

## Acidity and Activity of Fluorinated Mordenites

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Samples of mordenite catalyst treated with 0.125 and 0.25 M HF aqueous solutions showed appreciable aluminum removal and small amounts of residual fluorine after treatment. More concentrated HF (1.5 M) caused silicon to be leached from the zeolites and the unit cell dimensions were decreased slightly; the surface areas were also significantly affected by this latter treatment. Infrared studies of these samples suggest that small amounts of impregnated fluoride enhance strong Lewis acidity and weak Brønsted acidity. For all except the most severely treated catalyst, the activity for cumene conversion was fairly high. It appears that aluminum-associated Brønsted sites are the active sites for this reaction, and those catalysts with less aluminum can deactivate quickly as their active sites are blocked with coke. © 1987 Academic Press, Inc.

### INTRODUCTION

The incorporation of fluorine in oxide catalysts enhances their activity for acid-catalyzed hydrocarbon reactions such as cracking, isomerization, alkylation, polymerization, and disproportionation (1, 2). Fluoride is thought to replace surface O or OH; because fluorine is more electronegative than the groups it replaces it increases the polarity of the lattice, thereby increasing both the acidity and reactivity of the surface.

The modification of alumina by fluorination is not uncommon because otherwise it is not very active for acid-catalyzed hydrocarbon reactions (2). Much less work has appeared in the literature on fluorinated zeolites because these catalysts are already highly active for such reactions. Lok *et al.* (3, 4) found that the treatment of zeolites with diluted fluorine gas affected the samples in a manner which depended on the severity of the fluorination. Becker and Kowalak recently reported the results of a study of the modification of H mordenite with ammonium fluoride solutions and gaseous CHF<sub>3</sub> (5). Also it has been reported in the recent patent literature that the high-silica pentasil zeolites exhibit enhanced Brønsted acidity and therefore improved

catalytic activity after treatment with various fluorine-containing compounds (6, 7). Some of the patent studies (6b, 7a) suggest the use of aqueous HF solutions for fluorination, and it was for this reason that the present study of the HF treatment of mordenite, an industrially important siliceous zeolite, was undertaken.

### EXPERIMENTAL

*Reagents.* Pyridine used for the infrared adsorption studies was ACS grade, distilled, and degassed by several freeze-pump-thaw cycles, and stored over molecular sieves before use. Aqueous HF was prepared from ACS-grade HF. Cumene (Eastman reagent grade) was purified by passing it through a column containing Al<sub>2</sub>O<sub>3</sub> to remove hydroperoxide and then it was distilled before use.

*Fluorination of zeolites.* Mordenite (NH<sub>4</sub> form) obtained from Union Carbide was deammoniated at ca. 550°C for more than 2 h in a tube for which one end was connected to a pump, the other end being open. The hydrogen mordenite so formed (HM) was used as the parent catalyst for the fluorination studies. The zeolite was fluorinated by wet impregnation with an aqueous solution of HF (details given below) and the

slurry so formed was then stirred and slowly evaporated to dryness at 60°C.

*X-ray study.* X-ray powder diffraction patterns of the samples were recorded over a  $2\theta$  range of 5 to 60° at a scan rate of 2° per minute with the aid of a Norelco/Philips diffractometer using  $\text{FeK}\alpha$  radiation filtered through manganese. The samples were heated overnight at 110°C prior to the X-ray studies.

*Infrared spectra.* Infrared spectra were measured at  $2\text{ cm}^{-1}$  resolution on a Nicolet 8000 Fourier transform spectrometer. The infrared cell used was fitted with calcium fluoride windows and connected to the vacuum system and the reagent inlets by Teflon joints. Approximately 10 mg of the zeolite powder was accurately weighed and then pressed into a 13-mm-diameter self-supporting wafer which was placed in the IR cell. The standard pretreatment consisted of evacuating while slowly increasing the temperature to 500°C at which time oxygen was admitted and left overnight at the same temperature to remove any carbonaceous contaminants. The sample was finally evacuated at 500°C and then cooled to room temperature. Pyridine (used as a probe molecule) was then admitted at its saturated vapor pressure into the IR cell at room temperature. The cell was kept at 100°C for 1 h followed by desorption successively at 200, 300, 400, and 500°C for 1 h in each case. IR spectra were recorded at room temperature.

