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# The Effect of Sodium Poisoning on Dealuminated Y-Type Zeolites

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Dealuminated zeolites prepared both hydrothermally and using silicon tetrachloride were investigated to determine the effect of sodium addition on their catalytic activities. These materials were found to have drastically reduced activities upon sodium addition with each sodium atom effectively neutralizing the catalytic activity previously thought to be due to five framework Brønsted acid sites. These results are interpreted to mean that isolated framework Al atoms are a necessary but insufficient condition for strong acidity, and only about one-fifth of the framework Al atoms are associated with this strong acidity. Extraframework Al is believed to impart, through inductive effects, strong acidity to these framework Brønsted sites. An infrared study of the hydroxyl region revealed bands at 3675 and 3595–3610 $cm^{-1}$($\pm 2$ $cm^{-1}$) that are attributed to protons associated with two different types of extraframework aluminium oxide or oxyhydroxide. A band at 3695 $cm^{-1}$ is attributed to $Na^+$ interacting with water which is hydrogen-bonded to a framework oxygen atom. A narrow band at 3602 $cm^{-1}$ is attributed to a highly acidic Brønsted site in the zeolite lattice. © 1989 Academic Press, Inc.

## INTRODUCTION

The origin and development of strong acid sites during the dealumination of Y-zeolite is a phenomenon which has been under investigation for the last two decades. Progress in this area of research has been described in several reviews (*1–6*). Dealuminated Y-zeolite is used extensively in the refining industry as a component in fluidized cracking catalysts, and therefore, the nature of the active sites in these materials is of practical importance. The dealumination procedure exposes these zeolites to rigorous conditions which extensively modify many aspects of the zeolite structure. Determining which of the many changes is responsible for the remarkable activity observed in these materials is the key to understanding the nature of the active sites. However, separating the effects of the different variables, which include the change in the unit cell size, the degree of isolation of the framework aluminum atoms, the change in the extraframework aluminum concentration, and even the change in the residual cation content, poses a difficult problem.

Pine *et al.* (*7*) correlated the unit cell size with zeolite stability, selectivity, and activity for dealuminated, rare-earth, and hydrogen-exchanged Y-type zeolites. Since the unite cell parameter is a function of the Al content in the zeolite it is also a measure of the number of acid sites, as well as their degree of isolation. Therefore in practical catalytic systems the unit cell size becomes an effective method to predict catalytic activity. On a more fundamental level, however, this may be an oversimplification of the complex modifications occurring in these systems.

Several studies have suggested that strong acidity is related to the presence of isolated framework aluminum atoms (*7, 8*). In our laboratory, it has been demonstrated that the activity for hexane cracking and cumene dealkylation reached a maximum at ca. 32 Al per unit cell and decreased linearly with decreasing framework Al content for dealuminated zeolites (*9, 10*). This constant turnover frequency supported the

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view that the isolated aluminium atoms were responsible for the strong acidity and that each active center had a similar acid strength. The role of the extraframework Al was not determined in the previous studies and its effect continues to be debated in the literature (*11–13*).

Nock and Rudham (*11*) found that removal of the extraframework Al resulted in a catalyst with improved resistance to deactivation. They concluded that the effect of the extraframework Al was detrimental, and its removal led to decreased coke formation and hence prolonged catalytic activity. The authors suggest that complete removal of the extraframework Al occurs, which even after acid washing is unlikely (*14*). Nock and Rudham (*11*) report a total Si/Al ratio on the basis of chemical analysis, and consequently there is no measure of the amount of extraframework Al remaining in the lattice. Beyerlein *et al.* (*8, 12*) concluded that indeed some amount of extraframework aluminum was an essential ingredient in the generation of strong acidity. Samples prepared with ammonium hexafluorosilicate, which yielded dealuminated zeolites having almost no extraframework Al, were compared with similarly prepared samples exposed to a mild steaming. The steamed samples, although of similar framework Al concentration, had extraframework Al and also showed a dramatic increase in carbonium ion activity. The possibility that an interaction between a framework Brønsted site and an extraframework Lewis site gives rise to super acidity has been suggested previously (*4*).

Lago *et al.* (*15*) observed that the activity of HZSM-5 for hexane cracking increased by about a factor of 4 upon mild steaming of the catalyst. Selective Cs-poisoning studies indicated that a few very acidic –OH groups were formed by the modification of one member of a paired Al region of the zeolite. This aluminum acts as a strong electron withdrawing center for the remaining tetrahedral Al, thus creating a stronger Brønsted site. The concentration of the more active sites was about 6% of the tetrahedral framework aluminum. These sites exhibited a specific activity 45–75 times greater than that of a normal site in HZSM-5.

In a recent study by Corma *et al.* (*16*) the idea of "hidden acid sites" was proposed. The isomerization and disproportionation of *m*-xylene was examined using zeolites which were dealuminated by reaction with silicon tetrachloride. A maximum in activity was observed when 19 Al atoms remained in the framework, and a maximum in TOF was observed when the framework Al content equaled ca. 17 Al atoms. On the basis of infrared results in which a fraction of the Brønsted sites remained unconverted to pyridinium ions upon addition of pyridine, it was concluded that certain sites were inaccessible to both pyridine and *m*-xylene. It was concluded that by modifying classical predictions of zeolite acidity with this new concept of "hidden acid sites" one could explain all Brønsted acid-catalyzed reactions in dealuminated zeolites.

Residual monotonic cations have been shown to have a dramatic negative effect on the activity for H–Y-zeolites (*17–19*). In these early studies normal Y-zeolites were examined, and their $Na^+$ content ranged from ca. 0.2 to 10 wt%. Moreover, Beyerlein *et al.* (*8*) showed that in dealuminated zeolites residual sodium cations decrease the isobutane cracking activity. From their sodium-poisoning results it was concluded that only one-third of the framework aluminum atoms were associated with strong acidity throughout the $Si/Al \geq 5$ composition domain. This result appears to contradict the conclusion that a Brønsted site of equivalent acid strength is associated with every framework Al atom for $Si/Al \geq 6$.

