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A Study of Dealuminated Faujasites

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We have examined a series of steamed and chemically dealuminated faujasites, with lattice parameters varying from 2.4488 to 2.4242 nm, using a range of techniques in order to obtain a better understanding of the acid sites in these materials. Temperature programmed desorption (TPD) and thermogravimetric analysis (TGA) measurements of isopropylamine showed that only a fraction of the sites associated with framework Al give rise to Brønsted-acid sites, as determined by decomposition of the amine between 575 and 650 K. Infrared spectroscopy indicated that these acidic sites are associated with the hydroxyls observed in a band at 3640 cm^{-1}. No significant differences were observed for TPD–TGA of isopropylamine or for propene oligomerization between a steamed and a chemically dealuminated H–Y having nearly the same lattice parameter; however, TPD–TGA measurements of isopropanol suggest that additional reaction sites are present in the steamed sample for this probe molecule. *n*-Hexane cracking measurements at 748 and 798 K indicate that turnover frequencies (molecules reacted/site sec) are significantly enhanced by steaming, but that acid leaching reduces the activity back to that observed for a chemically dealuminated material. Microcalorimetry measurements for pyridine and isopropylamine provided no evidence for the presence of special sites in steamed materials. It is suggested that the enhanced cracking activities observed in steamed faujasites are not due to the enhanced acidity of the hydroxyl sites.

INTRODUCTION

One of the most interesting questions in the area of acid catalysis in zeolites regards the role of dealumination, and the resulting nonframework Al, in changing the catalytic activity of faujasites. It has been demonstrated that the hydrocarbon cracking activity increases sharply during the initial phases of dealumination, then decreases as more and more Al is pulled out of the framework (1). The method used to dealuminate the catalyst is also important. Materials which have been dealuminated by steaming have been shown to be considerably more active for hydrocarbon cracking than those which have been dealuminated chemically to the same framework Al content (2, 3). Steamed zeolites differ from chemically dealuminated zeolites mainly in that they contain a considerable amount of nonframework Al.

Exactly how nonframework Al affects catalytic activity is not known, and three general possibilities exist. First, the nonframework species could, itself, be a catalytic site. Second, nonframework species could interact with framework Al sites to stabilize the negative charge on the lattice following the removal of acidic protons (3). In this case, the nonframework alumina would simply increase the strength of the Brønsted-acid sites which are primarily the result of tetrahedral framework Al. Third, nonframework alumina could work in a symbiotic manner with nearby Brønsted-acid sites, increasing the rate at which a protonated molecule reacts to form products. For example, the alumina could promote bond scission of carbonium ions formed at the Brønsted sites without affecting the strength of the Brønsted sites. There are obviously a number of variations on these general mechanisms for the promotion of catalytic activity by nonframework Al, but they can at least be placed loosely within these categories.

In an attempt to address these questions and further develop techniques for characterizing the acidic properties of faujasites, we have investigated a series of well-characterized H–Y zeolites using a variety of techniques. The materials we investigated had a wide range of bulk Al contents and were dealuminated both chemically and by steaming. As a measure of site concentrations, we used simultaneous temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) of isopropylamine and isopropanol (4). In a previous study of steamed fluid-catalytic-cracking (FCC) catalysts, it was shown that the amount of isopropylamine which decomposed to propene and ammonia between 575 and 650 K in TPD–TGA measurements correlated very well both with the lattice parameter of the faujasite component of the catalyst and with the cracking activity of the catalyst for a light gas-oil feed (6). Based on the observation of an isopropylamine decomposition feature at the same temperature in TPD–TGA measurements on high-silica zeolites (5), this feature was identified as being due to strong Brønsted-acid sites and the amount of decomposition is

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therefore directly related to the concentration of those Brønsted-acid sites. From results on a series of H(Na)–Y catalysts, it was shown that only those sites associated with the high-frequency 3640 cm^{-1} hydroxyl are strong enough to cause decomposition of the amine (7). Complimentary information is obtained from TPD–TGA of isopropanol. Like isopropylamine, isopropanol decomposes at Brønsted-acid sites in high-silica zeolites in a stoichiometry of one per site (4); however, it also reacts to propene and water on the Lewis sites present in pure alumina (8). Given that isopropylamine does not react in appreciable amounts on the Lewis sites on pure aluminas (20), the difference between the amounts of isopropanol and isopropylamine which decompose in TPD–TGA provides an additional measure of the acid-site concentration. To determine site strengths, we measured *n*-hexane cracking rates and differential heats of adsorption of selected bases (9, 10).

Our results confirm that the reaction of isopropylamine in TPD–TGA measurements occurs exclusively at Brønsted sites resulting from tetrahedral framework Al. The presence of nonframework Al does not appear to have any influence on the results of these measurements. We also reproduced the high catalytic activity observed previously for ultrastable faujasites, but microcalorimetry measurements do not indicate the presence of any unusually strong acid sites. This suggests that the increased hydrocarbon cracking activity observed for materials containing nonframework Al is probably not due to unusually strong acid sites.

EXPERIMENTAL

Sample Preparation and Characterization

Most of the materials used in this study were provided by the PQ Corp., and the physical characteristics of each sample are summarized in Table 1. PQ(7) is a typical USY catalyst which was prepared by steaming between 650 and 730 K followed by ammonium ion exchange. The other PQ samples were steamed a second time at higher temperatures (for example, PQ(10) was steamed between 705 and 790 K) and leached with a mineral acid at pH <0.5 to 0.7. Bulk Al concentrations were determined by atomic absorption spectroscopy and are reported in Table 1, along with the relative porosities determined from oxygen uptakes at $P/P_0 = 0.4$ and 77 K. The porosities ranged from 0.289 to 0.321 cm^3/g, in reasonable agreement with the ideal porosity of faujasite.

