JOURNAL OF CATALYSIS **101**, 132–141 (1986)

Acid Catalysis by Dealuminated Zeolite-Y

I. Methanol Dehydration and Cumene Dealkylation

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Received August 30, 1985; revised April 18, 1986

A series of dealuminated Y-type zeolites was prepared by reaction of HY with $SiCl_4$ at elevated temperatures. Methanol dehydration and cumene dealkylation were used as test reactions to probe acid sites of weak and moderate strength, respectively. Zeolites dealuminated at temperatures up to 550°C exhibited catalytic activity for both reactions, but samples dealuminated at 750°C were relatively inactive. Both for methanol dehydration and for cumene dealkylation the activity was linearly proportional to the number of framework aluminum ions over the range from 0 to 14 aluminum ions per unit cell. Thus, assuming one acid site per framework aluminum ion, the turnover frequency (TOF) was essentially constant in this range. The activity of catalysts containing ca. 30 Al/u.c. was less than expected for both reactions, probably because of diffusional limitations. Moreover, a normal HY zeolite exhibited much less activity than anticipated on the basis of its framework aluminum content. The difference in TOF between the dealuminated and the HY zeolite suggests that the latter material has a large number of weak acid sites. The difference was accentuated by the more demanding cumene dealkylation reaction. © 1986 Academic Press, Inc.

INTRODUCTION

Ultrastable Y-type zeolites are an important class of materials due to their increased chemical and thermal stability, with respect to normal HY zeolites. Zeolite-Y is made ultrastable by the removal of aluminum from the framework. The dealumination can be effected through the use of steam (*1–3*), chelating agents (*4*), or by treatment of the zeolite with silicon tetrachloride (*5*). It also has been found that HCl can effect the removal of aluminum from ultrastable zeolites, without excessive loss of crystallinity (*6*). There are several reviews which describe the preparation of ultrastable zeolite-Y with emphasis on steam-stabilized samples (*7–9*).

There is interest in ultrastable zeolite-Y partly because of the similarity in chemical composition to the ZSM pentasil zeolites which were developed by Mobil (*10–12*). ZSM zeolites have certain properties, such as specific shape selectivity with respect to reactants and products, and slow deactivation during catalysis, which are a direct result of the zeolitic structure and chemical composition (*13, 14*). These pentasil zeolites were found to be very active in the conversion of methanol to hydrocarbons (*10*).

Catalysis by ultrastable zeolite-Y has been somewhat less studied than by ZSM zeolites. It has been found that dealuminated Y-type zeolites are active in cumene cracking (*15*) and 2-propanol dehydration (*16*). Zeolites with a Si/Al ratio of about 4 were found to be most active in 2-propanol dehydration, while samples with a Si/Al ratio of greater than 4 were found to be less active (*16*). Similar behavior was observed in the catalytic cracking of cumene (*15*). In

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0021-9517/86 $3.00

n-pentane isomerization, another acid-catalyzed reaction, catalytic activity was found to be directly proportional to zeolite acidity, i.e., inversely proportional to the Si/Al ratio of the zeolite (*17*). In a study by Beaumont and Barthomeuf (*18*) it was found that activity for isooctane cracking was independent of dealumination for up to 33% aluminum removal. This was thought to result from the fact that the first 30% of the aluminum abstracted was associated with weak acid sites while dealumination past 33% resulted in destruction of strong acid sites.

Although most of these previous studies dealt exclusively with materials of moderate Si/Al ratio, Bremer *et al.* (*19*) studied zeolite-Y having Si/Al ≥ 6.7 and found that the cracking activity of hexadecane increased linearly with respect to the number of aluminum ions per unit cell. Of note is a study of the catalytic conversion of methanol to ethylene over dealuminated mordenite samples (*20*). Here, experiments were performed using zeolites with Si/Al ratios of 41 and 82. It was found that these materials were more active than nondealuminated mordenite samples and of comparable activity to HZSM-5 samples. Moreover, the dealuminated zeolites exhibited catalytic activity which did not decay rapidly with time.

