohol conversion reactions depends on the atmosphere in the following order: vacuum > air >  $\text{N}_2$  >  $\text{H}_2$  > moist  $\text{N}_2$ .

The concentrations of individual aromatic hydrocarbons in aromatics and the ratios of xylene isomers do not vary significantly due to the change in the atmosphere.

The results of H-ZSM-5 [II, XIII, and XIV] (Tables 3-6) show that the variation in the heating rate has only a small effect on

the distribution of hydrocarbons in the two alcohol conversion reactions.

The variation of the concentration of the aromatics in the hydrocarbons and that of the individual aromatic hydrocarbons (viz., benzene, toluene, xylenes, and ethyl benzene) in aromatics with the number of strong acid sites on the zeolite in the methanol and ethanol conversion reactions is shown in Figs. 11 and 12. The data on H-Na-ZSM-5 zeolites having the same Si/Al ratio as that of the zeolites used in the present investigation but with different degrees of  $\text{H}^+$  exchange (23) are also presented in the figures.

#### DISCUSSION

The acid sites on the H-ZSM-5 zeolites measured by the pyridine adsorption

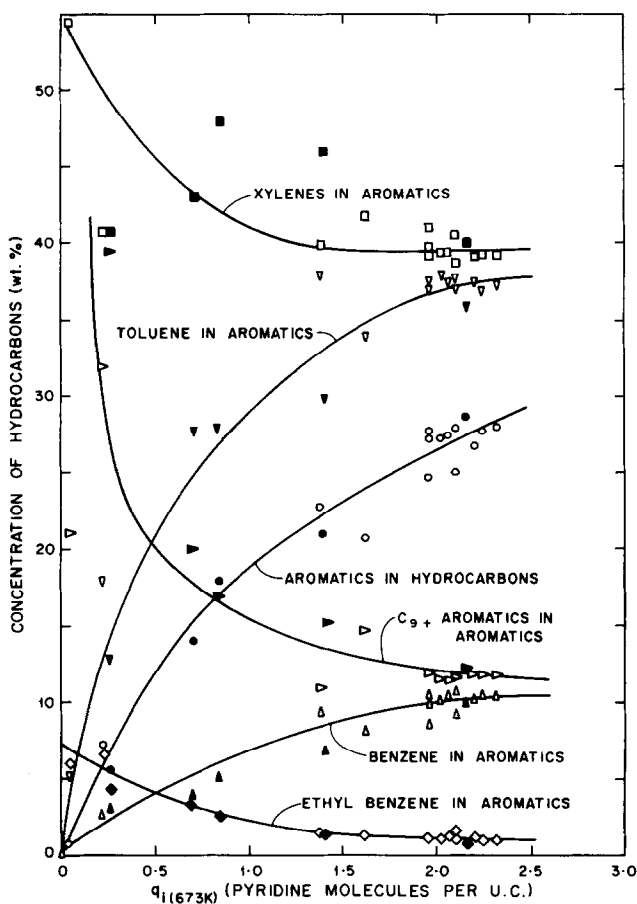


FIG. 11. Dependence of the distribution of aromatics formed in the reaction of methanol on the corresponding irreversible adsorption of pyridine molecules at 673 K [ $q_{1(673\text{ K})}$ ] on the H-ZSM-5 zeolites. Solid symbols represent data on H-ZSM-5 zeolites obtained from  $\text{NH}_4$ -ZSM-5 zeolites having different degrees of  $\text{NH}_4^+$  exchange under identical deammoniation conditions. Open symbols represent the present data.

method are divided into two groups: the sites that adsorb pyridine irreversibly at  $\geq 673\text{ K}$  which are considered strong acid sites and the remaining ones which are the weak acid sites. This distinction is supported by the fact that the ir band at  $3605\text{ cm}^{-1}$  for the hydroxyl groups (which are responsible for the strong Brønsted acidity) in H-ZSM-5 zeolite presaturated with pyridine at lower temperatures could be recovered (24) only after desorbing the chemisorbed pyridine on the zeolite at about 673 K.

Both the TPD and STD methods give the number of strong acid sites and essentially

give the distribution of weak acid sites. The second method gives quantitative information on the distribution of weak acid sites while the first gives information that is more qualitative in nature.