TABLE 1

Physical Characteristics of the Samples Used in this Study

Sample	Bulk Al Al/u.c.	u.c. size (nm)	Framework Al[a] Al/u.c.	O_2 uptake cm^3/g
CD(12)	29	2.4488	26.0	0.296
PQ(7)	43	2.4478	25.7 (30.7)	0.321
PQ(10)	33	2.4318	8.6 (6.4)	0.281
PQ(20)	17.5	2.4292	5.6 (5.8)	0.293
PQ(30)	12.0	2.4269	3.3 (1)	0.315
PQ(60)	6.2	2.4266	3.0 (<1)	0.306
PQ(71)	5.3	2.4244	0.6 (<1)	0.289
PQ(85)	4.4	2.4252	1.5 (<1)	0.286

[a] Values in parentheses were determined using ^{29}Si NMR.

The CD(12) sample was prepared by a double dealumination of an ion-exchanged NaY zeolite (PQ Corp., Valfor CP-6300) with ammonium hexafluorosilicate using procedures based on those outlined in the literature (2, 11). In the first step, 3.00 g of ion-exchanged PQ(5) was added to 200.00 g of a solution containing 12.20 g of ammonium acetate in deionized water. While this mixture was being heated in a vessel at 350 K, 2.00 g of a solution containing 0.90 g of ammonium hexafluorosilicate in 25.00 g of ammonium acetate was added dropwise. This mixture was stirred at 350 K for 3 h, filtered, and then dried in an oven at 470 K for 20 min. Following a second ammonium ion exchange with an ammonium sulfate solution, a second dealumination step was performed which was identical to the first except that the starting weight of the zeolite was 1.00 g and the other ingredients were scaled back proportionally.

The samples were characterized by X-ray diffraction and all gave sharp peaks with no amorphous halo. Lattice parameters were determined using the peaks between 50 and 60° 2θ, with the (222) line of NaCl, which had been added to the samples as a physical mixture, used as an internal reference. The lattice parameters, shown in Table 1, have been shown to be linearly related to the framework Al content according to the equation

$$Al_f = 107.1 \times (a_0 - 24.238),$$

where a_0 is the unit cell parameter in angstroms (12). ^{29}Si NMR was also used to measure the framework Al content on selected samples and gave essentially identical results to those obtained from the lattice parameters (13). It should be noted that the bulk Al content for each of the steam-dealuminated samples is significantly higher than the framework Al content, indicating the presence of significant amounts of extraframework Al.

The unactivated CD(12) sample was also examined using ^{27}Al NMR at a resonance frequency of 39.71 MHz. The pulse length of 0.25 μsec, which corresponded to a $\pi/20$ rotation of the bulk magnetization measured using a 1.0 *M* $AlNO_3$ solution, should be sufficiently small to observe ^{27}Al nuclei having different quadrupolar coupling constants with equal intensity. By comparing the intensities of the CD(12) and PQ(5) samples, we determined that the bulk Al content of this sample was very close to the framework content from the lattice parameter and that only tetrahedral Al was present in this sample. Therefore, CD(12) provides an excellent comparison for the steam-dealuminated samples.

Measurement Techniques

The conditions and equipment used for the TPD–TGA experiments have been described elsewhere (4–7). Between 5 and 15 mg of zeolite were placed on the sample pan of a Cahn microbalance which was then evacuated with a turbomolecular pump to $\sim 10^{-7}$ Torr. The sample temperature was then ramped to 750 K at 20 K/min before being cooled back to room temperature. From the lattice parameter measured on PQ(7) after this treatment, it was shown that the vacuum was sufficient to prevent steaming. The samples were exposed to ~10 Torr of adsorbate for ~5 min and then evacuated for 2 h to remove some of the weakly bound species. The temperature of the sample was then ramped at 20 K/min using a mass spectrometer and the microbalance to monitor the desorption process. In each case, the sample weight returned to its initial value following a TPD–TGA experiment and successive measurements on the same sample gave identical results. We did not attempt to calibrate the areas under the TPD peaks and all coverages reported in this paper were determined from the weight changes in given temperature regions.

n-Hexane cracking rates were measured in a differential tubular flow reactor. Approximately 50 mg of catalyst was supported inside a $\frac{3}{8}$ in. stainless-steel tube using Pyrex wool. Quartz chips placed at the reactor entrance served to preheat the feed gases and to reduce the residence time in the reactor. A dry nitrogen carrier gas was bubbled through liquid *n*-hexane, maintained at 273 K using an ice bath, and products were measured using an on-line gas chromatograph. Samples were activated *in situ* by heating stepwise from room temperature in 100° increments, holding the reactor at each temperature for $\frac{1}{2}$ h. For each rate determined in this study, the conversion was measured as a function of reactor space time up to conversions of ~5%, with the rate obtained from the initial slope of a plot of conversion versus space time. Between measurements, only dry nitrogen was passed over the catalyst and no catalyst deactivation was observed during the rate measurements. The catalysts were exposed to hexane for only a few minutes during the entire course of the rate measurements. Prior to measurements on the faujasite samples, cracking rates were determined on an H-ZSM-5 sample. The turnover frequencies (molecules reacting/Al site sec) on H-ZSM-5 were found to agree with those reported by Haag and co-workers within the uncertainty of our measurements (14, 15).

The calorimetry experiments were performed on a Calvet-type heat-flow microcalorimeter which was designed and constructed in our laboratory. Details about the apparatus and the experimental procedures have been described elsewhere (16, 17). Relatively large samples (500 to 600 mg) were typically used in the instrument; however, the cubic sample chamber (2.54 cm on each side) was designed to be large enough so that the bed height was relatively shallow (~1 mm) in order to minimize concentration gradients. Also, the gas doses were held at the temperature of the measurements, 480 to 500 K, in order to avoid adsorption on the walls of the dosing volume, which can lead to significant errors in the heats obtained in the initial pulses. A typical gas does was 10 to 20 μmol, and the total heat evolved during a given pulse was determined by integrating the heat flux with respect to time. In all cases, the signal from the heat-flux meters was found to return to the baseline within less than 20 min and there was no need for baseline correction.