*Cumene cracking.* The cumene cracking studies were carried out in a continuous flow, fixed-bed reactor. The reactor was made of stainless-steel with an inside diameter of 15 mm. It was packed with alternating layers of quartz wool, and between these layers the catalyst (100 mg) was placed. The catalyst was activated by heating at 500°C for 2 h with a helium flow rate of  $60\text{ cm}^3\text{ min}^{-1}$ . After activation the catalyst was cooled to 400°C. The cumene was contained in a presaturator, held at 20°C, through which the carrier gas, helium, was passed at a measured flow rate ( $30\text{ cm}^3\text{ min}^{-1}$ ). The reaction was then carried out

over a 7.5-h period. Samples of the feed and products were collected every 16 min in a sample loop collector, equipped with a CDS-111 data processor. The column was 6 ft  $\times$   $\frac{1}{8}$  in. o.d., stainless steel, packed with 5% Bentone-34 + 5% Diisodecylphthalate on 60- to 80-mesh Chromosorb W. The GC signals (suitably corrected for detector sensitivity) were used to calculate the total number of moles of each aromatic product in the output stream. The total conversion is defined as the sum of all aromatics except cumene divided by the sum of all aromatics including cumene.

## RESULTS AND DISCUSSION

### *Elemental and X-ray Analyses*

The results of elemental analyses, X-ray powder diffraction (XRD) studies, and surface area measurements on the mordenite samples used in this study are collected in Table 1. This table also includes the carbon content measured for used samples from the catalytic studies (to be discussed later). As can be seen, the amount of fluorine retained in the zeolite is quite small, being less than 0.4% in all cases. This range of values is similar to that found to be most active by Becker and Kowalak (5); they found that above 0.43% F cumene conversion in their pulse reactor decreased.

The overall composition of the zeolite will influence its physical and chemical properties, and Sanderson electronegativity values have been found in previous studies to correlate reasonably well with certain properties of this type of zeolite (8–10). The Sanderson electronegativity values of the zeolites prepared for this work are summarized in Table 1. The unit cell compositions required to calculate these values were computed by assuming that in HM each Al present requires one H for charge compensation, and that each  $\text{F}^-$  incorporated in the fluorinated samples replaces one  $\text{OH}^-$  group. As can be seen, sample F3, which contains the largest amount of  $\text{F}^-$  and the smallest quantity of Al, has the most electronegative surface.

TABLE I

Details of Preparation and Analyses of Samples

Sample	HF treatment <sup>a</sup>		Elemental analyses <sup>b</sup> (wt%)			Si/Al	S <sup>c</sup>	Lattice parameters (Å)			Surface area <sup>d</sup> (m <sup>2</sup> g <sup>-1</sup> )	C <sup>e</sup> (wt%)
	Concn (M)	Vol (ml)	Si	Al	F			a	b	c		
HM	—	—	31	3.9	0.00	8.0	4.189	18.17	20.16	7.43	319	na <sup>f</sup>
F1	0.125	40	31	3.4	0.09	9.1	4.194	18.18	20.21	7.45	331	5.77
F2	0.250	40	33	2.7	0.23	12.2	4.200	18.16	20.24	7.47	348	6.58
F3	0.250	80	32	1.5	0.38	21.3	4.231	18.15	20.19	7.46	308	2.57
F4	1.50	20	27	3.6	0.14	7.5	4.186	18.05	20.07	7.42	264	2.93
F5	1.50	33	28	3.8	0.16	7.4	4.185	18.01	20.07	7.42	110	0.27