Poisoning of stronger acid sites of the H-ZSM-5 zeolites (with different Si/Al ratios) (23) has shown that the cumene cracking and *o*-xylene isomerization reactions occur on the acid sites which adsorb pyridine irreversibly at the temperatures above 570 K. Since these reactions are catalyzed only by protonic acid sites, the observed conversion of cumene or *o*-xylene can be taken as a measure of the protonic acid sites (which

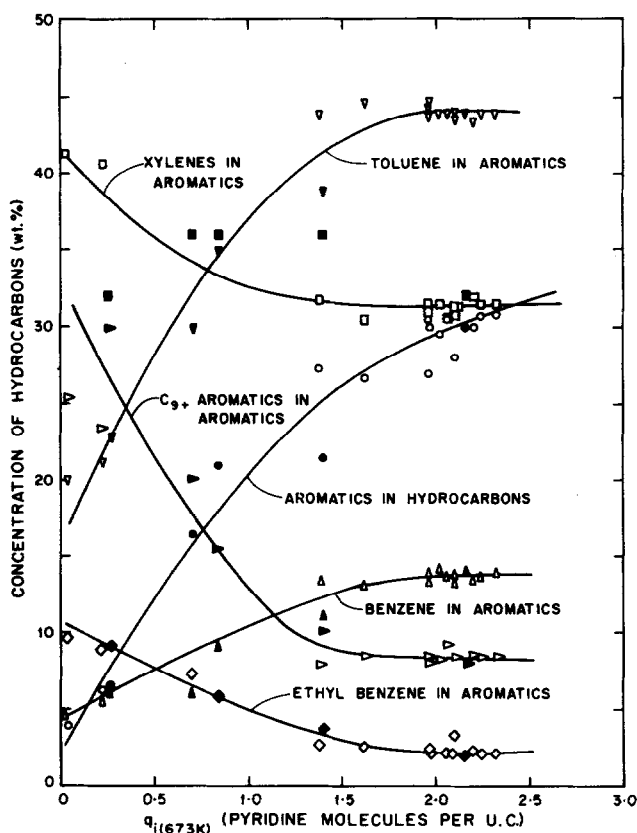


FIG. 12. Dependence of the distribution of aromatics formed in the reaction of ethanol on the corresponding irreversible adsorption of pyridine molecules at 673 K [ $q_{1(673\text{ K})}$ ] on the H-ZSM-5 zeolites. Solid symbols represent data on H-ZSM-5 zeolites obtained from  $\text{NH}_4\text{-ZSM-5}$  zeolites having different degrees of  $\text{NH}_4^+$  exchange under identical deammoniation conditions. Open symbols represent the present data.

adsorb pyridine irreversibly above 570 K) on the zeolite; the variation in the conversion with the change in the deammoniation conditions is related to the corresponding change in the protonic acid sites on the zeolite.

#### *Effect of Deammoniation Temperature*

The results point to a strong influence of the deammoniation temperature on both the acid strength distribution and catalytic properties (viz., the activity in the cumene cracking, *o*-xylene isomerization reactions, and the distribution of hydrocarbons formed in the methanol and ethanol conversion reactions) of H-ZSM-5 zeolite. The changes in the activity and selectivity are

attributable to the decrease in the number of strong protonic acid sites due to the dehydroxylation of the zeolite that occurs when the deammoniation temperature is increased. To a small extent, this decrease in the number of acid sites may also result from the dealumination at higher temperatures. The ir spectroscopic study of the hydroxyl groups responsible for the strong Brønsted acidity and the adsorption of pyridine on H-ZSM-5 has shown (24) that the Brønsted acidity decreases as the calcination temperature is increased. The XPS study of H-ZSM-5 [II and V] (25) has shown that the deammoniation at higher temperatures results in an increase in the surface concentration of aluminum on the



zeolite. A similar observation was made by Vedrine *et al.* (24) in the dehydroxylation of H-ZSM-5 at high temperature. This increase in the surface concentration is attributed to the dealumination.

It has been noted that there is a decrease in the amount of pyridine irreversibly adsorbed at 673 K when the deammoniation temperature is increased (Fig. 6a). Also, there is a decrease in the height of the ir band corresponding to the hydroxyl groups ( $3605\text{ cm}^{-1}$ ) responsible for strong Brønsted acidity and a decrease in the pyridinium ions ( $1550\text{ cm}^{-1}$ ) when the dehydration temperature of H-ZSM-5 is increased [Figs. 3 and 6 in Ref. (24)]. The fact that the decreases in all three cases follow the same trend indicates that the irreversible adsorption of pyridine is essentially a measure of the protonic acid sites in H-ZSM-5 zeolite. This is probably because the Brønsted acid sites are easily accessible to the pyridine molecules, while the Lewis acid sites formed due to dehydroxylation are not because of restricted accessibility of the base to the structural sites resulting from its size and binding mode to Lewis acid sites (24).