Infrared spectroscopy has been used extensively in an attempt to relate the structure of these materials with their catalytic properties. The nature of the bands developed upon dealumination has been a topic of debate. Jacobs and Uytterhoeven (*20*) observed a broad band at 3600 $cm^{-1}$

and attributed this to nonacidic lattice hydroxyl groups near Al defect positions in the framework (silanol nests). It was determined that these species could not be removed by alkaline extraction, which seemed to rule out the possibility that this band was due to hydroxyaluminum species, as proposed earlier by Ward (*21*). Anderson and Klinowski (*22*), however, found no correlation between a similar band at 3610 $cm^{-1}$ and the intensity of the $^{29}Si$ NMR peak corresponding to silicon atoms associated with hydroxyl nests. They concluded, therefore, that the 3610 $cm^{-1}$ band is due to extraframework Al(OH) species. It was postulated that the removal of the species by alkaline extraction was inhibited because of their location, which was probably within the sodalite cages. A band was also observed at 3675 $cm^{-1}$, and this was assigned to framework Si–OH groups at defect sites.

Kubelkova *et al.* (*23*) observed an OH band at ca. 3620 $cm^{-1}$, which developed upon dealumination with $SiCl_4$. Since these species were only weakly acidic or inaccessible to pyridine, it was assumed that these hydroxyls were closely related to the presence of extraframework Al. They concluded that during washing with water, hydroxide complexes of Al are formed. The Al atoms removed from the framework were assumed to remain in extraframework positions as cations or oxide clusters where they compensated the lattice charge and exhibited strong Lewis acidity.

On the basis of X-ray radial distribution functions Shannon *et al.* (*13*) determined that the extraframework Al, present in the hydrothermally dealuminated zeolites, exists as boehmite-like species. Pseudoboehmite, AlOOH, has infrared bands at 3670–3680 $cm^{-1}$ which are near in wavenumber to the extraframework Al hydroxyl bands at 3660–3670 $cm^{-1}$ in the zeolites. It was further postulated that the nonframework aluminum species were located in the supercages and not in the macropores, on the basis of the constrained size of the clusters which were observed. The possibility that other aluminum species were present elsewhere in the zeolite was not ruled out.

Lohse *et al.* (*24*) conducted an IR and $^1H$ NMR study in which hydrothermally treated NaH–Y was prepared both with extraframework Al and with up to 80% of the nonframework Al removed by acid-leaching. Upon dealumination Lohse *et al.* (*24*) observed a broad band at 3606, a band at 3693, and a shoulder at 3675 $cm^{-1}$. Upon acid-leaching of the samples these bands were greatly reduced and Lohse *et al.* (*24*) concluded that they resulted from nonframework AlOH species. Through proton NMR it was determined that the ratio of the number of aluminum hydroxide species to the number of extraframework Al atoms was small, implying that condensation to higher molecular weight Al species was occurring.

In the study by Corma *et al.* (*16*), infrared bands at 3680–3625 $cm^{-1}$ and 3560 $cm^{-1}$ were attributed to OH groups in the supercages and OH groups associated with six-member rings, respectively. Bands at 3600 and 3610 $cm^{-1}$ were also reported. The 3600 $cm^{-1}$ band was attributed to an extraframework AlOH species, while the 3610 $cm^{-1}$ band was assigned to an extraframework silica–alumina phase. The 3600 $cm^{-1}$ band was reported to be nonacidic, while the band at 3610 $cm^{-1}$ was found to be highly acidic in agreement with their results on acidic amorphous silica–alumina.

In the present work, a systematic study of the effect of $Na^+$ addition to Y-zeolite has been carried out. The focus is on the range between 0.03 and ca. 0.8 wt% $Na^+$. This study on sodium poisoning allows us to resolve, in part, the diverse observations and conclusions reached for the assignment of hydroxyl bands in the infrared region. The effect of the $Na^+$ on the IR results and the catalytic activity for hexane cracking provides additional insight into the origin of strong acidity in dealuminated Y-zeolite.

## EXPERIMENTAL

The starting material used in this study was a NaH–Y-zeolite (Union Carbide LZ-Y62 with a reported total Si/Al ratio of 2.55, and a $Na_2O$ content of 2 wt%). The NaH–Y material was further modified by either silicon tetrachloride treatment or hydrothermal treatment.

The silicon tetrachloride-treated zeolites were prepared by first placing ca. 5 g of 12 to 20 mesh NaH–Y-zeolite in a quartz tube with an internal diameter of ca. 18 mm. The material was then carefully dehydrated by heating at a rate of 0.9°C/min to a final temperature of 400°C and held there for a minimum of 2 h under flowing UHP $N_2$. After dehydration the zeolite was allowed to cool to room temperature before contacting it with the silicon tetrachloride. The $SiCl_4$ was contained in a gas drying tube at 0°C. Nitrogen was bubbled through the $SiCl_4$ and introduced into the zeolite bed. The temperature of the zeolite was increased at a rate of 5°C/min to 200°C, at which point the $SiCl_4$ flow was discontinued and pure $N_2$ was passed over the zeolite until a final temperature of 590°C was attained. The temperature was maintained at 590°C for several hours to sublime off part of the $AlCl_3$ produced during dealumination and to provide an opportunity for the lattice to heal. In all cases some amount of extra-framework Al was retained in the zeolite.

The hydrothermally treated materials were prepared by placing ca. 5 g of 12 to 20 mesh NaH–Y-zeolite in a quartz tube with an internal diameter of ca. 16.5 mm. Steam from a flask of boiling water was passed through heated lines at a flow rate of 30 cc/min over the zeolite bed which was maintained at a temperature of 600°C. The length of time which the zeolite was exposed to the steam was varied between 2 and 6 h to produce a range of silicon-to-aluminum ratios.