<sup>a</sup> Using 5.0 g HM.<sup>b</sup> Si and Al were determined by neutron activation analysis at AECL Ltd., Ottawa, Ontario, Canada. Fluoride was analyzed with an ion-sensitive electrode after removal from the zeolite surface by treatment with NaOH.<sup>c</sup> Sanderson electronegativity; see Refs. (10–12).<sup>d</sup> Surface areas were measured by the BET technique using a Micromeritics Model 2200 instrument.<sup>e</sup> wt% C remaining on the surface after toluene extraction of samples used in catalytic cracking of cumene under conditions described in text.<sup>f</sup> Not available.

One possible consequence of HF treatment is a modification of the crystal structure due to attack on the zeolite framework by the fluorination agent. In previous studies, the X-ray powder diffraction pattern has been used to detect changes in crystallinity after fluorine treatment. Lok *et al.* (3, 4), for example, who used diluted F<sub>2</sub> gas for fluorination, observed substantial changes in XRD peak intensity and small shifts to higher 2θ values, particularly for those samples treated under “severe” conditions. These shifts were attributed to a decrease in unit cell size associated with dealumination and structure stabilization. Kokotailo *et al.* (7), who used dilute HF treatment, reported weaker and broader lines in the XRD patterns after fluorination. In the work reported here a more detailed analysis of the XRD powder patterns, which are shown in Fig. 1, was carried out. A least-squares fitting program was used to obtain the unit cell dimensions from the measured positions of known reflections (11); about 12 lines were used for each sample.

Three different concentrations of HF solution were used: 0.125, 0.25, and 1.50 M. As can be seen by comparing the elemental

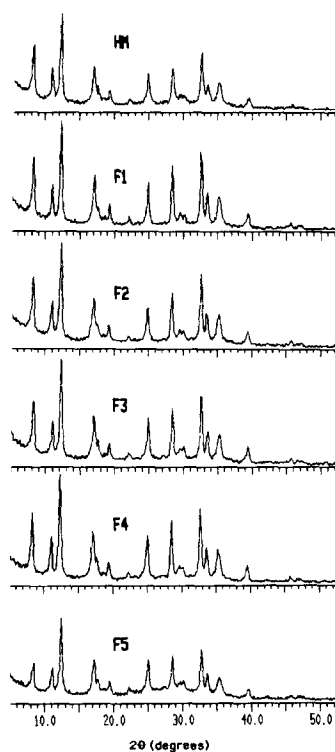


FIG. 1. X-ray powder diffraction patterns for zeolite samples described in Table I.

analyses and the X-ray data for these samples, treatment with either 0.125 *M* HF or 0.25 *M* HF did not affect significantly the unit cell dimensions or the weight percentage of silicon, but aluminum was leached from the samples. Treatment with the more concentrated HF did produce a small decrease in unit cell dimensions, but while silicon was removed from the lattice the aluminum content of these two samples did not change appreciably. This result is consistent with the very recent observation from NMR studies that treatment of aluminosilicates with concentrated fluoride solutions results in preferential removal of silica from the lattice (12). It is worth noting that no significant variation in X-ray line width was found for any of these samples, and only the most severely treated sample, F5, showed reduced line intensity. Apparently the X-ray line width and intensity are not sensitive indicators of aluminum extraction.

Mild treatment with dilute HF (0.125 *M*, 0.250 *M*) resulted in only minor changes in the surface areas of these samples; initially a very small increase was noted, but with the larger volume of 0.250 *M* HF a small decrease was found. Sample F4, prepared with 20 ml of 1.50 *M* HF, showed a slightly larger reduction in surface area (14%), and sample F5 showed a severe reduction to only 110 m<sup>2</sup> g<sup>-1</sup>. It may be that the pores of this last sample are partially blocked by amorphous material leached from the zeolite framework.