RESULTS

TPD–TGA of Isopropylamine

The TPD–TGA curves for isopropylamine on CD(12), PQ(7), and PQ(60), shown in Fig. 1, are qualitatively similar to those published earlier for other zeolites (4, 17, 18). In all cases, we observe a well-defined feature desorbing from the samples as propene (m/e = 41) and ammonia (m/e = 17) between 575 and 650 K, the same temperature range that was observed for decomposition of isopropylamine on high-silica zeolites like H-ZSM-5 (18). This high-temperature feature has previously been shown to be due to adsorption of the amine at Brønsted-acid sites and occurs by decomposition of the ammonium ion by a mechanism similar to the Hofmann elimination reaction. Based on studies of Fe- and Ga-substituted ZSM-5 (19, 20), the decomposition temperature was shown to be insensitive to the strength of the acid site; but the quantity of amine which reacts in this temperature region does provide a good measure of the Brønsted-acid site concentration.

The remaining amine molecules desorb intact (m/e = 44) at lower temperatures. The peak between 300 and 450 K is observed on all zeolites we have investigated, independent of whether Al is present or not. It is assigned to weak adsorption, possibly associated with silanols, and will not be considered further. However, desorption of unreacted isopropylamine between 450 and 600 K was not observed on high-silica zeolites. Two possible explanations can be given for the desorption of unreacted amine at these higher temperatures. First, isopropylamine has been observed to desorb in this region from alumina (21). This may explain at least some of the desorption for PQ(7) and PQ(60), but the CD(12) sample did not contain appre-

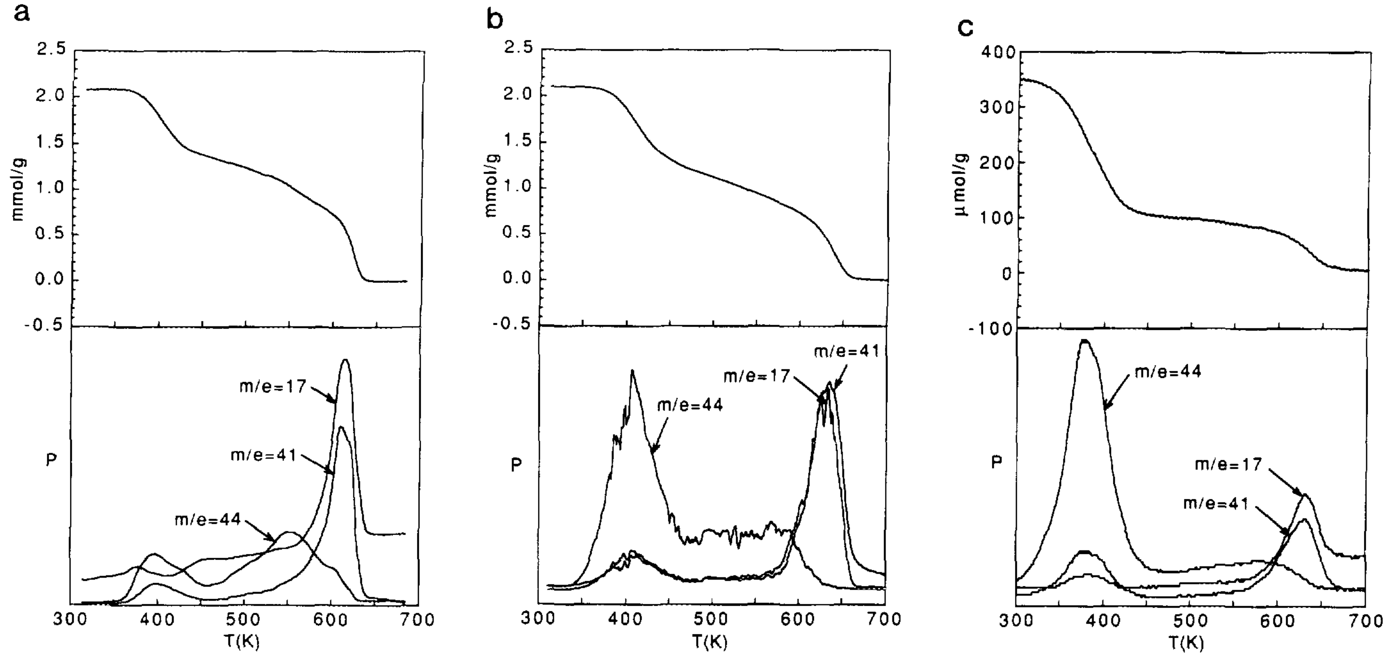

FIG. 1. TPD–TGA of isopropylamine on (a) CD(12), (b) PQ(7), and (c) PQ(60).

ciable amounts of extraframework Al. On PQ(5), a similar unreactive feature was shown to be due to desorption from the hydroxyls associated with a low-frequency band at 3540 cm^{-1} in the infrared spectrum (7). This result was reproduced on CD(12), as shown in Fig. 2. Following a saturation exposure of isopropylamine and heating to 450 K in vacuum, both the 3640 and the 3540 cm^{-1} peaks were absent in the infrared spectrum. After heating to ~550 K in vacuum, the 3560 cm^{-1} peak reappeared. The 3640 cm^{-1} feature reappeared only after heating the sample to above 650 K.

It is informative to consider the amount of isopropylamine which desorbs at high temperatures as a function of Al content in the zeolite. The values for each of the samples investigated are shown in Table 2. We did not attempt to integrate the peaks in the desorption curve and all of the numbers were obtained from the mass changes at the specified temperatures. From Table 2, it is clear that the number of amine molecules which desorbed at high temperatures is strongly affected by the framework Al content and these molecules must be associated with framework Al. While the uncertainty in the framework Al content for samples with lattice parameters less than ~2.428 nm is significant, it is also clear that the number of molecules desorbing at high temperatures was less than or equal to the framework Al content in each case. There are a number of factors which could lead to site concentrations being less than framework Al contents, including inactive hydroxyls (as in Fig. 2), the presence of cations other than protons for balancing the framework charge, steric interactions between molecules at adjacent sites, and inaccessible sites. However, based on previous work (22) with larger amines in PQ(7) and on the fact that the amount of isopropylamine which desorbed above 450 K on a series