Prior to any catalytic runs, the residual 2 wt% $Na_2O$ was removed from the NaH–Y materials. This was carried out by ammonium ion exchange with $NH_4NO_3$. After modification the zeolites typically were exchanged four times, 6–12 h each, in 1 *M* $NH_4NO_3$ at 70°C. In order to reintroduce controlled amounts of sodium, the zeolite was ion exchanged in an aqueous solution at 70°C for 8 h. Four series of catalysts were prepared. In two cases, series B and C in Table 1, the samples were calcined (at 350°C in air for 8 h) after $NH_4NO_3$ exchange, to remove extraneous filter paper remaining in these batches. This calcination step apparently removed the filter paper and partially deamminated the samples. Analysis of the noncalcined materials revealed that the sodium exchange had been complete; i.e., almost all of the $Na^+$ in solution was exchanged into the zeolite. The calcined samples had sodium contents much lower than expected on the basis of complete ion exchange. For example, sample C-3 was ion exchanged in a solution containing sufficient sodium to produce a sample with $Na^+/Al_f = 0.3$; however, the resulting zeolite had a $Na^+/Al_f = 0.1$. This is attributed to the favorable ion exchange of $Na^+$ with $NH_4^+$ relative to the proton.

After ammonium ion exchange, each of the zeolites was checked by X-ray diffraction for crystallinity, and the unit cell size was determined relative to $Pb(NO_3)_2$. The X-ray diffraction patterns were obtained with a Seifert-Scintag PAD II diffractometer, and the framework aluminum content was determined as described previously (*9*, *25*). All samples had good crystallinity as determined by X-ray diffraction. Sodium-poisoned samples A-1 and A-2 were checked after reaction and found to have good crystallinity. The Si/Al ratio was also checked by $^{29}Si$ solid-state nuclear magnetic resonance (SSNMR) using an equation derived by Engelhardt and coworkers (*26*). The $^{29}Si$ SSNMR spectra were obtained with a Bruker MSL 300 spectrometer. Zirconium oxide rotors were filled with ca. 0.2 g of hydrated zeolite, and the samples were spun at the magic angle at 3000 Hz to remove line broadening due to

TABLE 1

Analyses of Zeolite Samples

| Catalyst | $a_0$ (Å) | Al ions per unit cell | | | $Na^+$ (wt%) | $Na^+/Al_f$ |
|---|---|---|---|---|---|---|
| | | Framework[a] | Total | Extraframework | | |
| A-0[b] | 24.381 | 15.3 | 35.3 | 20 | 0.02 | 0.007 |
| A-1 | | | 33.2 | 18 | 0.23 | 0.1 |
| A-2 | | | 33.6 | 18 | 0.49 | 0.2 |
| B-0[c] | 24.434 | 21 | 53 | 32 | 0.03 | 0.009 |
| B-1 | | | 54 | 33 | 0.14 | 0.041 |
| B-2 | | | 54 | 33 | 0.15 | 0.044 |
| C-0[c] | 24.490 | 27 | 54.2 | 27 | 0.02 | 0.007 |
| C-1 | | | 54.7 | 27 | 0.25 | 0.066 |
| C-2 | | | 53.3 | 26 | 0.29 | 0.076 |
| C-3 | | | 52.3 | 25 | 0.39 | 0.10 |
| D-0 | 24.574 | 36 | 54.6 | 18.6 | 0.04 | 0.008 |
| D-1 | | | 55 | 19 | 0.37 | 0.07 |
| D-2 | | | 55 | 19 | 0.83 | 0.17 |

[a] As determined by X-ray, assuming $Na^+$ exchange has no effect.

[b] Series A prepared by silicon tetrachloride treatment.

[c] Series B and C calcined before $Na^+$ exchange.

homonuclear or heteronuclear interactions. Collection times ranged from 2 to 3 h. The total Al content of the samples was determined using atomic absorption (AA) analysis and the inductively coupled plasma (ICP) technique. The difference between the total number of aluminum atoms per unit cell and the number of framework aluminum atoms per unit cell yields the extraframework Al content. The $Na^+$ content was determined using the ICP technique.

The infrared spectra of the hydroxyl groups were obtained using a Digilab FTS-40 Fourier transform spectrometer equipped with a MCT detector. The zeolites were pressed into self-supporting wafers having a mass per unit area between 5 and 10 mg/cm$^2$. The wafers were pretreated under the same conditions as the catalytic samples, except they were degassed under vacuum rather than flowing $N_2$. In both cases the temperature never exceeded 400°C.

The hexane cracking activity was determined in a glass U-tube reactor with an internal diameter of 4 mm. The amount of catalyst was kept constant and was chosen such that the conversion for the most active catalyst was less than 10%. Typically, 45 mg of 20–45 mesh zeolite particles (pressed at 5000 lb/in$^2$) was placed in the reactor and held in place with quartz wool. The reactor was then packed with quartz chips which served to preheat the gases. Further modification of the catalyst during preatreatment was minimized by careful dehydration at lower temperatures. The zeolite was activated under flowing $N_2$ by heating the sample in 1-h increments at 100,200, and 300°C and then for 2 h at 400°C. The temperature was controlled by an external thermocouple to ±1°C.

After pretreatment, the reactor was bypassed and the flow of gas was diverted through a hexane saturator at 0°C, and after 30 min the reactant flow of hexane was analyzed by GC. The hexane was then passed through the zeolite bed which was maintained at 350°C. The flow rate was determined by a bubble meter and was maintained at ca. 20 cc/min. After 5 min on stream, the activity was determined by product analysis ($C_1$–$C_6$ hydrocarbons) using an on-stream gas chromatograph (GC). Nitrogen was used as an internal standard. The small fluctuation in the amount of hexane reactant was also corrected. The GC was a Carle 111 chromatograph used isothermally at 150°C. The column was a 3-m Porapak Q. The activity was based on the weight of the zeolite, rather than the total catalyst weight. The form of the extraframework Al affects the total zeolite molecules weight. Since the exact form of the extraframework Al is difficult to ascertain separate calculations were performed on the basis of the extraframework Al existing in the form of $AlO_2$, AlOOH (boehmite), and $Al_2O_3$. In all cases the trends observed were similar, and the results for AlOOH are reported.