### Infrared Studies

**Hydroxyls.** Hydrogen mordenite has OH stretching bands at about 3745, 3650, and 3610 cm<sup>-1</sup>. The hydroxyls which give rise to the 3745-cm<sup>-1</sup> band are present in all zeolites and are only weakly acidic (13). These hydroxyls have been attributed to terminal silanols, and they may also contain some contribution from hydroxyl nests which are formed upon dealumination (14, 15). The hydroxyls responsible for the 3650-cm<sup>-1</sup> band are known to be nonacidic, while

TABLE 2  
IR Data for Mordenite Samples

Sample	Infrared intensity <sup>a</sup>			
	Hydroxyls <sup>b</sup>		Pyridine bands <sup>c</sup>	
	3745	3610	1545(B)	1455(L)
HM	28.1	5.0	4.4	10.2
F1	26.6	8.8	10.6	19.9
F2	24.5	7.0	8.5	21.0
F3	19.0	4.1	2.4	4.0
F4	3.5	1.3	1.9	1.9
F5	0.2	0.0	0.0	0.2

<sup>a</sup> Absorbance per gram of catalyst, at the given wavenumbers.

<sup>b</sup> Prior to pyridine adsorption.

<sup>c</sup> After pyridine adsorption and desorption (at 400°C) as described in the text.

those which produce the band at 3610 cm<sup>-1</sup> are very acidic and are responsible for the activity of mordenite for acid-catalyzed reactions. These highly acidic hydroxyls are associated with aluminum atoms of the zeolite (13, 16).

The 3650-cm<sup>-1</sup> band does not show any significant change with fluorination. The 3745- and 3610-cm<sup>-1</sup> bands change intensity with fluorine content of the catalyst, as shown in Table 2. As fluoride is thought to replace surface hydroxyls, these bands would be expected to decrease in intensity as the percentage of F increases. For the 3745-cm<sup>-1</sup> band, the expected behavior is observed for HM, F1, F2, and F3. F4 shows a further decrease in intensity at 3745 cm<sup>-1</sup>, although the percentage of F retained in the catalyst is less than that for either F2 or F3. Presumably the more concentrated HF used to prepare F4 has modified the external surface of the zeolite (and hence affected the terminal silanols); note that the wt% of Si is significantly lower for F4 (and F5). Rather surprisingly, the aluminum-associated 3610-cm<sup>-1</sup> band does not show the expected decrease in intensity with fluorine content. Instead, an initial increase in intensity is observed; the 3610-

$\text{cm}^{-1}$  band is stronger in both F1 and F2 than it is in the parent HM. This intensity increase when the number of hydroxyl groups responsible for the absorption presumably is decreasing must be attributed to an increase in absorptivity of the remaining OH groups as they become more acidic, under the influence of the fluoride. It has been reported that the absorptivity of aromatic hydroxyls (more acidic) is greater than that of aliphatic hydroxyls (less acidic) (17). If this same correlation can be applied to surface hydroxyls, then the initial increase in intensity at low F content suggests that the  $3610\text{-cm}^{-1}$  hydroxyls are more strongly affected by the addition of fluorine than those responsible for the  $3745\text{-cm}^{-1}$  band, for which no increase in absorbance is seen.

**Adsorbed pyridine.** The acidity of the zeolites was characterized from the Fourier transform infrared spectra of adsorbed pyridine. The change in the population of Brønsted and Lewis sites as determined from absorbances of the characteristic bands of the pyridinium ion ( $\text{PyH}^+$ ) at  $1545\text{ cm}^{-1}$  and of Lewis-adsorbed pyridine (LPy) at ca.  $1460\text{ cm}^{-1}$  as a function of fluorine content are shown in Table 2. It is clear (and not unexpected) that treatment with the most concentrated HF used ( $1.5\text{ M}$ ) affected the surface characteristics of samples F4 and F5. F5 in particular shows very little acidity of either type, and F4 has substantially reduced activity, despite having a substantial surface area and moderate F content.