The earlier acidity data on the heats of adsorption of ammonia (26) show that when the dehydration temperature is increased from 655 to 1075 K, the total number of strong acid sites of H-ZSM-5 (obtained by HCl treatment) are decreased by about 31% while on the other hand, the acid strength of the remaining sites is increased considerably. The increase in the dehydration temperature does not cause an appreciable change in the acidity distribution of H-ZSM-5 [Figs. 3 and 4, Ref. (26)] as measured by the microcalorimetric heats of adsorption of ammonia (26); hence it seems that the acidity data obtained by this method cannot be related to the catalytic properties of H-ZSM-5 zeolite.

The results of the microcalorimetric heats of adsorption of ammonia and of the ir and ESR investigations (24, 26) have indicated that upon dehydroxylation at elevated temperature, the Brønsted acid sites

of H-ZSM-5 are irreversibly converted to Lewis acid sites. The present investigation shows that the total number of acid sites as well as the number of strong protonic acid sites (as measured by the adsorption of pyridine) on the zeolite obtained at the deammoniation temperature of 1073 K are decreased when the zeolite is rehydrated at 773 K.

The sharp increase in the *p*- to *o*- and *p*- to *m*-xylene ratios and also in the concentration of *p*-ethyl toluene in ethyl toluenes in both the alcohol conversion reactions on the zeolites obtained at the higher deammoniation temperatures (above 873 K) (Fig. 9 and Tables 3 and 5) may be mostly attributed to a very small but progressive change in the channel diameter of the zeolite caused by extensive dehydroxylation accompanied by dealumination, while the distribution of other aromatics (Fig. 8) may be affected by the decrease in the strong protonic acid sites due to dehydroxylation of the zeolite with the increase in the deammoniation temperature.

The decrease in the catalytic activity of the zeolite in the cumene cracking and *o*-xylene isomerization reaction with the increase in the deammoniation temperature (Fig. 6a) confirms that these reactions occur only on protonic acid sites. Further, from the decrease in the concentration of aromatics in hydrocarbons with the increase in the deammoniation temperature (Fig. 8), it can also be concluded that the aromatization in both the alcohol-to-hydrocarbon conversions on the zeolite occurs only on protonic acid sites. The retention of hydrocarbons on the zeolites obtained at higher deammoniation temperatures (above 873 K) in the alcohol conversion reactions may be mostly due to strong adsorption of long-chain hydrocarbons (27) which were not converted to aromatics (which desorb easily) due to low acidity.

#### *Effect of Deammoniation Period*

Both the TPD (Fig. 1b) and STD (Figs. 3 and 5b) data of pyridine point to an appre-

ciable decrease in both the total number of acid sites and the number of strong acid sites of the zeolite due to an increase in the deammoniation period. The conversion of cumene and *o*-xylene (Fig. 6b) and the concentration of aromatics in the hydrocarbons formed in both the methanol and ethanol conversion reactions (Fig. 10) on the zeolite decrease with the increase in the deammoniation period in the same manner in which the irreversible adsorption of pyridine at 673 K decreases with the deammoniation period (Fig. 6b).

The progressive change occurring in the acidity, the catalytic activity in the cracking and isomerization reactions, and the product selectivity in the alcohol conversion reactions due to increase in the deammoniation period are mainly attributable to the dehydroxylation of the zeolite resulting in a decrease in the concentration of the hydroxyl groups responsible for the strong Brønsted acid sites.

#### *Effect of Atmosphere*

The data on the zeolites obtained in different atmospheres [viz., N<sub>2</sub>, H<sub>2</sub>, air, and moist N<sub>2</sub>] and in their absence, viz., under vacuum, indicate that both the acid strength distribution (Figs. 2b, 3–5) and the catalytic properties depend on the atmosphere. The deammoniation under vacuum is most satisfactory as both the total and strong acid sites, the catalytic activity in the cracking and isomerization reactions, and the concentration of aromatics in the alcohol conversion reactions on the zeolite were found to be maximum in this case, whereas, deammoniation in the presence of moist nitrogen is the least satisfactory.

The observed changes in the catalytic activity and the product selectivity are reflected by the corresponding change in the strong acid sites, a deviation from this in a few cases might be due to a shift in the strength distribution of the strong acid sites toward the lower or higher energy side.

Comparison of the data on the zeolites obtained in the deammoniation in the flow

of nitrogen with and without the presence of moisture shows that the presence of moisture causes significant decrease in both the acidity and catalytic activity and selectivity (for the aromatic hydrocarbons) in the reactions studied, probably because of dealumination to a small extent.