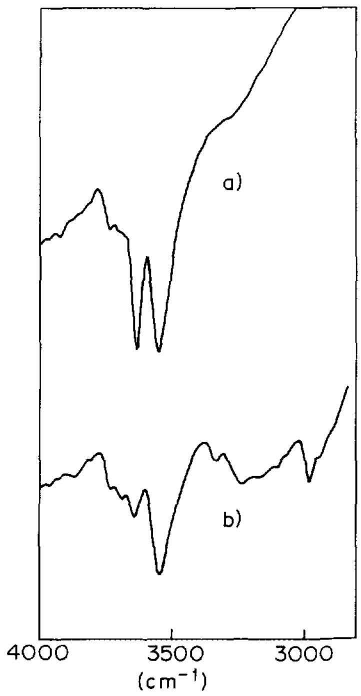

FIG. 2. Infrared spectra of CD(12) at room temperature following (a) heating of the sample to 700 K in vacuum, and (b) exposure to isopropylamine followed by heating in vacuum at 450 K.

TABLE 2

Summary of the TPD–TGA Results

Sample	T_p for IPA	Amine molecules/u.c.		Alcohol molecules/u.c.	
		450–700 K	575–700 K	300–500 K	380–500 K
CD(12)	413	16.0	10.1	16.5	13.2
PQ(7)	413	15.0	9.4	21.7	17.3
PQ(10)	411	8.6	5.2	11.5	9.2
PQ(20)	402	4.8	2.5	6.7	5.4
PQ(30)	399	2.3	1.5	2.9	2.3
PQ(60)	405	1.3	1.0	1.2	1.0
PQ(71)	394	1.4	0.8	1.1	1.0
PQ(85)	405	0.9	0.8	0.9	0.8

of H(Na)–Y samples was equal to the proton concentration (the most highly exchanged on the H(Na)–Y samples had a higher site concentration than any of the other samples investigated in this present study (7)), steric effects do not appear to be a significant problem.

TPD–TGA of Isopropanol

As discussed in the Introduction, the desorption of isopropanol is of interest for comparison with isopropylamine and because isopropanol decomposes at Lewis-acid sites, such as those present on pure alumina, which do not cause the reaction of isopropylamine. Also, the temperature at which reaction of isopropanol occurs in TPD is strongly dependent on the type of sites that are present in the solid. Isopropanol molecules associated with Brønsted-acid sites on high-silica zeolites like H-ZSM-5, H-ZSM-12, and H-mordenite react between 400 and 405 K in TPD (5). In comparison, the reaction of isopropanol to propene and water on alumina was found to be strongly dependent on the sample, but was above 440 K for even the most acidic aluminas (8).

Representative TPD–TGA curves for isopropanol on CD(12), PQ(7), and PQ(60) are shown in Fig. 3, and are again similar to those reported for high-silica zeolites like H-ZSM-5. A fraction of the isopropanol (m/e = 45) desorbed unreacted from each of the samples, mainly below 400 K. Since isopropanol has been observed in this temperature region on pure silica, we do not attempt to assign this desorption state to acid sites in the faujasites (7).

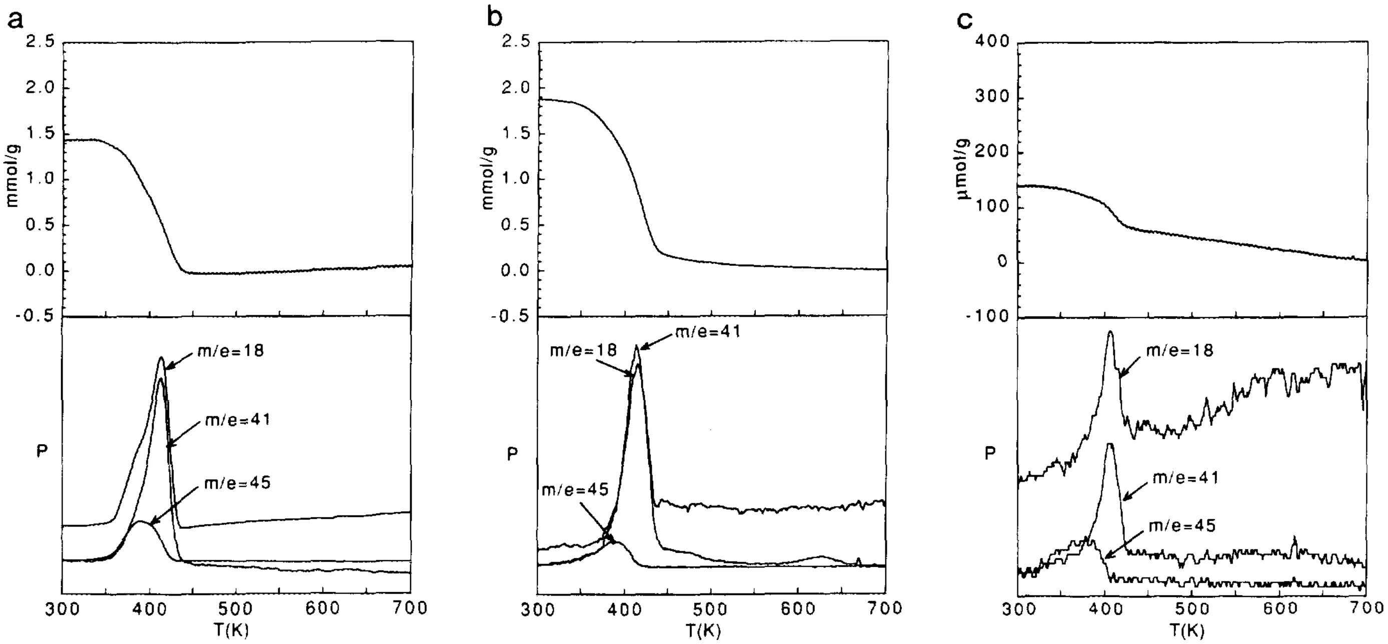

FIG. 3 TPD–TGA of isopropanol on (a) CD(12), (b) PQ(7), and (c) PQ(60).