For samples HM, F1, F2, and F3 the trends in acidity are readily explained. As can be seen from Table 2, the number of Brønsted sites which retain pyridine after desorption at  $400^\circ\text{C}$  increases above that observed with HM in samples F1 and F2 and then decreases in F3. This behavior is consistent with the increase in acidity noted above for the  $3610\text{-cm}^{-1}$  hydroxyls in the absence of pyridine. Similarly, after  $400^\circ\text{C}$  desorption, the Lewis-pyridine band is stronger for F1 and F2 than for HM, despite their reduced aluminum content. This con-

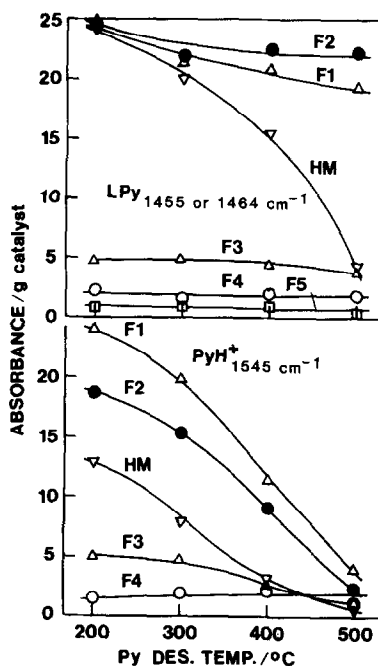


FIG. 2. Absorbance per gram of catalyst for pyridine remaining on Lewis sites (LPy, band at  $1455$  or  $1464\text{ cm}^{-1}$ ) and Brønsted sites ( $\text{PyH}^+$ , band at  $1545\text{ cm}^{-1}$ ) after desorption at  $200$ ,  $300$ ,  $400$ , and  $500^\circ\text{C}$ .

firms that fluorination also enhances Lewis acidity.

The number of Brønsted and Lewis sites of different relative strength can be measured from the thermodesorption of pyridine, since as the desorption temperature is increased only pyridine adsorbed on stronger sites will remain. Figure 2 shows the absorbances of the  $\text{PyH}^+$  and LPy bands after pyridine was desorbed at progressively higher temperatures. From a comparison of the curves for samples HM, F1, and F2 it appears that mild fluoride treatment enhances the strong Lewis sites (those which retain pyridine at  $500^\circ\text{C}$ ) and the weak Brønsted sites (those which retain pyridine at  $200^\circ\text{C}$ ). The number of Lewis sites in F3 is reduced (although they all appear to be strong) compared to the first three samples, probably because of the smaller number of accessible aluminum sites in this sample (see also next section). This lower quantity of aluminum in F3

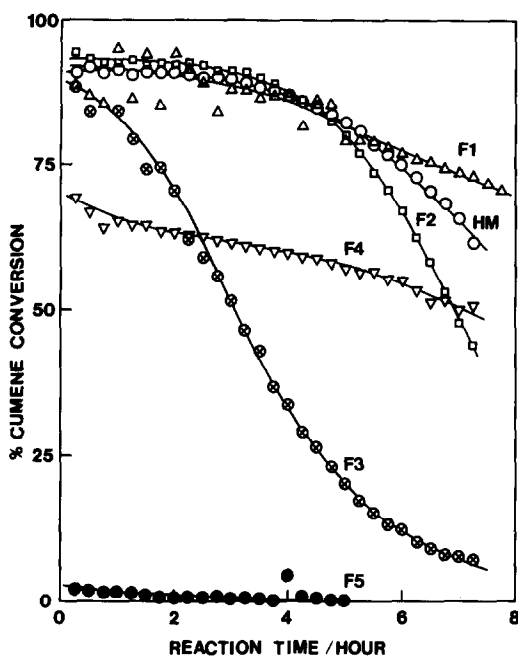


FIG. 3. Cumene conversion at 400°C as a function of time on stream.

would also explain the reduced  $\text{PyH}^+$  band intensity noted above for this sample, as the active Brønsted sites are associated with aluminum atoms (13, 16).