The purpose of our study was to examine the catalytic activity of dealuminated Y-type zeolites with respect to cumene dealkylation and methanol dehydration. The former reaction is generally believed to require acid sites of medium strength, whereas the latter is thought to require only weak acid sites of Brønsted or Lewis character. In part II of this series, activity for hexane cracking, which requires strong acid sites, will be reported. Comparisons will be made between HZSM-5 and Y-type zeolites which were dealuminated with silicon tetrachloride or steam dealuminated. Of particular importance here is the effect of aluminum concentration on catalysis, since total acid-site concentration is proportional to framework aluminum concentration. Thus, a series of zeolites which were dealuminated to different extents was employed in this study. Recent analytical advances make it possible to determine the *framework* aluminum content (*21*) which is essential for a study of this type since considerable amounts of *extraframework* aluminum may remain in a zeolite after dealumination (see below).

EXPERIMENTAL

Zeolite Samples

The starting material used in the preparation of dealuminated Y-type zeolites was a Linde ammonium Y zeolite, designated NH_4NaY (2% residual Na_2O content). This zeolite was dealuminated without pretreatment, or after an ammonium ion exchange. The ion exchange was a stringent treatment involving 1 *M* NH_4^+ (from NH_4NO_3) at 60°C for 12 h. Ammonium-exchanged samples were filtered and dried in air at 120°C for 6 h. This treatment produced a crystalline zeolite-Y in which the sodium was essentially 100% exchanged with NH_4^+ ions. The resulting sample is denoted NH_4Y.

The standard dealumination process involved first heating the zeolites, under programmed conditions (5°C/min), to 100, 200, 300, and 400°C under an N_2 (Matheson, ultrahigh purity grade) purge of 50–100 ml/min. Each plateau temperature was maintained for 1 h. Heating under an inert atmosphere is important in that it results in the removal of water from the zeolite and, therefore, prevents the formation of HCL when $SiCl_4$ is used later in the dealumination process. The preheating was done slowly and in stages to prevent "steaming," or formation of steam-stabilized zeolite-Y. Since steam-stabilized zeolites can be produced during heat treatments performed under "deep-bed" conditions (*9*), zeolite bed depths were kept shallow: ca. 2.0 cm (1.5 g starting zeolite contained in a 20-mm-diameter quartz reactor) or less. The shallow bed, combined with slow heat-