Unlike the case for silica, however, some of the alcohol on each of the faujasites also decomposed to propene (m/e = 41) and water (m/e = 18). Since the amounts of unreacted alcohol leaving the sample after evacuation were relatively small and a significant fraction of this desorbed below 380 K, we used the weight change between 380 and 500 K to determine the approximate amount of alcohol which reacted on each of the samples. These values are shown in Table 2, along with the weight changes between 300 and 500 K, which provide an upper limit for the number of sites that cause reaction.

Table 2 shows that the site concentrations which cause isopropylamine (575–650 K) and isopropanol (380–500 K) reaction in TPD are similar for the high-silica materials, but there are more sites which cause the reaction of isopropanol than cause the reaction of isopropylamine on the high-alumina materials. In the high-silica materials, the fact that both probe molecules give the same site concentrations shows that the same sites are involved in both reactions on these materials. Since isopropylamine reacts *only* at strong Brønsted-acid sites, isopropanol must be reacting at these same sites. There is no evidence for any additional product formation on nonframework Al in the high-silica materials, which may indicate that the nonframework Al is inaccessible for adsorption, possibly because accessible alumina has been removed by acid leaching, leaving only that alumina which is present in the sodalite cages.

For the high-alumina materials, there are two types of sites which could be responsible for the additional reaction of isopropanol over isopropylamine. First, based on the results for PQ(5) (7) and CD(12) which do not contain extraframework Al, there must be weak hydroxyl sites which allow the intact desorption of isopropylamine but cause the reaction of isopropanol. This has been discussed in a separate paper, where it was shown that these weak sites are associated with the 3540 cm^{-1} hydroxyl band in the infrared spectrum (7). On the other high-alumina materials, such as PQ(7), reaction of isopropanol may also occur on nonframework alumina. This may account for the difference in the amounts of isopropanol which react on PQ(7) and CD(12), since both of these materials have the same framework Al content; however, all of the isopropanol reacts in a narrow temperature range on PQ(7), considerably below the temperature at which isopropanol reacts on pure aluminas. Therefore, it is not possible to assign the additional reaction sites to ordinary alumina.

The peak decomposition temperatures, also shown in Table 2, varied between 393 and 413 K and were reproducible to within less than 5 K; but there do not appear to be any obvious trends in the data with respect to Al content or lattice parameter. In particular, there is no obvious difference between the results for CD(12) and PQ(7), materials which show significantly different hydrocarbon cracking activities, as will be discussed shortly. While the decomposition temperature is probably not the most accurate measure of acid strengths, the results from our study suggest that there are no significant differences in the strengths of the sites in the various faujasite catalysts.

Propene and Ethene

Olefin oligomerization provides an additional qualitative test of acid strengths on zeolites (23). On H-ZSM-5, propene reacts rapidly at room temperature to form large oligomers in the zeolite at the Brønsted-acid sites, while the zeolite must be heated to ~370 K for the analogous reaction of ethene to occur (24). Since the oligomerization of olefins must be initiated by the protonation of the olefin, the difference between propene and ethene is due mainly to the increased stability of the secondary carbenium ion formed from propene compared to the primary carbenium ion formed by ethene (25). In TPD–TGA measurements, the oligomers formed by both propene and ethene crack to form a large number of hydrocarbon products, beginning at ~400 K. This cracking temperature for the oligomers is an additional measure of the site activity.

In this study, we compared the steamed PQ(7) and the chemically dealuminated CD(12) in order to determine whether any intrinsic differences between these samples could be observed from olefin adsorption; however, the oligomerization properties for CD(12) and PQ(7) were very similar. Propene oligomerization occurred readily at room temperature and 10 Torr on both samples, with final uptakes of 179 mg/g for PQ(7) and 148 mg/g for CD(12). That these weight increases were due to oligomerization was shown by the fact that evacuation did not decrease the weight and that these coverages, 4260 and 3520 μmol/g, are much higher than the Brønsted-acid site densities on these materials. Assuming the density of the oligomers is approximately that of typical hydrocarbons, ~0.8 g/cm^3, and that the accessible volume is given by the oxygen uptake, the uptake after reaction corresponds to filling ~50% of the pore volume on both samples, suggesting that the reaction proceeds at a large fraction of the sites until the pores are blocked. Ethylene did not oligomerize at significant rates on either sample up to 400 K for 10 Torr, indicating that there are differences between H–Y and H-ZSM-5. Whether this difference is due to the strength of the sites or to differences in the adsorption properties of the ZSM-5 and Y crystallites is not clear. It may be that the ZSM-5 pore structure causes an increased coverage of the monomer olefin so that the bimolecular oligomerization reaction proceeds at a faster rate.

The intermediates formed by olefin oligomerization have been shown by ^{13}C NMR to bond to the zeolite lattice through the lattice oxygen to form an alkoxide species (26, 27). These alkoxide species exhibit reaction properties which are virtually identical to that of carbenium ions and should be similar to species formed in catalytic cracking. It was therefore of interest to examine the cracking of the zeolite oligomers using TPD–TGA. The results for the two H–Y samples are shown in Fig. 4, with the TPD curves obtained while monitoring m/e = 41 and 55 in the mass spectrum. Previous measurements on H-ZSM-5 showed that a large number of olefin products are formed during desorption, from ethene to the various isomers of heptene (24), and a complete mass spectrum of the products desorbing from the H–Y samples appeared to indicate the same result. While the peak at m/e = 41 is a major fragmentation product in the mass spectrum of propene, it is also observed for many other olefins. The peak at m/e = 55, a major fragmentation product for C_4H_8 and larger olefins, demonstrates that a significant fraction of the products have molecular weights larger than that of propene.