#### Catalytic Studies of Cumene Cracking

Under the conditions of the catalytic experiments, benzene was the major aromatic product (ca. 95%) with a small amount of ethylbenzene (1–3%) and toluene (<2%). The total of other aromatics represents less than 2% of the input cumene. These others presumably consist mainly of methylstyrene; however, this compound was not clearly resolved in the gas chromatogram. It is expected that the propene produced after dealkylation of cumene may readily undergo a variety of secondary reactions, giving a number of aliphatic light hydrocarbons ( $\text{C}_1$ – $\text{C}_4$ ) in the products (18). In this study these hydrocarbons were not resolved.

The initial activity of the parent H-mordenite for cumene conversion is very high (ca. 90%), as can be seen in Fig. 3. The

increased Brønsted and Lewis acidity of samples F1 and F2 (see Fig. 2) does not increase this already high initial conversion. The conversion of cumene produced by sample F3 is also very high initially, although it deactivates very rapidly (see discussion below). Sample F4 shows a somewhat reduced initial activity, and F5 has almost no catalytic activity at all. These trends in initial activity confirm that Lewis sites do not play a major role in cumene cracking over these catalysts. As the samples were activated at 500°C prior to reaction, the number of Lewis sites on the samples might be expected to be in the order of the strong sites identified in the pyridine-IR studies, i.e.,  $\text{F2} > \text{F1} \gg \text{HM} \approx \text{F3} > \text{F4}$ , and this order is quite different from the observed initial activity order. As can also be seen from Fig. 2, the number of Brønsted sites retaining pyridine after high-temperature desorption (500°C) is very small, and very similar for all catalysts. Apparently with pyridine it is difficult to characterize the stronger Brønsted sites on these catalysts.

The deactivation of these catalysts with time on stream shows some significant differences. Samples HM, F1, and F2 behave in a very similar manner for the first 5 h, after which F1 deactivates more slowly than the parent HM while F2 deactivates more quickly. F3 loses its high initial activity very quickly, while F4, which showed only moderate activity initially, deactivates very slowly, and after 7 h is performing much better than F3.

Deactivation of these catalysts can occur as a result of coke formation. The amount of carbon remaining on the used catalysts after toluene extraction is given in Table 1, and this can be taken as a measure of the relative amount of coke formed. As expected, more carbon is found on F2 than on F1, and F4, which deactivates slowly, contains only about half as much carbon. Sample F3, which deactivates very rapidly, contains less residual carbon than either F1 or F2—approximately the same amount as F4. F5, which is virtually inactive, de-

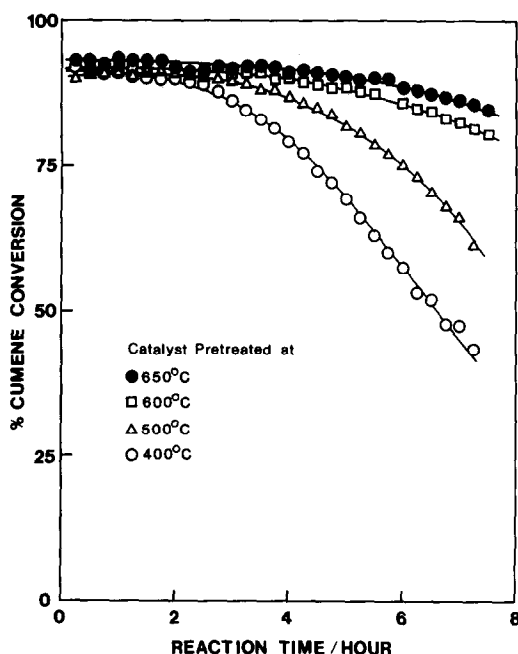


FIG. 4. Cumene conversion at 400°C on H mordenite (HM) pretreated at different temperatures.

velops only a very small amount of carbon.