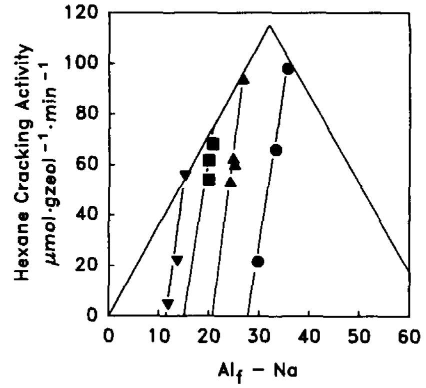


FIG. 1. The dependence of hexane cracking activity on the framework Al content for four series of $Na^+$-poisoned catalysts. Each $Na^+$ is assumed to poison one framework Al atom. (▼) A series, (■) B series, (▲) C series, (●) D series. The solid line represents the theoretical activity based on isolated Al atoms (*10*).

## RESULTS

*Catalytic results.* Previous work in our laboratory (*9, 10*) has demonstrated a linear dependence of cracking activity on the framework Al content up to a maximum of ca. 32 framework Al atoms per unit cell. This maximum corresponds very well with the predicted maximum number of isolated Al atoms (those with no next-nearest tetrahedral Al atoms in the four-member ring) possible in the Y-zeolite lattice (*27*). Zeolites prepared by both steaming and treatment with $SiCl_4$ had activities which fell on a common line. Moreover, samples dealuminated by the two methods to the same framework aluminum content exhibited similar catalytic activities for hexane cracking. This apparent constant turnover frequency per framework aluminum was interpreted to mean that each framework Al and its associated proton contributed equally to the activity of the zeolite. Because of the difficulty involved in preparing a zeolite with a Si/Al ratio of ca. 6 with no extraframework Al, the role of such a cationic species is difficult to ascertain. To approach the problem of zeolite acidity from another direction the effect of adding a poison to these materials was examined. The sodium ion was chosen because of its ease of addition, its relative stability under high pretreatment temperatures, and its relevance to practical systems.

The hexane cracking activity was then determined for each of the series of catalysts and the results are plotted in Fig. 1. The nonpoisoned materials fall on a line which reaches a maximum at ca. 32 Al/u.c. This line also represents the number of isolated Al atoms in the framework on the basis of a model. According to this model there would be a theoretical maximum at ca. 30 isolated Al atoms (*27*). As additional Al atoms are placed into the framework, the isolated Al tetrahedra in the four-ring would decrease until no isolated Al atoms remain when a total of 65 framework Al atoms are present in the unit cell. As one moves to the left of the maximum, the number of isolated Al atoms also would decrease, thus reducing the total number of possible acid sites.

As $Na^+$ is added to the zeolite the total number of acid sites is reduced. The abscissa in Fig. 1 represents the number of framework Al which remains unpoisoned after the addition of sodium. Each sodium ion was assumed to poison one framework Al atom, or more correctly one Brønsted acid site associated with each framework Al atom. The effect of the $Na^+$ poisoning

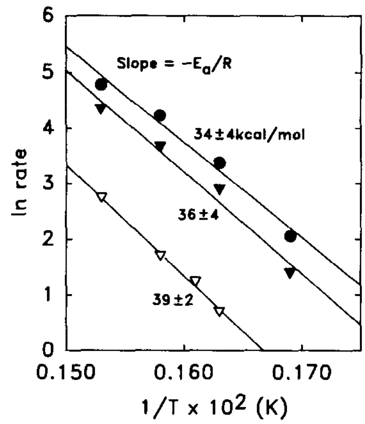


FIG. 2. Arrhenius plots for the catalysts (●) D-0, (▼) A-0, and (▽) A-2.

was found to be dramatic over the entire range of Si/Al ratios examined. The slopes of the poisoning lines appear to be similar over this range for both the hydrothermally prepared and the silicon tetrachloride-treated materials. Assuming that each framework Al contributes equally to the activity of the zeolite, it was determined from the slope of each poisoning curve that one sodium atom could effectively poison ca. 5 Al atoms. Beyerlein *et al.* (*8*) observed a similar result for their hydrothermally treated material (Si/Al = 5.1) and reasoned that only a fraction of the sites were active for the conversion of isobutane. In fact, it was concluded that only one-third of the framework aluminum atoms were responsible for the strong acidity observed in these materials. Although qualitatively the results presented in this study and those reported by Beyerlein *et al.* (*8*) are similar, in that the activities of the $Na^+$-poisoned materials are much less than would be expected, quantitatively they are significantly different.

It is notable that the results reported by Beyerlein *et al.* (*8*) are for the rate of carbonium ion formation in the conversion of isobutane carried out at 500°C, while in this study the rate of hexane cracking was examined at 350°C. To determine the effect of temperature on the fraction of framework atoms poisoned by $Na^+$ a series of sodium-poisoned materials was run at 380°C. While the hexane cracking activity increased by 150% in the unpoisoned case, the fraction of poisoned sites remained essentially the same. Temperatures higher than 400°C were not attempted because of the problem of zeolite dehydroxylation.

Arrhenius plots are shown in Fig. 2 for the following catalysts: A-0, A-2, and D-0. These three were chosen because they span the range of aluminum contents, $Na^+$ contents, and activities. The temperatures ranged from 320 to 380°C. The activation energies ranged from 34 ± 4 kcal/mol, for the most active catalyst, to 39 ± 2 kcal/mol for the least active catalyst, which are within the range reported for alkane cracking reactions (*28*). All of the activation energies are within experimental error of one another. At 380°C, the unpoisoned catalysts with the highest activities had conversions slightly higher than 10%, and therefore the actual activation energies may be slightly greater than that determined from the plot.