With respect to reaction temperature, also, the TPD–TGA curves are virtually identical to each other and to those reported earlier for H-ZSM-5, with olefin products desorbing between 400 and 500 K. The fact that cracking of the oligomers occurs in the same temperature range on both steamed and unsteamed H–Y and on H-ZSM-5 suggests either that the interactions between the oligomers and the zeolite lattice are unimportant in this reaction or that the interactions between the zeolite lattice and the carbenium-ion-like species are similar, independent of zeolite structure or pretreatment. In either case, the implication for catalytic cracking is that the reaction properties of the intermediate, once formed, are not strongly affected by the zeolite properties.

n-Hexane Cracking Rates

n-Hexane cracking rates were measured on selected samples as an additional measure of acid strengths. (Note: Catalytic activity and acidity are sometimes used interchangeably, but are very different concepts which should *not* be confused. Catalytic activity may well increase with acidity, but factors other than acidity will affect catalytic activity.) All rates were determined in flowing N_2, using the vapor pressure of *n*-hexane at 273 K, by measuring the initial slope of a plot of conversion versus residence time. Initial experiments were performed on an H-ZSM-5 sample in order to test the performance of the reactor, and the turnover frequencies (molecules of *n*-hexane which reacted per acid site per second) were found to be indistinguishable from those reported by Haag and coworkers (14, 15), whose data are shown for comparison in Table 3. Rates on the H–Y samples were measured at two temperatures, 748 and 798 K, which were chosen to avoid bimolecular reactions. The rates are reported as turnover frequencies in Table 3 at 748 and 798 K, along with the activation energies calculated from the two data points. The site densities used in calculating the turnover frequencies were the site concentrations which caused the reaction of isopropylamine in TPD–TGA between 575 and 700 K, shown in Table 1.

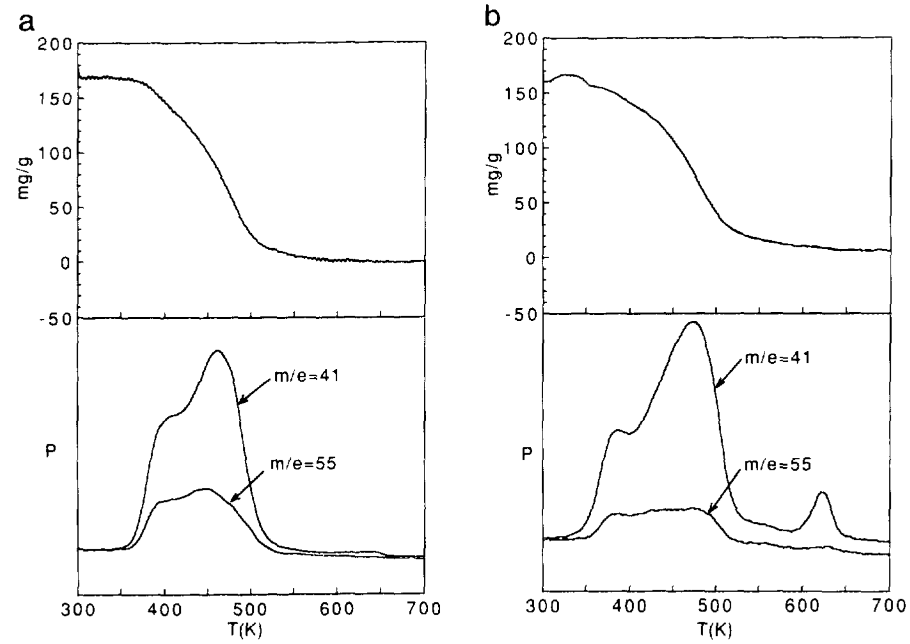

FIG. 4 TPD–TGA of propene on (a) CD(12) and (b) PQ(7).

TABLE 3

Summary of the *n*-Hexane Cracking Results for Selected Samples

Sample	Site conc.[a] μmol/g	TOF × 10^3, 748 K molec. site^{-1} sec^{-1}	TOF × 10^3, 798 K molec. site^{-1} sec^{-1}	E_a kcal/mol
CD(12)	860	0.69 ± 0.07	2.5 ± 0.3	31 ± 6
PQ(7)	850	6.8 ± 0.7	14 ± 1	17 ± 4
PQ(10)	450	0.38 ± 0.04	1.5 ± 0.2	33 ± 6
PQ(20)	230	1.5 ± 0.2	6.4 ± 0.6	34 ± 6
PQ(71)	70	1.0 ± 0.1	3.2 ± 0.3	28 ± 5
PQ(85)	60	0.34 ± 0.03	1.5 ± 0.2	35 ± 5
H-ZSM-5[b]		5.8		

[a] Determined from the amount of amine desorbing between 575 and 700 K in the TPD–TGA data (Table 2).

[b] Data taken from Ref. 14 and scaled from 760 to 47 Torr assuming a first order dependence of the rate on pressure (15), and from 723 to 748 K using an activation energy of 30 kcal/mol (15).

The first thing to notice is that the turnover frequencies are very similar on all of the materials, with the exception of H-ZSM-5 and PQ(7). Even these materials exhibit rates within a factor of 10 from the rest, suggesting that one need not develop an entirely new picture for understanding the sites. This implies that the Brønsted-acid sites which are probed by isopropylamine must be primarily responsible for the catalytic activity for *n*-hexane cracking under the conditions of our measurements. Other factors affect the catalytic activity, but not by orders of magnitude. As reported by others (2), PQ(7), the ultrastable Y catalyst, was the most active of the faujasites, being approximately 5 to 10 times as active as CD(12), even though the two materials had essentially the same framework Al content and the same number of acid sites as measured by isopropylamine. The activation energy is also significantly lower on PQ(7). Since the main difference between PQ(7) and CD(12) is the presence of nonframework Al in PQ(7), the nonframework Al is probably responsible for the change in catalytic activity (3). It is also interesting that the dealuminated samples, which had then been acid leached to remove some of the nonframework Al after steaming, exhibited turnover frequencies and activation energies more similar to CD(12) than to PQ(7). While each of these samples still contained significant amounts of nonframework Al, the species responsible for enhancing activity is removed by acid leaching. Given that the alumina which could not be removed by acid leaching is probably in the sodalite cages, we suggest that the alumina responsible for activity enhancement on PQ(7) is in the channels and accessible to the reactant molecules.

