JOURNAL OF CATALYSIS **119**, 426–440 (1989)

The Assay of Acid Sites on Zeolites as Measured by Ammonia Poisoning

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Received December 12, 1988; revised May 8, 1989

The decomposition of neopentane was studied with and without selective site poisoning with NH_3. The lethal dose, which was just sufficient to kill the catalytic activity, was estimated for each of a series of H-mordenites, H–Y and H–ZSM-5 zeolites, all with Si/Al ratios higher than 7.0, i.e., over silica-rich compositions where ideally all the sites are supposedly identical. It was found that poisoning no more than 10% of the sites (counted as lattice aluminum ions) was sufficient to eliminate the activity. Some ramifications of these observations are discussed. Unpoisoned and partially poisoned zeolites were investigated using ^{13}C-MASNMR following adsorption of isopropanol-2-^{13}C. These findings clearly show the efficacy of adsorbed NH_3 in repressing formation of polymeric surface residues. © 1989 Academic Press, Inc.

INTRODUCTION

Recently we have reported on the effects of varying the Si/Al ratio on the activity and selectivity of several different H-zeolites in the cracking of small paraffin molecules (*1*). Neopentane, because of its unique structural features, was a useful probe for the qualitative assay of the acidity (the concentration and strength of the active Brønsted sites). Its decomposition mechanism has been considered previously (*2*). The Brønsted sites of H–Y, H–M (mordenite), and H–ZSM-5 zeolites and even of amorphous silica–alumina catalysts supposedly attack the carbon–carbon bonds of neopentane yielding CH_4 and the *t*-butyl carbenium ion as primary products. This ion may vary in stability, and consequently in lifetime, on these different surfaces. This feature was postulated to be a determining factor in controlling the extent of secondary reactions.

Neopentane contains only primary hydrogens. Since no H_2 was formed, these evidently cannot be attacked by Brønsted protons as can the tertiary H of isobutane; CH_4 is formed instead. Moreover, no evidence was obtained for hydride transfer from neopentane to an existing carbenium ion. If this occurred, C_5 products derived from the isopentyl carbenium ion would be produced, but these were not observed. Hence, in the simplest case, a proton was discharged from the *t*-butyl ion back to the catalyst and equimolar amounts of CH_4 and isobutene appeared in the products. When the ion lifetime was sufficiently long, however, substantial concentrations of isobutene and the *t*-butyl ion were present simultaneously in the catalyst bed, and oligomerization and other secondary reactions occurred, most noticeably the formation of large amounts of paraffinic products (*1, 2*).

Linear relationships between catalytic activity for paraffin cracking and the extensive factor of the acidity (taken as framework Al/g) have been reported for the high

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0021-9517/89 $3.00

silica-containing zeolites H–ZSM-5 and H–Y (*3–5*). These have been interpreted to mean that the Brønsted sites of these materials are sufficiently remote from each other so that they are all essentially identical, i.e., that the rates simply reflect changes in the extensive factor of the acidity. The present work casts doubt upon this assumption. Its goal was to estimate the number of active sites by poisoning with NH_3 and to ascertain their relative strengths. It was thought that this information would be helpful in discriminating between the effects of intensive vis-a-vis extensive factors of the acidity on the catalytic activity and selectivity. The results indicated that some additional factors need be considered.

TABLE 1

Chemical Composition and Pore Volumes of Zeolites

Catalyst	(Si/Al)[a]	Al atoms/g × 10^{-20}	Pore volume (ml/g)[b]
H–ZSM-5(35)	35	2.8	0.20 (0.18)
H–Y(8.1)	13	11.0	0.30 (0.32)
H–M(7.3)	—[c]	11.9	0.21 (0.20)
H–M(11)	—[c]	8.3	0.20 (0.20)
H–M(17)	—[c]	5.7	0.21 (0.20)
H–M(27)	—[c]	3.5	0.21 (0.20)
H–M(65)	—[c]	1.4	0.10 (0.20)

[a] These are Si/Al ratios obtained by NMR; the chemical analysis values are in parentheses following zeolite, e.g., H–Y(8.1).