#### *Effect of Heating Rate*

The results show that the large variation in the heating rate employed for attaining the final deammoniation temperature does not cause any significant change in either the acid strength distribution or the catalytic properties. This fact indicates that the H-ZSM-5 zeolite has a very high stability toward thermal shocks.

#### *Correlation of Acidity and Catalytic Properties of H-ZSM-5 Zeolites*

The dependence of the cumene and *o*-xylene conversions (Fig. 7) and the concentration of aromatics in the hydrocarbons formed in the methanol and ethanol conversions (Figs. 11 and 12) on the H-ZSM-5 zeolites (obtained under the different deammoniation conditions and also under the same deammoniation conditions but with different degrees of H<sup>+</sup> exchange) on the amount of irreversibly adsorbed pyridine at 673 K clearly shows that a close relationship exists between the catalytic properties and the number of strong acid sites measured by the pyridine adsorption.

In the case of the isomerization of *o*-xylene the conversions are less than 20%; hence the conversion values closely approximate a direct index of catalytic activity (22). Figure 7 shows a linear relationship between the strong acid sites and the catalytic activity in the isomerization reaction on the zeolite. Since the isomerization, cracking, and the aromatization (involved in the conversion of alcohols) reactions are catalyzed by protonic acid sites, the present correlations also show that pyridine adsorption is essentially a measure of the protonic acid sites on H-ZSM-5 zeolite.

The present work clearly establishes the suitability of pyridine for measuring the acid strength distribution of H-ZSM-5 zeolite, particularly when the acidity data are to be correlated with the activity and selectivity of H-ZSM-5 zeolite. Ammonia is a poor choice for this purpose as measurements with it give the number of both the Lewis and Brønsted acid sites on H-ZSM-5.

#### CONCLUSIONS

The following conclusions are drawn from the results obtained from the studies on H-ZSM-5 zeolites obtained under different deammoniation conditions from  $\text{NH}_4$ -ZSM-5.

The acidity due to both the weak and strong acid sites of the H-ZSM-5 zeolite depends on the deammoniation conditions (viz., temperature, period, and atmosphere) employed for its preparation from  $\text{NH}_4$ -ZSM-5. The changes in the acidity caused by the variation in the deammoniation conditions are directly reflected on the catalytic activity in the cracking and isomerization reactions and on the product selectivity in the alcohol-to-hydrocarbon conversion reactions. The acidity, catalytic activity, and product selectivity of the zeolite are strongly affected when deammoniation temperature is increased above 873 K. These properties are changed appreciably when the period of deammoniation at 773 K is increased from 1 to 48 hr. These properties are found to be dependent on the atmosphere in which the deammoniation is carried out (viz., air,  $\text{N}_2$ ,  $\text{H}_2$ , moist  $\text{N}_2$ ) and also on the absence of it (viz., vacuum). Deammoniation under vacuum is the most satisfactory, and deammoniation in the presence of water vapors is the least satisfactory. The heating rate at which the deammoniation temperature (773 K) was attained (ranging from the lowest rate of  $2.5 \text{ K} \cdot \text{min}^{-1}$  to the highest obtained when the temperature is taken to 773 K directly by flash heating) has no significant effect on

the acidity and catalytic properties of the zeolite.

The activity in the cumene cracking and *o*-xylene isomerization reactions and the extent of aromatization and distribution of aromatics in the alcohol conversion reactions could be correlated satisfactorily to the number of strong acid sites, measured in terms of the irreversible adsorption of pyridine at 673 K on the zeolites. The possibility of correlating the catalytic properties with the acidity clearly establishes the suitability of the use of pyridine as the base in characterizing H-ZSM-5 zeolites for their acidity distribution. Pyridine selectively measures protonic acid sites on H-ZSM-5 zeolite as Lewis acid sites, formed due to the dehydroxylation, are not easily accessible to it.

In both the alcohol conversion reactions, the extent of aromatization and distribution of aromatics are strongly dependent on the strong protonic acid sites on the zeolite. The formation of aromatics increases with the increase in the number of strong acid sites. The distribution of aromatics varies with the strong acid sites as follows: when the number of strong acid sites is increased, the concentrations of benzene and toluene increase, while the concentrations of xylenes, ethyl benzene, and  $\text{C}_{9+}$  aromatics decrease.

Deammoniation at higher temperatures ( $>1073 \text{ K}$ ) causes extensive dehydroxylation which leads to a drastic change in protonic acidity. A very significant increase in the selectivity for the *para* isomer of xylene and ethyl toluene indicates the possibility of the alteration of the channel diameter of the zeolites, probably due to dealumination at the higher deammoniation temperatures.

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