TABLE 1

Summary of Preparation for NH_4Y and Dealuminated Zeolite Samples

Zeolite	Synthesis procedure
NH_4Y (HY)	Linde NH_4NaY (2% Na_2O by weight) was subjected to a NH_4^+ ion exchange (1 *M* NH_3NO_3, 60°C, 12 h): essentially 0% Na was present after this treatment
DY550-1	NH_4NaY dealuminated with $SiCl_4$: programmed heating, under $N_2/SiCl_4$ flow, at 5°C/min, from 25 to 550°C. Sample held at 550°C for 3 h under $N_2/SiCl_4$ flow
DY550-2	NH_4NaY dealuminated as in DY550-1. Sample then subjected to NH_4^+ ion exchange (1 *M* NH_4NO_3, 60°C, 12 h)
DY550-3	Sample DY550-1 was subjected to 1 *M* HCl (60°C, 12 h)
DY550-4	NH_4NaY first subjected to NH_4^+ ion exchange (1 *M* NH_4NO_3, 60°C, 12 h) then dealuminated as in DY550-1
DY750-1	NH_4NaY subjected to NH_4^+ ion exchange (1 *M* NH_4NO_3, 60°C, 12 h), as shown above, to yield NH_4Y. Sample was dealuminated with $SiCl_4$: programmed heating, under $N_2/SiCl_4$ flow, at 5°C/min, from 25 to 750°C. Sample held at 750°C for 6 h. Final zeolite washed with 1 *M* HCl (60°C, 12 h)
DY-750-2	Same procedure as DY750-1 including HCl wash, but $SiCl_4$ treatment at 750°C maintained for 12 h
DY750-3	Same procedure as DY750-1, but $SiCl_4$ treatment at 750°C, maintained for 12 h and final zeolite was not washed with HCl
DY750-4	Same procedure as DY750-1, including HCl wash, but $SiCl_4$ treatment at 750°C maintained for 24 h
DY-(Si/Al)	A series of NH_4NaY zeolites dealuminated with $SiCl_4$: 2 g samples, programmed heating under $N_2/SiCl_4$ flow to selected temperatures from 200 to 570°C. Samples held at maximum temperature for 0–4 h under $N_2/SiCl_4$ flow. After reaction at lower temperatures (200–350°C) sample temperature raised to 530°C under N_2 flow. Samples washed with deionized water and then subjected to NH_4^+ ion exchange (1 *M* NH_4NO_3, 70°C, 12 h, 3 times)
SDY	NH_4NaY dealuminated with steam: programmed heating, under N_2/H_2O (8 psi H_2O) flow, from 25 to 600°C. Sample held at 600°C for 1 h under N_2/H_2O flow. Sample cooled under steam and then exposed to NH_4^+ ion exchange (1 *M* NH_4NO_3, 60°C, 12 h). Sample heated, under dry N_2, to 500°C for 1 h
HZSM-5	Zeolite sample obtained from Mobil

ing and N_2 purge, resulted in production of a dehydrated HY and not a steam-stabilized zeolite-Y.

After the final heating, at 400°C, the HY samples were cooled to 25°C under N_2 purge. At this stage the N_2 was directed through $SiCl_4$ (Aldrich, 99%), maintained at 0°C, and over the zeolite sample. Upon exposure to the $N_2/SiCl_4$ purge, the samples were heated under programmed conditions (5°C/min) to a final temperature of 550 or 750°C. Samples were maintained at this final temperature from 3 to 24 h. After this period the $SiCl_4$ flow was halted, and the samples were purged with N_2 at the final operating temperature for 1 h to remove any remaining $AlCl_3$ and $SiCl_4$. The samples were then cooled under N_2 to 25°C.

As a variation of this treatment one series of zeolites (DY-(Si/Al)) was prepared by exposing a NH_4NaY sample to flowing $N_2/SiCl_4$ at lower temperatures, e.g., 200°C, and then heating the sample to 570°C in pure N_2. This procedure resulted in zeolites which were less completely dealuminated.

After exposure to silicon tetrachloride the samples were washed with 2 liters of deionized H_2O in a Büchner funnel, under aspiration. Some dealuminated zeolites were then dried in air at 120°C for 6 h while others were ion exchanged in a 1 *M* NH_4NO_3 solution or treated in a 1 *M* HCl solution (60°C, 12 h), washed again with H_2O and then dried in air at 120°C for 6 h. Specific samples and treatments are listed in Table 1.

TABLE 2

Analyses of Zeolite Samples

Zeolite	Unit cell constant a_0 (Å)	Al ions per unit cell		Si/Al ratio	
		Framework[a]	Total[b]	Framework	Total
NH_4Y	24.746	54.4	56	2.53	2.48
DY550-1	24.288	5.3	27	35.2	6.81
DY550-2	24.263	2.7	9.1	70.1	20.8
DY550-3	24.241	0.32	7.4	600	26.0
DY550-4	24.256	1.9	35	100	5.42
DY750-1	24.315	8.2	7.4	22.4	21.2
DY750-2	24.254	1.7	4.2	112	45.0
DY750-3	24.250	1.3	5.5	147	34.5
DY750-4	24.220	0.0	32	∞	6.07
SDY	24.536	31.9	54	5.02	2.94
HZSM-5[c]				26.5	26.5

[a] Based on unit cell parameter.
[b] Based on atomic absorption data.
[c] All Al assumed to be in the framework.