[b] Numbers in parentheses indicate theoretical pore volumes.

[c] These values are presently unavailable because the four topologically nonequivalent T-atoms in mordenites make this determination by ^{29}Si-NMR intractable. Hence, upper limits of the lattice aluminum ion concentration are given.

EXPERIMENTAL

Catalysts. Three different zeolites were used: H–ZSM-5(35), a gift of Mobil Oil Corp., Linde-Y (LZY-62), and Norton Z900H mordenite. The first was used as received; according to Haag and coworkers (*3b*), its Si/Al ratio is too high for it to be noticeably affected by mild steaming. Moreover, NH_4^+ exchange measurements showed that essentially all of the aluminum ions occupied framework positions. The LZY-62 was dealuminated following standard hydrothermal treatment procedures, then exchanged twice with NH_4NO_3, and extracted with HCl (1.0 *M* at 60°C for 2 h) to remove Na^+ and extralattice aluminum. The H-mordenite was similarly dealuminated by refluxing in HNO_3 of suitable concentration for various lengths of time. The good agreement obtained between the measured and the theoretical pore volumes of all the catalysts verified the effectiveness of the cleaning procedure (Table 1).

Apparatus and pretreatment of zeolites. A conventional all glass high vacuum BET system was used for volumetric measurements. The catalysts were loaded into quartz tubes fitted with stopcocks so that besides these, gas could be flowed over the zeolites for purposes of pretreatment and for making the microcatalytic pulse measurements. Highly purified He (<1 ppm max. impurity) was used for the latter. For the ^{13}C-NMR measurements, the tube containing the zeolite with adsorbed alcohol could be sealed by closing its stopcocks, removed from the apparatus, and opened in a drybox where the MASNMR rotors were loaded. Close fitting plug lids were sealed with minimal amounts of Apiezon M stopcock grease. All the preparations were pretreated in O_2 at 500°C and then evacuated to 10^{-5} Torr for 1 h at the same temperature before exposure to 2-propanol-2-^{13}C vapor at room temperature.

The chromatographic separations were made using (a) for ammonia, an 8′ × ¼″ column of HAYESEP P, 60/80 (Alltech Ass.), thermostated at 80°C; (b) for hydrocarbons, a 15′ × ¼″ column filled with 20% dibenzylamine on Chromosorb PAW 80/100, and held at 0°C. The He flow rate was ~60 cm^3/min in both cases.

Reactants. Neopentane was Aldrich Research Grade (99.9%). The anhydrous ammonia from Matheson and was specified 99.99% pure. The 2-propanol-2-^{13}C was obtained from ICON; it had a stated isotopic purity of >98%. The He carrier gas was passed through a Matheson purifier; it tested pure to better than 1 ppm (*2*).

Reaction tests. The catalytic experiments were performed in a conventional pulse reactor system. An absolute calibration of the GLC system was made by varying the pressure in a doser whose measured real volume was 1.57 ± 0.03 cm^3; thus the integrated peak area of each gas could be converted into micromoles. A known amount of reactant was passed over the catalyst and the products were collected in a trap at −195°C for 5 min before flashing onto the chromatographic column. CH_4 and H_2 (if present) could be removed in a second trap filled with 5-Å sieves at −195°C placed downstream from the TCD detector used for the first column. Provision was made to measure these gases separately. The fraction of reactant converted was taken as the sum of the micromoles of the product molecules recovered (calculated as C_5) divided by the micromoles of neopentane injected. Separate batch experiments reported earlier (*2*) showed that over 90% of the reactant was recovered in the products in this way. The overall mass balances (gases plus residue) accounted for 94 to 96% of both C and H. The excess hydrogen required to produce the paraffinic products was furnished by the corresponding hydrogen deficient residue (*2*).

The poisoning experiments, using either NH_3 or H_2O, were generally performed using a *standard procedure*. In these cases a known (excess) amount of NH_3 was adsorbed on the catalyst at room temperature and then desorbed in flowing He at increasing temperatures between 400 and 500°C. This NH_3 was collected in a trap downstream at −195°C and was measured using GLC techniques (for small amounts) or volumetrically in the attached BET system (for larger amounts). The amount remaining on the zeolite could then be accurately calculated by difference.