These results may be understood if it is assumed that the active sites for cumene conversion are those highly acidic Brønsted acid sites which are associated with the aluminum atoms in the zeolite. Table 1 shows that the aluminum content decreases from HM to F1, F2, and F3, but F4 contains almost the same amount of Al as does HM. Since presumably in all these catalysts some of this aluminum is located at inaccessible sites inside the zeolite framework, the number of catalytically active sites could be considerably less in F3 than in the other four active catalysts. To illustrate this point, if it is arbitrarily assumed that say 1.0% of the aluminum in each zeolite is inaccessible, then the catalytically active sites would be proportional to 2.9, 2.4, 1.7, 0.5, and 2.6, respectively, for the catalysts HM, F1, F2, F3, and F4. If this were the case, then the ratio of active sites in say F2 to F3 would be 1.7 : 0.5, or 3.4 : 1. Any increase in the amount of inaccessible aluminum above the arbitrarily assumed 1.0% would of course increase this ratio. Thus F3 would

be expected to be most susceptible to poisoning by coke (even by relatively small amounts), F2 to be next most susceptible, and HM, F1, and F4 to be most resistant to coke poisoning. This is in agreement with the observed rates of deactivation (see Fig. 3), except that HM deactivates slightly more rapidly than F1. Perhaps the slightly larger surface area in F1 may expose more active sites that are present in HM.

To confirm the importance of Brønsted sites on these catalysts, a study of the parent H mordenite was undertaken. Samples of this catalyst were activated at different temperatures between 400 and 650°C and spectra of adsorbed pyridine were obtained. Catalytic studies were also carried out on these samples; the results of these studies are presented as Fig. 4. As can be seen, the catalysts activated at higher temperatures deactivate more slowly. This is consistent with the conclusion of Marczewski and Wojciechowski (19) that the rate of catalyst deactivation is related to the Brønsted site concentration, because the pyridine-IR results show that activation at higher temperatures causes a decrease in the concentration of Brønsted sites, but an increase in the concentration of Lewis sites.

#### CONCLUSION

For mordenite catalysts, XRD and surface area measurements have shown that treatment with dilute HF ( $\leq 0.25 M$ ) does not seriously affect the structure of the catalysts. Elemental analysis shows that small amounts of fluorine are incorporated, and aluminum is leached from the samples. Treatment with more concentrated HF (1.5  $M$ ) causes silicon to be removed from the structure and does decrease the size of the unit cell slightly. With a larger volume of this more concentrated HF, the surface area was found to be substantially reduced (sample F5). Infrared studies both of the OH stretching region of these samples and of adsorbed pyridine have shown that the incorporation of small amounts of fluoride

enhances both the Brønsted and Lewis acidity, but in different ways; it enhances strong Lewis acidity and weak Brønsted acidity.

The initial activities of these catalysts for cumene conversion are similar for the parent mordenite and for the three samples treated with dilute HF. The sample treated with a smaller amount of 1.5 M HF showed an initial activity which was reduced by about the same amount as its surface area, compared to the parent HM. The final sample, treated with a larger volume of 1.5 M HF, showed a severe reduction in surface area and virtually no acidity or activity for cumene conversion.

The deactivation of this series of catalysts at longer reaction times appears to be related to the aluminum content—in general, the lower the aluminum content, the more rapid the rate of deactivation. It is assumed that deactivation occurs via coke poisoning of the active sites, which are thought to be those aluminum-associated hydrogens responsible for the 3610-cm<sup>-1</sup> band in the infrared spectrum. A study of the reactivity of H mordenite activated at different temperatures confirmed that the active sites are Brønsted acid sites.

#### ACKNOWLEDGMENT

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