A steam-stabilized (or steam-dealuminated) zeolite-Y was prepared according to the method of Ward (*3*). A sample of Linde NH_4NaY was heated under N_2/H_2O (415 Torr H_2O) flow at 5°C/min, to 600°C, held at 600°C for 1 h and cooled under the flow of steam. Sodium was then removed through a NH_4^+ ion exchange, and the resulting zeolite was heated to 500°C (5°C/min) under N_2 flow for 1 h.

X-Ray diffraction was used to determine the unit cell parameters of the zeolite samples. Lead nitrate was employed as an internal standard. From the unit cell constants, the concentration of framework aluminum atoms was calculated using the equation (*21*):

$$N_{\mathrm{Al}} = 107.1(a_0 - 24.239). \qquad (1)$$

Here, N_{Al} is the number of framework aluminum atoms per unit cell and a_0 is the measured unit cell constant. An estimated error of ±0.5 Al atom per unit cell is inherent in the technique. Total zeolitic aluminum was determined using atomic absorption spectroscopy on digested zeolite samples (*21*). These analytical techniques confirm that in many samples both framework and *extraframework* aluminum were present (Table 2). The term "*extraframework*" includes all nonframework aluminum.

Catalytic Reactions

The zeolites listed in Table 1 were studied as catalysts for methanol dehydration and in the dealkylation of cumene. Catalyst samples were prepared from the pure zeolite materials or by mixing the zeolite with silica (Davison 952 grade SiO_2) in order to keep conversions low. Also, in the methanol dehydration reaction, the purpose was to limit the reaction to the formation of dimethyl ether and prevent further dehydration to hydrocarbons. In most cases, less than 20% of the reactant material was converted to products.

Most of the catalyst samples were pressed into wafers (10,000 psi), broken, and sieved: the 20–45 mesh portion was used in the reactions. For each experiment, approximately 0.10 g (0.07–0.15 g) of catalyst was loaded into a 10-mm tubular microreactor, giving a bed depth of about 1.0 cm.

For the methanol dehydration tests on the DY-(Si/Al) series a loosely packed bed of zeolite powder was used to minimize diffusional problems. The reactor was packed with Pyrex beads or quartz chips which both positioned the catalyst sample near an external thermocouple and served as a preheating stage for reactant gases. This reactor was attached to a Pyrex manifold wherein both catalyst pretreatment and the catalytic reaction could be performed. During both pretreatment and reaction, helium or nitrogen was used as a vector gas. Nitrogen also was used as an internal standard in some of the activity measurements.

Pretreatment involved heating the catalyst samples to 100, 200, 300, and finally 350°C. The samples were maintained at each plateau temperature for 1 h (2 h at the final pretreatment temperature). During these pretreatments, helium was kept flowing through the catalyst bed (17.5 ml min^{-1}) to effect the removal of H_2O and NH_3. The pretreatment temperature was limited to 350°C in order to minimize the defect structure which might result from dehydroxylation of the zeolite. In a separate experiment the amount of NH_3 evolved by 350°C was measured and found to be equivalent to 90% and 80% of the ammonia content of the NH_4Y and $SiCl_4$-treated samples, respectively. Infrared spectra of zeolite wafers that had been heated to 350°C under vacuum revealed no residual NH_4^+ band at ca. 1450 cm^{-1}. Ammonia apparently is more efficiently removed from the wafer because of its geometry and because of the small amount of zeolite contained therein.

After pretreatment the catalyst temperature was adjusted to the value necessary for the particular experiment being performed, the helium or nitrogen flow was then directed through a saturator containing the liquid reactant (kept at 0°C in all cases), and through the catalyst bed. Upon passage through the catalyst bed the flow was then directed, with the use of switching valves, through a Carle 111 gas chromatograph which was operated under isothermal conditions. During the methanol dehydration reaction, where it was necessary to separate lower hydrocarbons, methanol, dimethyl ether, and water, a 3-m Porapak Q (80–100 mesh) column was employed. For separation of propylene, benzene, and cumene, during the cumene dealkylation reactions, a 3-m Bentone 34 on Chromasorb W column was used. Both columns were maintained at 120°C in a helium purge of about 20 ml min^{-1}. The flow of He, through the saturator and onto the catalyst bed, was kept at 17.5 ml min^{-1} during the reactions.