In some cases, small measured amounts of either NH_3 or H_2O were flushed from a doser located upstream from the reactor onto the zeolite with He; the amounts added in this way were always smaller than the lethal dose determined by the standard technique. The reactor was either held at room temperature or at 400°C. In either case, any gas not retained on the catalyst was collected in a liquid nitrogen trap located downstream and then measured. It may be remarked that the NH_3 or H_2O retained by the catalyst is kinetically controlled. Complete desorption into the flowing He stream should occur given sufficient time. At any given temperature, however, after desorption to a given coverage the desorption rate became immeasurably slow. These "stable states" are reported in the figures and tables.

NMR experiments. A few exploratory ^{13}C-MASNMR spectra were collected at room temperature using a Brücker MSL-300 instrument. A MAS probe was used with alumina rotors which were spun at rates up to 4.5 kHz. Block decay measurements are reported here.

The pretreated samples were loaded with 2-propanol-2-^{13}C at room temperature; either propanol alone or NH_3 followed by 2-propanol was adsorbed on the solid. The amount of gas to be adsorbed (0.2 C_3H_7OH/Al and/or 0.5 NH_3/Al) was measured using the BET system; on exposure to the zeolite these gases were rapidly and essentially completely adsorbed. In tests performed with H–M(7.3) and H–Y(8.1) the rotors were left in a desiccator for 2 weeks and then the spectra were recorded a second time. No significant changes were observed between the spectra taken 2 weeks apart with either sample.

RESULTS

Kinetic Studies

H–mordenites. Previously (*1*), the activities of these materials for the cracking of neopentane, *n*-hexane, and isobutane

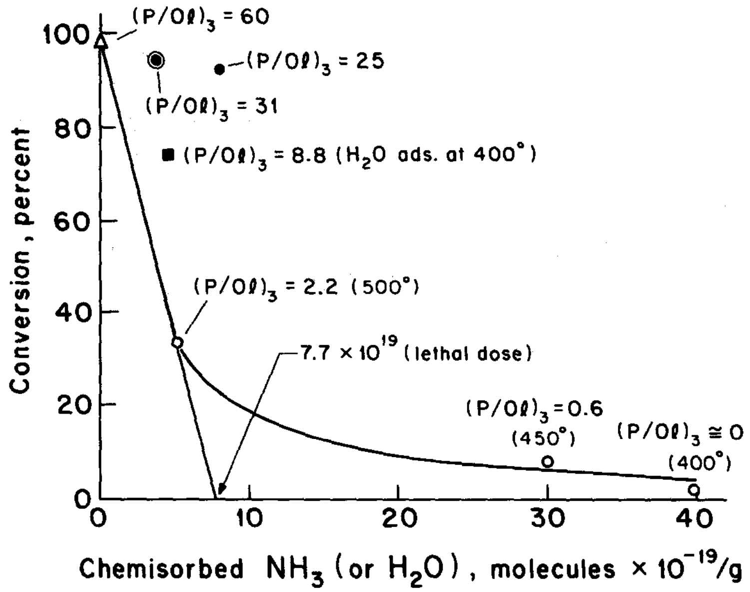

FIG. 1. The effect of preadsorbed ammonia on the cracking activity of 400 ± 4 mg of H–M(7.3) containing 119 × 10^{19} Al sites/g. The reaction temperature was 400°C and the pulse size was 1.54 × 10^{19} molecules of neopentane; the He flow rate was 90 cm^3/min and $(P/Ol)_3$ is the propane/propene ratio from each test. Δ represents the unpoisoned activity, and ○ the results of the experiment in which excess ammonia was adsorbed and then desorbed at the temperatures indicated in parentheses. ● and ■ represent data taken after pulses of either NH_3 or H_2O, respectively, were carried by He onto the unpoisoned catalyst at 400°; ◉ represents two overlapping points using NH_3 pulses.