*Infrared studies.* In an attempt to correlate structure and catalytic activity an infrared study was conducted on the hydroxyl region of these materials. Small differences in the wafer densities for a given series of catalysts were corrected by assuming that the band due to the terminal Si–OH groups was unaffected by the addition of sodium; i.e., the intensity of the band at 3745 $cm^{-1}$ was kept constant. The results for a silicon tetrachloride-treated series with 15 framework Al atoms/u.c. are shown in Fig. 3. Spectrum a (catalyst A-0), which is that of the nonpoisoned material, consists of six bands. There are two SiOH bands: one at 3745 $cm^{-1}$, which results from terminal hydroxyl groups in the lattice (*4*), and one at 3739 $cm^{-1}$, which is possibly due to silanol groups in the hydroxyl nests. There are two bands at 3635 and 3560 $cm^{-1}$ which are associated with the traditional Brønsted sites found in a normal H–Y zeolite. There are two additional bands at

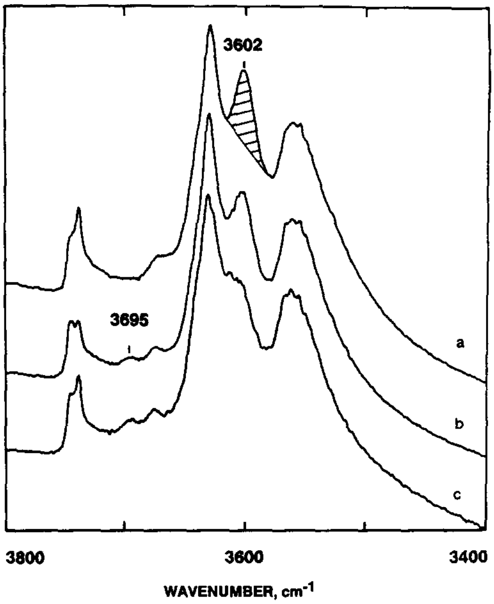


FIG. 3. Infrared spectra of the hydroxyl region for a $SiCl_4$-treated zeolite (series A, with $Al_f = 15.3$) with various amounts of $Na^+$ added as a poison: (a) 0.02 wt% $Na^+$, (b) 0.23 wt% $Na^+$, (c) 0.49 wt% $Na^+$.

3675 and 3602 $cm^{-1}$. As one moves down the series, the spectra reflect the addition of small amounts of $Na^+$ to the zeolites (see Table 1, catalysts A-1 and A-2). The changes in the nonacidic Si–OH band at 3739 $cm^{-1}$ are ignored since small changes in $Na^+$ level are not expected to affect these hydroxyl bands. In the acidic hydroxyl region of the spectra, the addition of sodium appears to be affecting only the 3602 $cm^{-1}$ band. By comparing the catalytic activity for this series of samples with the intensity of the 3602 $cm^{-1}$ band it is evident that as the catalytic activity approaches zero, the intensity of the band is almost completely diminished. Relative areas for the 3602 $cm^{-1}$ bands and catalytic activities are compared in Table 2. The bands at 3630 and 3550 $cm^{-1}$ appear to be unchanged at these levels of sodium ion poisoning. A band at 3695 $cm^{-1}$, however, appears to be growing in with sodium addition, and this will become more evident in the steamed samples.

The hydroxyl region of the hydrothermally prepared materials is complicated by the large excess of extraframework hydroxyl species relative to the $SiCl_4$-treated materials. Many of the conclusions drawn about trends of the hydrothermally treated samples are clarified through comparison with the $SiCl_4$-treated infrared data.

Figure 4 is a series of infrared traces for the hydroxyl region of a steamed sample with 27 aluminum atoms per unit cell which was poisoned with $Na^+$. Spectrum a in Fig. 3 has one large band at 3745 $cm^{-1}$, a broad group of peaks in the acidic hydroxyl region from 3650 to 3550 $cm^{-1}$, and a band at 3670 $cm^{-1}$. As found with the $SiCl_4$-treated sample the addition of $Na^+$ caused the 3602 $cm^{-1}$ band to decrease in intensity and a band to appear at 3695 $cm^{-1}$. The effect of the sodium ion addition is most noticeable between spectra a and b (which correspond to C-0 and C-2, respectively) since the difference in sodium levels is greatest. The band at 3602 $cm^{-1}$ in spectrum c (catalyst C-3) is not removed as completely as in spectrum c (catalyst A-2) of Fig. 3; however, this is because the sodium poisoning is not as extensive in series C. Moreover, comparison with the catalytic activity shows that this steamed material retains a large amount of activity. The band at 3695 $cm^{-1}$ grows much more noticeably with sodium addition in this steamed sample than with the previous $SiCl_4$-treated

TABLE 2

Correlation of 3602 $cm^{-1}$ Band with Activity

| Catalyst | Relative area of 3602 $cm^{-1}$ band | Relative catalytic activity |
|---|---|---|
| A-0 | 1.0 | 1.0 |
| A-1 | 0.50 | 0.40 |
| A-2 | 0.13 | 0.08 |
| C-0 | 1.0 | 1.0 |
| C-2 | 0.65 | 0.69 |
| C-3 | 0.56 | 0.58 |
| D-0 | 1.0 | 1.0 |
| D-1 | 0.65 | 0.66 |
| D-2 | 0.21 | 0.26 |