Cumene was obtained from Fisher (certified grade) and methanol from MCB (99 mol% min). During the catalytic experiments these were contained in a gas saturator. Prior to use, they were purged with He to remove all entrained gases. GC analysis of the reactants showed that this procedure was effective; i.e., no impurity peaks were evident (although there was still a small amount of water in the methanol).

RESULTS AND DISCUSSION

Sample Preparation

During the preparation of the $SiCl_4$-dealuminated zeolites several experimental parameters were found to be important in determining the aluminum content and crystallinity of the final product. The sample bed depth had a profound effect on the crystallinity of the zeolite product. Zeolite samples remained crystalline after $SiCl_4$ treatment only if the bed height was small (ca. 2.0 cm or less). The large degree of crystallinity is indicated by the XRD pattern of Fig. 1 for the sample DY550-2. When beds of larger depth (>5 cm) were used, NH_3 and H_2O were not removed as efficiently during the pretreatment. Upon exposure to $SiCl_4$ water caused the production of HCl which attacked the zeolite framework and resulted in loss of crystallinity.

Care was taken to ensure that the zeolites were uniformly dealuminated along the depth of the bed. Analyses of the top and bottom portions of the bed by XRD revealed identical unit cell parameters.

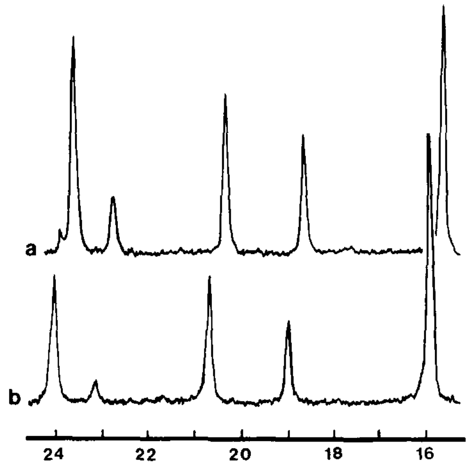

FIG. 1. X-Ray powder diffraction patterns of: (a) NH_4NaY (2% Na_2O), unit cell parameter of 24.746 Å; and (b) DY550-2, unit cell parameter of 24.263 Å

By controlling the gross parameters of zeolite bed depth and sample size, more subtle experimental parameters could be examined. The results obtained upon changing experimental variables such as NH_4^+ ion exchange, dealumination temperature, time of $SiCl_4$ exposure and HCl washings could be determined.

The samples DY750-1, DY750-2, and DY750-4 form a series which illustrates the effect of length of $SiCl_4$ exposure on the removal of framework aluminum. As the $SiCl_4$ flow time was lengthened from 6 to 12 h, and finally to 24 h, the number of framework aluminum ions per unit cell decreased from 8.1 to 1.7 and finally to zero. Within this series, however, the DY750-4 zeolite retained a rather large interstitial aluminum content. The reason for this anomally is most likely due to an ineffective HCl washing, since zeolites become more hydrophobic as more of the framework aluminum is removed.