showed maxima when plotted against the aluminum content or alternatively vs the Si/Al ratio. These maxima appeared at Si/Al ratios between 7 and 8. The most active preparation obtained on dealumination of the parent Norton 2900H will be considered first. The data of Fig. 1 relate the activity of H–M(7.3) for the cracking of neopentane to the amount of preadsorbed NH_3. The initial unpoisoned activity was first determined (first pulse). Then, after regenerating the catalyst, excess NH_3 was adsorbed at room temperature (12 × 10^{20} NH_3 molecules/g). The reactor was then heated to 400°C while the He flow was directed through the reactor. The desorbed NH_3 was trapped downstream (−195°C) for 30 min at the final temperature, vacuum transferred back into the BET system, and measured volumetrically. Now only 40 × 10^{19} NH_3/g remained adsorbed. A pulse (1.54 × 10^{19} molecules) of neopentane was now reacted over the catalyst at 400°C. This procedure (*2*) was repeated after NH_3 desorption at 450 and 500°C. Although the NH_3 retained in the catalyst after the 500° treatment was only about 4% of the total number of lattice Al, still this was enough to reduce the conversion to about one-third of its unpoisoned value. This poisoning plot was extrapolated to zero conversion to estimate the (arbitrarily defined) lethal dose necessary to kill the catalyst activity was 7.7 × 10^{19} molecules/g. Treatment with O_2 at 500°C completely removed the NH_3 and restored the initial activity.

After another regeneration using the standard pretreatment, a dose of ammonia (3.8 × 10^{19} molecules) was carried onto the catalyst by He at 400°C; it was quantitatively adsorbed as no NH_3 was collected in the downstream trap. After passing a test pulse of neopentane, the catalyst showed a short, white band followed by a dark line near the gas inlet, and the activity was nearly that of the original unpoisoned catalyst (solid circle). Moreover, the paraffin/olefin ratio (shown next to this point) was high, approaching that of the unpoisoned catalyst. This ratio may be taken as a measure of the extent of secondary hydride transfer reactions. Repeating the experiment using twice as much NH_3 gave virtually the same result. The addition of 4.5 × 10^{19} H_2O molecules reduced the activity further. Clearly the NH_3 was not uniformly adsorbed throughout the bed.

The results of similar experiments using H–M(17) are presented in Fig. 2. The poisoning plot corresponded well with the previous one, indicating a lethal dose of 6.4 × 10^{19} NH_3/g. There was, however, a very important difference. In two separate experiments in which pulses containing 3.5 × 10^{19} molecules of NH_3 were adsorbed on the unpoisoned catalyst either at 24° or at 400°C, the conversion data taken at 400° fell very nearly onto the poisoning plot curve and the catalyst was now almost uniformly gray. Evidently the NH_3 was able to spread throughout the bed with this catalyst suggesting that the intensive factor of its acidity was weaker than that of H–M(7.3).

The most highly dealuminated mordenite sample H–M(27) showed the same overall behavior (Fig. 3). The lethal dose was now only 4.7 × 10^{19} NH_3/g. Thus, in all three cases, the lethal dose corresponded to 10 ± 3% of the total number of the possible acid sites (the number of aluminum atoms/g).

The selectivity data obtained from unpoisoned and NH_3–poisoned H–M(7.3) catalysts are compared in Table 2 with those for other (unpoisoned) higher (Si/Al) ratio mordenites. Note that the extent of hydride transfer decreased with the NH_3 chemisorption as did the conversion. These trends paralleled the variations with the Si/Al ratio. Clearly, poisoning sites with NH_3 is equivalent to, but more than 10 times as effective as, removing sites by dealumination.