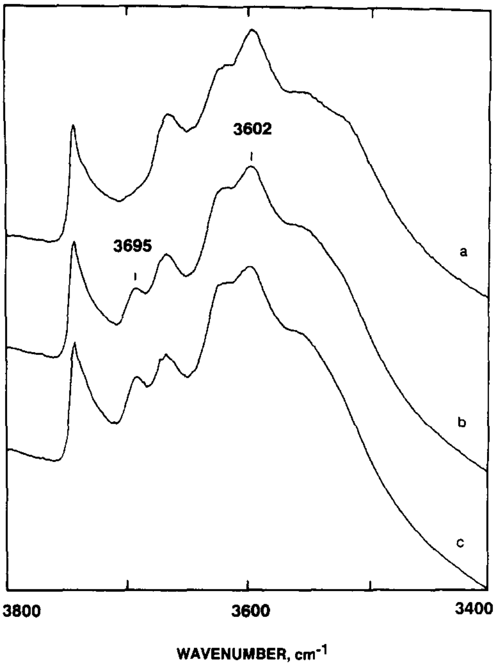


FIG. 4. Infrared spectra of the hydroxyl region for a hydrothermally prepared zeolite (series C with $Al_f$ = 27) poisoned with different amounts of $Na^+$: (a) 0.02 wt% $Na^+$, (b) 0.25 wt% $Na^+$, (c) 0.39 wt% $Na^-$.

sample. A band at 3670 cm$^{-1}$ is present in the nonpoisoned material and remains relatively unaffected by the addition of sodium. There is an additional shoulder at ca. 3535 cm$^{-1}$ which decreases slightly upon $Na^+$ addition.

Figure 5 depicts the infrared spectra of a hydrothermally prepared series of materials with 36 Al/u.c. Spectrum d represents a material which was prepared by contacting the zeolite with 1 *M* $NaNO_3$ at 70°C. This material had no detectable hexane cracking activity and is not represented in Fig. 1. The 3602 cm$^{-1}$ band decreases in intensity with increasing $Na^+$ content, and the decrease in intensity parallels that of the catalytic activity (see Table 2). The 3695 cm$^{-1}$ band again grows with the addition of sodium, reaching a maximum in the sample saturated with $Na^+$. The band at 3670 cm$^{-1}$ remains relatively unaffected, which is most evident in spectrum d of the zeolite containing the highest $Na^+$ content. Spectrum d has lost the characteristic Brønsted bands and only a broad band at 3595–3610 cm$^{-1}$ remains in this region. As in Fig. 4 the shoulder at ca. 3535 cm$^{-1}$ decreases with $Na^+$ addition.

A $SiCl_4$-treated sample with 21 aluminum atoms per unit cell was extensively $Na^+$-poisoned and the infrared spectrum (not shown) of this zeolite yielded a broad band at 3590–3640 cm$^{-1}$ with shoulders at 3680 and 3695 cm$^{-1}$ and with silanol peaks at 3740 and 3745 cm$^{-1}$.

Table 2 shows the correlation between the relative catalytic activity and the relative area of the 3602 cm$^{-1}$ band. The relative area of the 3602 cm$^{-1}$ band was determined by extending a straight line from the base of the right side of the 3602 cm$^{-1}$ band to the base of the left side of the band as demonstrated in Fig. 3. The areas were then determined by weight. Deconvolution of the infrared spectra was not attempted

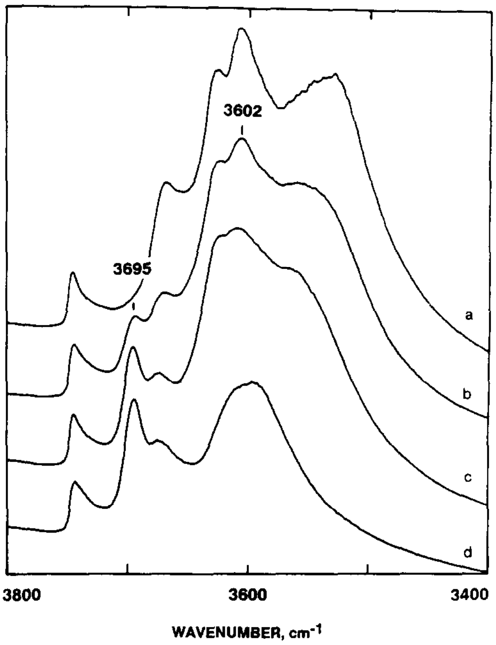


FIG. 5. Infrared spectra of the hydroxyl region for a hydrothermally prepared zeolite (series D with $Al_f$ = 36) poisoned with different amounts of $Na^+$: (a) 0.04 wt% $Na^+$, (b) 0.37 wt% $Na^+$, (c) 0.83 wt% $Na^+$. (d) Sample D-2 exchanged in 1 *M* $NaNO_3$.

because of the large number of overlapping bands, particularly in the steamed samples.

## DISCUSSION

Although other investigators have observed the effect of sodium poisoning in acidic zeolites (*17, 18*), it is obvious from this study that extreme care must be taken during the preparation of dealuminated zeolites to ensure that sodium is extensively removed if maximum activity is to be achieved in acid catalysis. In this study as little as 0.9 wt% $Na^+$ was enough to almost completely deactivate a zeolite with 15 Al/u.c. for hexane cracking. Sodium is a common contaminant in the laboratory found in water, glassware, and sweat, as well as the zeolite starting material.

*Mechanism of sodium poisoning.* The observed effect of the sodium poisoning (see Fig. 1) is much greater than would be predicted on the basis of a model in which each isolated Al atom is responsible for a Brønsted site of strong acidity. If this were the correct model one would expect that upon addition of $Na^+$, activity would decrease along the theoretical (and experimental) line which represents the activity due to the number of isolated framework Al atoms. For example, if one starts with 30 Al/u.c. and adds an amount of sodium equivalent to 6 $Na^+$ atoms/u.c., one would expect the resulting zeolite to have an activity equivalent to one with 24 Al/u.c. In fact, however, the resulting zeolite has almost no residual activity.

Two possible mechanisms for the effectiveness of the $Na^+$ poisoning are postulated. First, the sodium may be poisoning the active sites through some type of long-range interaction. Strong evidence for this hypothesis is given by Dyer and Singh (*29*), who examined the initial catalytic activity of $Na^+$- and $K^+$-exchanged mordenites for *n*-butane cracking. In this study $K^+$ was found to have a much larger detrimental effect than $Na^+$, and this was attributed to the differences in cationic radii and electronegativities. This implies that the poisons were not acting simply as cations replacing protons, but through some longer range interactions.