The effects of ion exchanging a dealuminated zeolite with NH_4^+ or washing with HCl are illustrated by the analyses of samples DY550-2 and DY550-3 (Table 2). Upon comparing samples DY550-2 and DY550-1 it is apparent that NH_4^+ ion exchange removed a large amount of the *extraframework* aluminum. The decrease in framework aluminum from 5.3 to 2.7 ions per unit cell results from variations which occur during sample preparation. Additional experiments carried out on identical samples confirm that NH_4^+ does not remove lattice aluminum. By contrast, HCl washing of DY550-1 removed 67% of the *extraframework* aluminum and 94% of the lattice aluminum to yield sample DY550-3. In evaluating this data one should keep in mind that there is an error of ±0.5 Al/unit cell in the analysis. The influence of NH_4^+ ion exchange suggests that part of the *extraframework* aluminum may be in an ion exchange form, perhaps as AlO^+. It was much more difficult to remove the framework aluminum from the samples dealuminated at 750°C (compare DY750-2 and DY750-3).

The differences in dealumination at 550 and 750°C become even more dramatic when one considers their catalytic behavior (see below). Nevertheless, from the results of Table 2, it is evident that the aluminum could be effectively removed both at 550 and at 750°C. For example, samples which were dealuminated at 750°C for 12 h (DY 750-3) and at 550°C for 3 h (DY 550-4), but were neither ion exchanged nor washed with HCl, experienced comparable amounts of framework aluminum removal, considering the differences in reaction time.

Catalytic Properties

Methanol dehydration. All of the zeolite samples listed in Table 2 exhibited some activity in the dehydration of methanol to dimethyl ether at 275, 300, and 325°C. The activity of the zeolite samples for methanol dehydration and the content of the catalysts that were used in this reaction (i.e., percentage zeolite and percentage SiO_2 diluent) are shown in Table 3. The DY-(Si/Al) series, which generally contained more framework aluminum, was active even at 190°C. If one plots activity versus frame-

TABLE 3

Activity for Methanol Dehydration

Zeolite	Catalyst composition[a] (wt% zeolite)	μmol MeOH converted[b] / g zeolite · min 275°C	300°C	325°C
HY	2.2	3510	HC[c]	—
DY550-1	5.0	838	1,250	—
DY550-2	5.0	482	576	—
DY550-3	100	23.7	28.9	—
DY550-4	5.1	1330	1,520	2340
DY750-1	100	13.9	18.8	27.3
DY750-2	100	2.4	5.6	6.4
DY750-3	100	5.4	15.0	33.7
DY750-4	100	19.5	27.9	34.2
SDY	2.5	6590	HC	HC
HZSM-5	1.0	3150	6,300	—
AMOR-Y	100	35.8	42.2	61.1
SiO_2	100 (SiO_2)	0.0	0.0	0.0

[a] Remainder was SiO_2.

[b] These values were taken at 275°C after 3–5 min on stream, then the temperature was increased to 300°C, etc. When dimethyl ether was the product, the loss in activity was small.

[c] HC indicates that conversion of methanol proceeds beyond dimethyl ether, to hydrocarbons.

work aluminum content for the DY-(Si/Al) series, there is good linear relationship up to 14 Al/u.c. as shown in Fig. 2. At higher aluminum content the activity did not increase proportionally, probably because of diffusional limitations which occur with this facile reaction. A DY-(Si/Al) zeolite and the SDY zeolite of similar framework aluminum content had essentially the same activity. Based on the framework aluminum content, and the associated number of Brønsted acid sites, the activity of the HY catalyst was considerably less than expected. These results can be understood if one assumes that the dealuminated zeolites had mainly strong acid sites in a concentration which was proportional to the framework aluminum content. Moreover, even for a reaction which is catalyzed by weak acid sites, the turnover frequency (TOF) on the strong acid sites is considerably greater than on weak acid sites. Thus, a DY-(Si/Al) catalyst containing only 12 Al/u.c. was as active as the HY catalyst which had 54 Al/u.c. and the commensurate number of weak acid sites.

When one compares the catalysts within the highly dealuminated DY550 series the relationship between framework aluminum content and activity is not so straightforward. For example, as indicated in Table 3 the DY550-4 catalyst was more active than the DY550-1 catalyst, even though the former had considerably less framework aluminum (Table 2). In this case the relatively large amount of *extraframework* aluminum in DY550-4 may serve as a Lewis acid to catalyze the dehydration reaction. Catalysis by these Lewis acid sites becomes significant only when the number of strong Brönsted acid sites becomes very small.