The product distributions shown in Table 2 are of some interest. In all cases the number of (C_3 + C_4) molecules produced was about equal to, or a little less than, the number of neopentane molecules reacted; the agreement was better the lower the

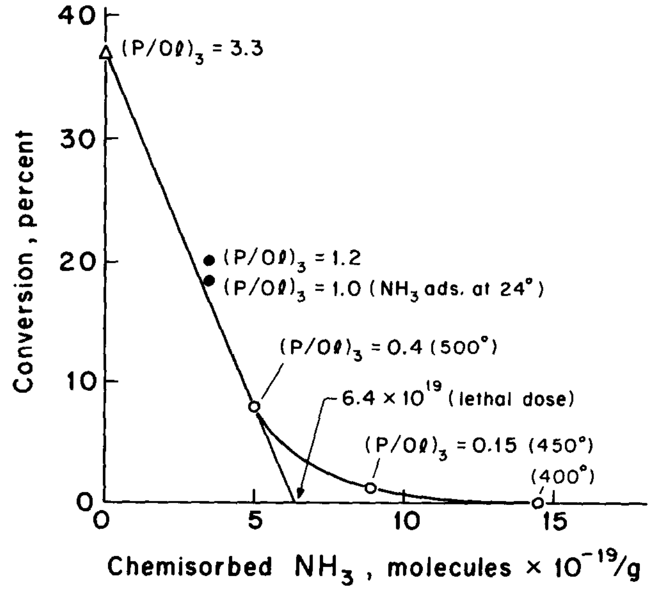

FIG. 2. The effect of preadsorbed ammonia on the cracking activity of H–M(17). Reaction conditions and symbols were as in Fig. 1. Catalyst weight was 400 mg; it contained 54 × 10^{19} sites/g.

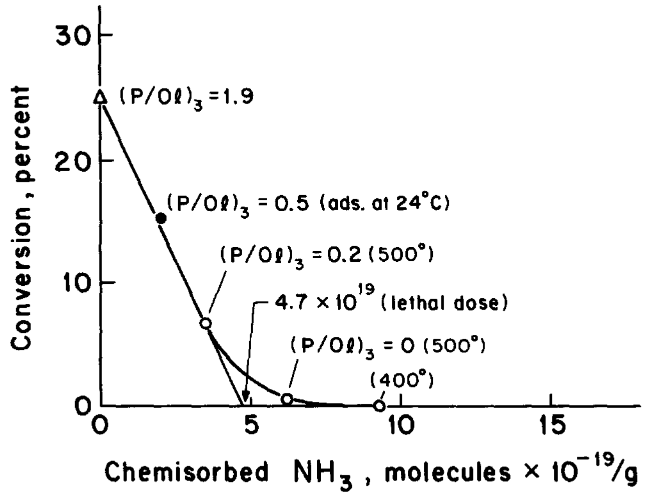

FIG. 3. The effect of preadsorbed ammonia on the cracking activity of H–M(27). Reaction conditions and symbols were as in Fig. 1. Catalyst weight was 400 mg; it contained 35 × 10^{19} sites/g.

conversion level. Isobutane was the largest single component of this fraction. The methane produced was always a little more than the neopentane reacted; this excess also increased with activity of the catalyst. This was a reflection of the increasing extent of secondary cracking of the isobutane formed to C_3 product. These trends have been noted before (*1*, *2*).

H–Y-zeolite (*8.1*). It is of interest to compare the result obtained with the mordenite samples with those of other zeolites having about the same extensive factor, i.e., the same lattice aluminum concentration (Table 3). This H–Y sample contains 1.1 × 10^{21} aluminum atoms/g; this is very close to that of H–M(7.3) which contains 1.2 × 10^{21} Al/g. As shown previously (*1*, *2*),

TABLE 2

NH_3 Poisoning of H–M(7.3)[a]

Pulse no.	Ads. NH_3 molec/g × 10^{-19}	Conv. %	Neo–C_5 reacted	CH_4	$C_3 + C_4$	$(P/Ol)_3$	$(P/Ol)_4$
			(molecules × 10^{-17})				
1[b]	0	98.	151	230.	147∞		23
2	40	1.0	1.6	2.5	1.4	0.0	1.5
3	38	3.3	5.1	6.2	4.0	0.1	2.8
4	36	6.8	11.	12.	10.	0.6	3.3
5	4.4	41.0	63.	86.	60.	4.5	11.
H–M(65)	0	1.9	3.0	3.1	3.0	0.0	2.4
H–M(27)	0	25.	38.	46.	35.	1.9	7.8
H–M(17)	0	37.	57.	78.	52.	3.3	12.
H–M(11)	0	59.	91.	132.	86.	7.6	13.