A second possibility is that only a fraction of the total Brønsted sites can be associated with the strong activity observed in these materials. The concept of zeolites having acid sites with differing strengths is not new. Early work by Barthomeuf and Beaumont (*19*) led them to conclude that strong and weak sites existed in these materials and dealumination removed the weak sites first. A further distinction must be made between the strong sites of Barthomeuf and Beaumont (*19*) and the fraction of sites responsible for the strong acidity observed in this work. The strong sites described in the present work would be only a fraction of the strong sites described by Barthomeuf and Beaumont (*19*). When 32 Al atoms remain in the lattice, it is assumed they are isolated and therefore, through electrostatic arguments, are all associated with strong acidity. The results of this study indicate that only a fraction of those remaining isolated Al atoms are responsible for the observed activity.

Jacobs *et al.* (*30*) studied the dealkylation of cumene and examined the hydroxyl region of the infrared spectra. A good correlation was found between the amount of pyridine required for complete poisoning and the number of acidic hydroxyls. This result was dismissed because the pyridine was known to react with Lewis sites as well as the framework hydroxyls. Instead, because the hydroxyls were found to decrease much more quickly than the initial activity, the activity was thought to be due to a fraction of the framework hydroxyls. Although qualitatively these results are opposite to what might be expected, on the basis of the current results, the overall interpretation is the same. In the current study the activity was found to decrease at the same rate as the 3602 $cm^{-1}$ band and to decrease much more *rapidly* than the acidic hydroxyls in general.

This finding is in qualitative agreement with the interpretation of Beyerlein *et al.* (*8*) that only one-third of the framework sites are responsible for the observed activity. A more dramatic effect of $Na^+$ poisoning, however, was observed in the present study. The difference between the fraction of strong sites determined by Beyerlein *et al.* (*8*) (one-third) and the fraction determined in the current study (about one-fifth) may be attributed to either the nature of the reaction itself or the difference in temperature at which the different reactions were conducted. Beyerlein *et al.* (*8*) examined the rate of carbonium ion formation, determined by the conversion of isobutane to propane, *n*-butane, and isopentane at 500°C, whereas, in the current study the conversion of hexane to lower hydrocarbons and isomers at 350°C was examined. To test the effect of temperature the hexane cracking was also carried out at 380°C. The fraction of poisoned sites effectively did not change; however, it is possible that at 500°C other factors such as sodium mobility or location affect the active sites.

Infrared spectra of the hydroxyl region provide information on the correct mechanism for the $Na^+$ poisoning, i.e., either long-range interactions or the fraction-of-sites model. It was expected that if the $Na^+$ was poisoning the zeolite through some type of long-range effect, the acidic hydroxyl bands would either shift frequencies noticeably or disappear almost completely as the catalysts became inactive. However, if the fraction-of-sites model was correct, the hydroxyl region in general would be expected to exhibit only minor differences, but specific minor bands would disappear. For example, one might expect only one Brønsted band to be affected, and in the case where 50% of the activity was lost, approximately 50% of one-fifth of the total Brønsted band intensity would be lost. Of course, this is an oversimplification as the extinction coefficients for all of the bands are not equivalent.

Upon examination of Fig. 3, it is clear that the infrared data of the hydroxyl region fit well with a fraction-of-sites model, with the 3602 $cm^{-1}$ band disappearing upon addition of small amounts of sodium. The 3602 $cm^{-1}$ band is formed upon dealumination and is present in both the hydrothermally prepared materials and the silicon tetrachloride-treated materials. The 3602 $cm^{-1}$ band is only a small fraction of the total intensity of the hydroxyl region, and the change in intensity from the original spectrum correlates well with the change in catalytic activity (see Table 2). Figures 4 and 5 show the same general trend with one difference being that a peak at ca. 3535 $cm^{-1}$ also decreases with increasing $Na^+$ content. Moreover, the majority of the Brønsted bands are unaffected and only these minor changes occur.

A qualitative argument against the mechanism based on long-range effects is the similarity of the slopes in Fig. 1. The slope is a measure of the degree of influence which the $Na^+$ has on the catalytic activity. Consider the series on the far left of the graph which contains 15 Al atoms per unit cell and the series on the right with about 36 Al atoms per unit cell. The concentration of Al atoms in the steamed sample with 36 aluminums is more than twice that of the sample with 15; however, the slopes are similar. If long-range effects dominated the poisoning mechanism, one might expect that the zeolite which has twice the concentration of acid sites would be poisoned much more effectively. Still further evidence is provided by the activation energy data. The activation energy was essentially the same for the three zeolites examined, indicating that the active site is not changing in nature, but only decreasing in number.

It is postulated that Al isolation is a necessary but insufficient condition for strong activity and that some additional factor is required for strong acidity (i.e., an extraframework cationic species). Assuming the fraction-of-sites model to be correct, one can predict what behavior might

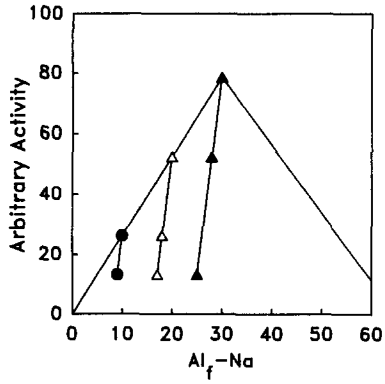
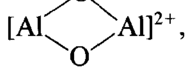


FIG. 6. Theoretical plot of the dependence of activity on framework aluminum content assuming that about one-fifth of the isolated framework aluminum atoms are responsible for the high activity observed in these dealuminated materials.

be expected, on the basis of the fact that only ca. 1 in 5 of the framework aluminum atoms is responsible for the strong acidity observed in these materials. Figure 6 was constructed by combining the fraction-of-sites model with the model in which isolated aluminum atoms are necessary for strong acid sites. The results are plotted in Fig. 6. This combined model gives results that closely resemble the trends observed in Fig. 1.