As a class of materials the DY750 series was markedly less active than the DY550 series, even though the total and framework aluminum content often was similar. The reason for this decrease in activity is unclear, although it may be related to the nature of the interstitial aluminum which

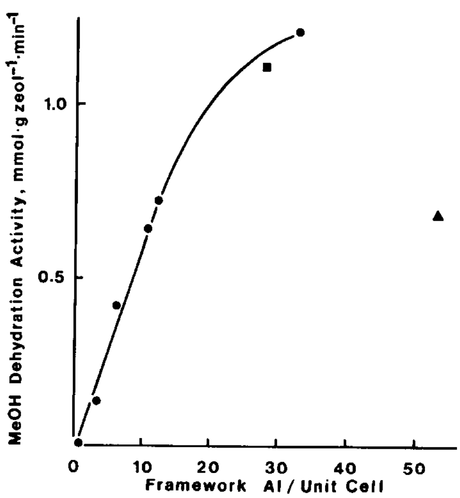

FIG. 2. (a) Dependence of catalytic activity for methanol conversion at 190°C on framework aluminum content: (▲) HY, (●) DY-(Si/Al), (■) SDY.

TABLE 4

Activity for Cumene Dealkylation from Flow Reactor

Zeolite	Catalyst composition[a] (wt% zeolite)	μmol Cumene reacted / g zeolite · min	
		290°C	340°C
HY	2.2	34.1	151
DY550-1	5.0	137	281
DY550-2	5.0	107	267
DY550-3	5.0	0.00	0.00
DY550-4	5.1	38.2	137
DY750-1	100	0.36	1.28
DY750-2	100	0.00	0.00
DY750-3	100	0.32	1.01
DY750-4	100	0.42	1.68
SDY	2.5	498	—
HZSM-5	1.0	223	339
SiO_2	100 (SiO_2)	0.00	0.00

[a] Remainder was SiO_2.

[b] Conversions were determined at 290°C after 3–5 min on stream, then the temperature was increased to 340°C.

apparently poisons the potential Brønsted sites and in itself is not capable of acting as a Lewis site.

Although the dehydration reaction initially was chosen as a probe for weak acid sites, reactions also were carried out under conditions which resulted in the formation of hydrocarbons from methanol. Over the dealuminated samples (DY550-1 and DY550-2) methanol was almost completely dehydrated at 400°C, and in addition to dimethyl ether, C_1–C_3 hydrocarbons were present in the product stream. Unlike the case with ZSM-5, no aromatic hydrocarbons were detected. Over a 3-h period the activity of these materials decreased 20–30%, compared to no loss in activity for the HZSM-5 sample. All samples were black upon removal from the reactor, indicating that coke had formed.

The crystallinity of the samples was checked by X-ray diffraction after several hours on stream. Even after reaction at 400°C the dealuminated zeolites exhibited good crystallinity; however, due to high-temperature exposure to water vapor the HY zeolite became amorphous. This loss in crystallinity was not observed for the HY zeolites when the dehydration reaction was carried out at 275–325°C. Even an intentionally prepared amorphous material (AMOR-Y) exhibited some activity at the higher temperatures.

Cumene dealkylation. At 290, 340, and 390°C cumene was dealkylated to form benzene and propylene. The catalysts typically were diluted with inert SiO_2, although the less active samples were used in an undiluted form.

As seen from Table 4 the dealuminated zeolites again fall into two regions of activity. The DY550 series exhibited moderate activity; whereas the DY750 series had very little activity.