The fact that the activation energy on PQ(7) is so dramatically different may be an indication of the reason for activity enhancement in this sample. We ruled out the possibility that diffusional limitations were responsible for the change in activation energy based on the fact that the calculated Thiele modulus was $\sim 10^{-3}$ on this sample and changing the total flow rate did not change the rates. We believe the best explanation for our results is that the mechanism is different on PQ(7). The bimolecular, hydride transfer mechanism has been shown to have a significantly lower activation energy than the unimolecular, nonclassical carbonium-ion mechanism in H-ZSM-5 (15). Therefore, the enhancement that one observes on PQ(7) may be due to factors other than changes in "acidity" of this material.

Microcalorimetry

To see whether the variations in the catalytic activity of the different samples could be related to acid strengths, we measured heats of adsorption for pyridine and isopropylamine on selected samples. Before discussing the calorimetric measurements, it should be noted that TPD–TGA results for pyridine on high-silica zeolites, like H-ZSM-5, exhibit a well-defined desorption feature corresponding to one molecule per acid site (17). In contrast, the TGA curve for pyridine adsorbed on PQ(7) showed only a continuous loss in weight. From the TPD–TGA results for isopropylamine on this sample (Fig. 1b) we know that the Brønsted-acid site density on PQ(7) is ~900 μmol/g, which is the same coverage reached for pyridine on PQ(7) at ~500 K. This suggests that pyridine may adsorb preferentially on the same sites as those responsible for the reaction of isopropylamine in TPD–TGA. It should also be noted that substantial amounts of pyridine cannot be removed from the ultrastable H–Y at 750 K, even for desorption from thin beds (~10 mg spread over a flat sample pan) in high vacuum. It is important to note that, based on calculations of desorption from porous samples (28, 29), one should not try to infer adsorption energetics from the desorption measurements (30).

In Fig. 5, the differential heats of adsorption for pyridine are shown as a function of coverage for PQ(7) at 480 K, with previously published results for PQ(30) and for an H-ZSM-5 sample with an Al content of 600 μmol/g shown for comparison (17). For PQ(30) and H-ZSM-5, the differential heats were approximately constant up to the site density determined by TPD–TGA of isopropylamine; however, the differential heats for pyridine on PQ(7) just show a continual decrease, starting from ~190 kJ/mol, the same value observed for PQ(30), and reaching ~150 kJ/mol at a coverage of 900 μmol/g.

The results for pyridine on PQ(7) are virtually identical to those published previously by Dumesic and co-workers on a US–Y catalyst, with one exception (31). Previously, it had been reported that steamed faujasites contain a small concentration of very strong sites with heats on the order of 250 kJ/mol; we found no evidence for these strong sites. We suggest that it would not be possible for us to observe them, if they existed, because the mobility of pyridine at even the weaker sites is limited at 500 K, as demonstrated by the TGA measurements. Molecules should not be able to migrate to the strongest sites; certainly, movement of the adsorbate between crystallites in the bed should not be possible. The initial heats should simply be a statistical average of the sites which are first exposed.

It is also interesting to compare the calorimetric results for pyridine on the three zeolite samples. In the case of H-ZSM-5, the differential heat of adsorption is ~200 kJ/mol for coverages less than one molecule/site, after which the heat drops precipitously. Measurements with other H-ZSM-5 samples have shown that this result is independent of the Si/Al ratio of the samples or sample preparation (19, 32). On PQ(30), the differential heats are slightly lower, ~190 kJ/mol; but they remain relatively constant up to a coverage equal to the Brønsted-acid site density. Therefore, these high-silica samples have heats that are actually slightly higher than that found on the ultrastable PQ(7), even though the *n*-hexane cracking activity on PQ(7) is the largest on a per site basis.

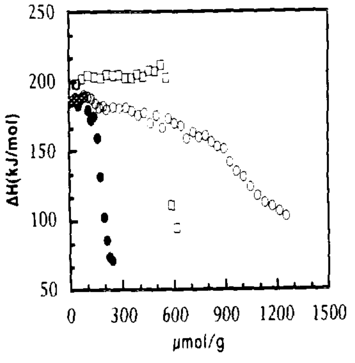

FIG. 5. Differential heats of adsorption for pyridine as a function of coverage at 480 K for PQ(7) [○], PQ(30) [●], and H-ZSM-5 [□].

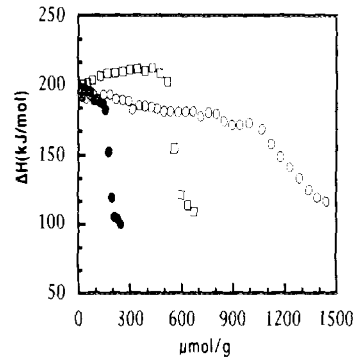

FIG. 6. Differential heats of adsorption for isopropylamine as a function of coverage at 480 K for PQ(7) [○], PQ(30) [●] and H-ZSM-5 [□].

In Fig. 6, the differential heats of adsorption for isopropylamine on PQ(7) are shown, with previous results for PQ(30) and H-ZSM-5 reported for comparison. Again, the heats of adsorption on PQ(7) fall with coverage; but the values are much more constant than those found with pyridine and the drop in the differential heats becomes much sharper at a coverage of ~900 μmol/g, the Brønsted-acid site density. The initial heat of adsorption on PQ(7), ~190 kJ/mol, is also close to the differential heat of adsorption on PQ(30).

The microcalorimetry results raise two important points. First, the site strengths on PQ(7), as measured by heats of adsorption for either pyridine or isopropylamine, are not stronger than those found on PQ(30) or H-ZSM-5. If one takes an average of the strengths by integrating the differential heats and dividing by the number of sites, the values on H-ZSM-5 and PQ(30) are clearly higher than the average heats on PQ(7). Since the catalytic activity of PQ(7) is considerably higher than that of PQ(30) and approximately equal to that of H-ZSM-5 on a per site basis, it appears that factors other than site strength are responsible for the differences in the catalytic activities.