*Assignment of hydroxyl bands.* The literature contains references to a band at 3600 $cm^{-1}$ (*4, 16, 20–24*) that is present in dealuminated materials; however, as demonstrated in this study the band at ca. 3600 $cm^{-1}$ has more than one origin. As noted previously part of the bands at ca. 3600 $cm^{-1}$ are nonacidic and may not even result from surface hydroxyl groups as the species responsible did not react with pyridine or ammonia. These results would agree with the behavior of the broad band at 3595–3610 $cm^{-1}$ in Fig. 4, spectrum d, which remains after the addition of sodium ions. By contrast the narrow band at 3602 $cm^{-1}$ is highly acidic, as demonstrated by its disappearance upon initial sodium addition. Kubelkova *et al.* (*31*) recently have reported a similar band at 3601 $cm^{-1}$ in a Y-type zeolite which had been dealuminated with $SiCl_4$. In steam-dealuminated zeolites it is postulated that previous workers were unable to distinguish the highly acidic band at 3602 $cm^{-1}$ because of its small intensity relative to the other peaks in this region, and particularly because of the dramatic effect which small amounts of $Na^+$ can have on the intensity of the band. In our earlier study (*9*), the apparent shift in the band at 3640 $cm^{-1}$ to lower wavenumbers may, in fact, have been a result of an unresolved band at 3602 $cm^{-1}$.

The cracking activity has been shown to be linearly dependent on the framework aluminum content (*9, 10*). The framework aluminum atoms are responsible for the Brønsted acid sites in these materials. Since the intensity of the 3602 $cm^{-1}$ band corresponds well with the activity of dealuminated zeolites (see Table 2), it is postulated that this band results from a highly acidic Brønsted site associated with the framework. In these dealuminated materials all of the aluminum atoms are assumed to be isolated since they electrostatically repel each other within the framework; however, the $Na^+$ poisoning results indicate that not all of the sites have similar strong acidities. The band at 3602 $cm^{-1}$ must be distinguished from the other Brønsted sites for reasons other than isolation. The possibility of an interaction between a Lewis acid and a Brønsted acid site has been proposed (*4*). A cationic species such as  $[Al(O)_2Al]^{2+}$, $Al(OH)^{2+}$, or a cationic oxyhydroxide located in the small cavities could enhance the activity through inductive effects. This model will be discussed more fully in a subsequent publication.

The band at 3695 $cm^{-1}$ increases with the addition of sodium in all cases. In earlier studies with Na–X and Na–Y (*32, 33*) a band at 3695 $cm^{-1}$ was attributed to the interaction of the $Na^+$ cation with residual water. A convincing correlation between various properties of monovalent cations and the band near 3700 $cm^{-1}$ has been presented (*34*), and the mechanism for the development of this band has been reviewed (*35*). Although one might expect that pretreatment at 400°C under vacuum would totally remove the $H_2O$ from the zeolite, weak bands at ca. 1650 $cm^{-1}$, which are consistent with the bending mode of water, remain in the spectra. The $Na^+$ would reside in a well-defined cationic location allowing a water molecule to hydrogen-bond to the framework oxygen which was once associated with strong acidity. The interaction between the free proton of the hydrogen-bonded water and the $Na^+$ would give rise to the cation-dependent band at 3695 $cm^{-1}$ as described by Ward (*35*).

Even after further addition of sodium, bands at 3695 and 3675 $cm^{-1}$ a broad band at 3595–3610 $cm^{-1}$ and the band due to terminal silanol groups remained (spectrum d, Fig. 5). The bands at 3675 and 3595–3610 $cm^{-1}$ are assigned to two different types of nonexchangeable extraframework Al species. Shannon *et al.* (*13*) report that their pseudo-boehmite model compounds had bands at 3670–3680 $cm^{-1}$, which agrees well with the band observed at 3675 $cm^{-1}$ in the present study. Addition of an excess of $NH_3$ to these samples (spectrum not shown) almost completely removed the silanol band at 3745 $cm^{-1}$, probably through H-bonding interactions, and only a broad band with greatly reduced intensity at 3595–3615 $cm^{-1}$ remained. Lohse *et al.* (*24*) reported that upon acid washing a broad band observed at 3606 $cm^{-1}$ was greatly reduced in intensity, relative to a band at 3675 $cm^{-1}$. In agreement with earlier studies the species responsible for the broad 3595–3610 $cm^{-1}$ band is assigned to an aluminum oxyhydroxide phase, which can be removed somewhat by acid leaching, but cannot completely hydrogen-bond with $NH_3$ as it contains internal hydroxide groups. Complete $Na^+$ poisoning of a $SiCl_4$-treated sample also revealed a broad band in this region (spectrum not shown).

## CONCLUSIONS

Models to explain zeolite acidity generally involve the aluminum distribution within the zeolite, with isolated framework aluminum atoms being responsible for the strong acidity. This study further demonstrates that the aluminum distribution is not the only factor which determines strong acidity. Evidence which suggests that only a fraction of these isolated Al atoms are responsible for the observed activity has been presented; implying that isolation is a necessary, but insufficient condition for strong acidity. When the Mikovsky and Marshall (*27*) model is combined with a fraction-of-sites model, good agreement with experimental results is obtained. This suggests that there is a statistical distribution of highly acidic centers, probably formed through an interaction with an extraframework cationic aluminum species. Small amounts of sodium can effectively eliminate these highly acidic centers. In this study, it was found that one sodium ion could effectively poison activity which was previously thought to be due to ca. 5 framework Al atoms. This is interpreted to mean that only about one-fifth of the framework aluminums are associated with sites having the strongest acidity. The fraction of active sites appears to be similar over a wide range of silicon to aluminum ratios.

Upon $Na^+$ addition the infrared intensity of a band at 3602 $cm^{-1}$ was found to decrease in a manner parallel to the catalytic activity. This band has been assigned to a framework hydroxyl group which functions as a strong Brønsted acid.

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