There also was a good correlation between dealkylation activity and the number of aluminum atoms per unit cell, as depicted in Fig. 3. Data for the DY-(Si/Al) series, as well as the SDY sample, are reasonably well fitted by a common straight line. The activity of the SDY sample may be a bit low due to diffusional limitations

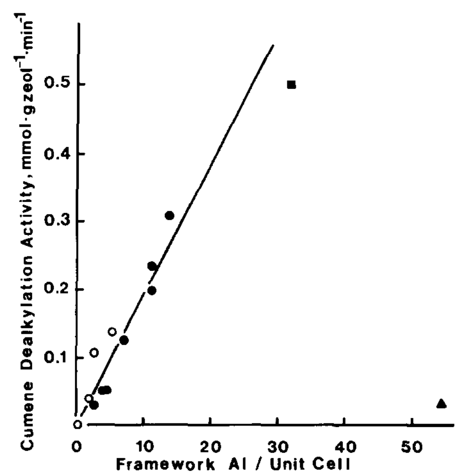

FIG. 3. Dependence of catalytic activity for cumene conversion at 290°C on framework aluminum content: (○) DY550 series, (●) DY-(Si/Al) series, (■) SDY, (▲) HY.

TABLE 5

Initial Activity for Cumene Dealkylation from Pulse Method

Zeolite	Catalyst composition[a] (wt% zeolite)	Conversion	
		mmol/g zeolite	mmol/g zeol · (Al/u.c.)
DY-16.8	5	1.3	0.12
DY-28.0	4	1.2	0.17
DY-47.6	6	0.55	0.13
DY-84.7	8	0.43	0.16

[a] Remainder was SiO_2.

[b] Fifty milligrams of mixed sample, $T = 290°C$, flow rate $= 40$ cm^3/min, 1 μl of cumene in the pulse.

within the zeolite particles. This linear relationship means that the TOF, based on framework aluminum, is nearly constant over a wide range of Si/Al ratios. It is further implied that the acid strength of the zeolite does not vary over this same range, at least to the extent that cumene dealkylation can probe the acid strength. These results are consistent with those found by Haag and co-workers (*23*), who studied hexane cracking over a series of HZSM-5 zeolites which had a wide range of Si/Al ratios.

In order to check the *initial* activity for several members of the DY-(Si/Al) series, a pulse reactor was employed. Because of the problems involved in extracting kinetic data from such an experiment, the results shown in Table 5 should be viewed as a relative activity. For samples which varied by a factor of 5 in the number of framework aluminum ions per unit cell, the turnover frequency based on these aluminum ions was essentially constant.

The odd member of the faujasite series again is HY, which exhibited an activity much less than anticipated on the basis of its aluminum content. The requirement of a stronger acid site for cumene dealkylation accentuates the difference between the more active dealuminated samples and the HY zeolite (Fig. 3). Clearly, the dealumination process enhances the acidity of the zeolite, but this may occur either via the *extraframework* aluminum or by generating a zeolite in which most of the alumina tetrahedra have no next-nearest alumina neighbors (*24*). These possibilities will be discussed more fully in a subsequent paper of this series.

The HZSM-5 sample had a Si/Al ratio which was approximately equivalent to the DY550-1 sample, yet the activity of the former was considerably greater than the latter. Moreover, the effect of temperature on activity suggests that the HZSM-5 zeolite may have been operating in a diffusion-limited region. Although the TOF, based upon structural aluminum, was essentially constant within a class of dealuminated zeolites, it appears that the TOF for HZSM-5 was considerably greater.

CONCLUSIONS

Dealumination at temperatueres up to 550°C gives rise to Y-type zeolites which are active for a methanol dehydration and cumene dealkylation. The activity for both reactions changed in a linear manner with respect to the number of framework aluminum ions which suggests a constant turnover frequency for each acid site. Normal HY, derived from NH_4Y, exhibited considerably less activity than expected, based on the number of aluminum ions per unit cell. Thus, this material contains a large number of only slightly acidic protons. Dealumination at 750°C rendered the zeolite essentially inactive as a catalyst for both reactions.

ACKNOWLEDGMENT

This work was supported by the U.S. Army Research Office.

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