Second, there appears to be considerable heterogeneity in the strength of the sites in PQ(7), based on the pyridine results, while the sites appear to be relatively uniform on PQ(30) and H-ZSM-5. In our opinion, this is the result of molecular interactions between molecules adsorbed at neighboring sites, rather than a true indication of differences between the sites. First, the initial heats on PQ(7) are similar to those found on the PQ(30); the difference between the two samples is that the differential heats on PQ(7) fall with coverage. Second, the apparent site heterogeneity in PQ(7) is much less for isopropylamine than for pyridine. If one were observing only changes in site strengths, one should expect a similar decrease for both adsorbates. Third, it is entirely reasonable that there could be strong repulsive interactions between adsorbate molecules in PQ(7). A coverage of 900 μmol/g corresponds to filling more than 20% of the available pore volume of PQ(7) with liquid pyridine. Since the sites must exist on the surface and not at the center of the supercage, this high coverage demonstrates that the adsorbate molecules are very close to one another when all of the sites are filled, and repulsive interactions could easily lead to a large decrease in the measured heats of adsorption with coverage. Repulsive interactions could arise from the ionic repulsion of two positively charged adsorbates, from steric interactions between neighboring adsorbates, or from changes in a protonic site due to adsorption at adjacent sites. If molecular interactions are responsible for the falling differential heats of adsorption observed on PQ(7), the implications for understanding catalytic cracking are significant. For catalytic cracking at high temperatures, at least for the conditions we employed in our study, the adsorbate coverages will be low. If all of the sites in PQ(7) are similar and if these sites are similar to those found in PQ(30), it is easy to understand why the cracking activities for *n*-hexane, on a per site basis, are similar for all of the samples.

DISCUSSION

In this study, we have used a wide range of techniques on a series of dealuminated faujasites in order to gain a better understanding of the nature of the acid sites in these materials. Several definite conclusions can be drawn from our results.

First, TPD of isopropylamine and other simple amines is useful for determining the concentration of the Brønsted-acid sites in steamed and chemically dealuminated faujasites, and all of the Brønsted-acid sites appear to be associated with framework Al. By counting only the molecules which react during desorption, one can obtain consistent values for the site concentrations which do not depend on the choice of amine as probe molecule (22). Desorption results for alcohols are affected by the presence of nonframework Al, and these measurements may provide complimentary information to amine desorption results.

The amine desorption results indicate that there is a significant difference between the framework Al contents and the site densities for the materials with higher Al contents, suggesting that only a fraction of the framework Al sites give rise to strong acid sites. This is the same result that had been obtained earlier for nondealuminated samples, and it was suggested that some hydroxyl sites (those associated with the 3540 cm^{-1} hydroxyl) are not Brønsted sites (7). Based on the fact that IR and TPD–TGA results for the chemically dealuminated sample, CD(12), are virtually identical to the results obtained earlier for nondealuminated H–Y, one can extend the conclusion that the 3540 cm^{-1} hydroxyls are not Brønsted-acid sites. Due to uncertainties in our ability to determine the framework Al content of the high-silica faujasites accurately, it is still unknown whether the ratio of sites to framework Al's approaches unity with further decreases in Al content.

The fact that framework Al content is significantly greater than the Brønsted-acid site density is very important for understanding the results of previous poisoning studies (33, 34). Several groups have used alkali poisoning of H–Y catalysts to demonstrate that catalytic activities decrease more rapidly than one would expect if each alkali ion simply eliminated the activity of one Al site. Based on our results, we suggest that the alkali ions affect only a single site and that the framework Al content is not a good measure of the absolute site concentration.

As in previous studies, we observed that the turnover frequencies for *n*-hexane cracking, calculated using site densities from amine desorption, vary with sample preparation conditions. However, we suggest that these changes in activity, while they may be very important for practical catalysts due to possible changes in selectivity, are not so dramatic that one needs to develop an entirely new picture of the acid sites. Steamed H–Y is more active on a site basis than chemically dealuminated H–Y, but the difference is only a factor of 5 to 10 (2). The question is what causes the variation in rates between the different samples? Only materials which contain nonframework AlO_x in the channels exhibit significantly higher activities and this enhanced activity can be removed by acid leaching. Our calorimetry results failed to find evidence for superacidic sites in the steamed materials and there was no correlation between the catalytic activities and the heats of adsorption on the three samples which were examined. Since significant H–D exchange rates for alkanes occur at much lower temperatures than that required for catalytic cracking (35), it appears that acidity, strictly defined as the ability of the solid to donate a proton to the adsorbate, is not the limiting step in the reaction. A factor of 5 to 10 in the reaction rates could be due to a number of factors, such as changes in the relative importance of hydride transfer (15), changes in the local adsorption isotherm due to structural defects (36), the assistance of alumina in C–C bond cleavage of the carbenium ion, or other factors (37).

Obviously, there is still much to learn about faujasites and catalytic cracking. In addition to the question about enhanced activity for steamed materials, we do not have a definitive explanation for the heterogeneity observed in the differential heats of adsorption on high-alumina materials or for the large difference in activity between the two types of hydroxyls, both of which are associated with framework Al. We believe that it may be possible to answer some of these questions using recently developed NMR techniques (38–40); however, as the present study makes clear, it will be very important to use a combination of techniques to make sure that the sites being investigated are the ones involved in catalytic reactions.

CONCLUSIONS

From this study, we conclude the following:

(1) TPD–TGA measurements of alkylamines provides a useful method for determining Brønsted-acid site concentrations in both steamed and chemically dealuminated faujasites.

(2) Only a fraction of the framework Al sites give rise to Brønsted-acid sites. The low-frequency hydroxyls at 3540 cm^{-1} are not strongly acidic.

(3) The rates for *n*-hexane cracking on all dealuminated faujasites are similar on a site basis. While the turnover frequencies on steamed materials are higher than those on chemically dealuminated materials by a factor of 5 to 10, no significant differences are observed in the adsorption properties of materials with similar framework Al contents or in the differential heats of adsorption. We suggest the increased activity of steamed materials is not due to an increase in the acidity of the hydroxyl sites.

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