[a] Reaction temperature, 400°C. Pulse size, 154 × 10^{-17} molecules of neopentane. He flow rate, 90 cm³/min. NH_3 was added after regeneration and this was followed by another pulse of neopentane. NH_3 was then allowed to desorb between pulses into flowing He for 1 h at 400°C or after increasing the temperature to 500°C (between 4 and 5). The last four rows obtained with more highly dealuminated mordenites are included for comparison.

[b] Data for the unpoisoned H–M(7.3) may be compared with the other catalysts listed below, and with NH_3-poisoned H–M(7.3).

TABLE 3

Lethal Doses of Ammonia Required to Suppress the Neopentane Cracking Activity of Several Zeolites

Catalyst	Al atoms × 10^{-19}	Lethal dose NH_3/g × 10^{-19}	Neo-C_5 conv%[a]	$(P/Ol)_4$	(iC_5/nC_5)[b]
H–M(7.3)	119	7.7	98	23	3.7
H–M(11)	83	—[c]	59	13	5.8
H–M(17)	57	6.4	37	12	6.2
H–M(27)	35	4.7	25	7.8	9.7
H=ZSM-5(35)	28	4.2	4.5	0.3	—[d]
H–Y(8.1)	110	2.9	4.3	2.5	∞

[a] Unpoisoned activities.

[b] $(i\text{-}C_5/nC_5)_{eq} = 2.6$ at 400°C.

[c] Not determined.

[d] This catalyst did not yield C_5 products at either 400 or 500°C.

the H–Y(8.1) has a much lower activity than H–M(7.3) as well as a much lower hydride transfer efficiency. Its behavior toward NH_3 poisoning was also completely different. In this case, the addition of very small amounts of NH_3 strongly poisoned the catalyst (Fig. 4). Also, in these experiments parts of pulses of NH_3 were carried through the reactor which was held at 400°C and collected in the −195°C trap. The data plotted have been corrected for this. Thus, the NH_3 was less strongly held on H–Y than on H–M, and the lethal dose was only about 3% of the maximum number of possible sites. Adsorbing an excess of NH_3 at 24°C and desorbing at temperatures between 400 and 500°C gave consistent results. Note that H–Y has a three-dimensional interconnecting pore system whereas H–M is a unidimensional system with

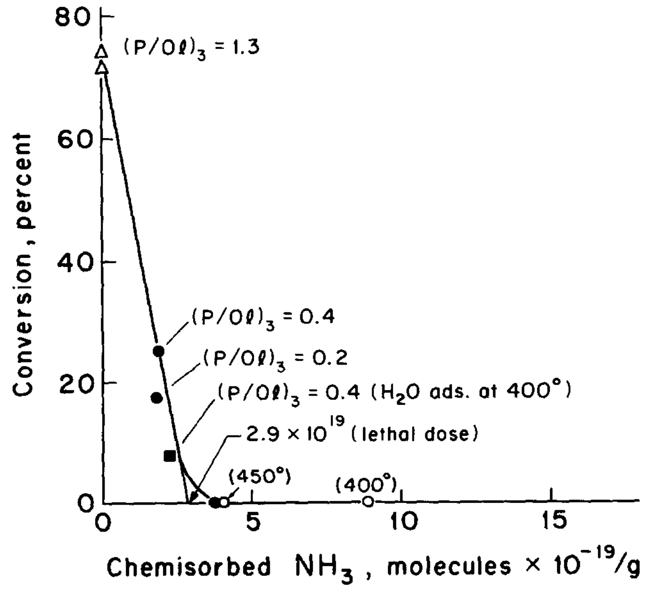

FIG. 4. The effect of preadsorbed ammonia on the cracking activity of H–Y(8.1). Reaction conditions were as in Fig. 1, except that He flow rate was 32 cm^3/min. Catalyst weight was 400 mg; it contained 110 × 10^{19} sites/g

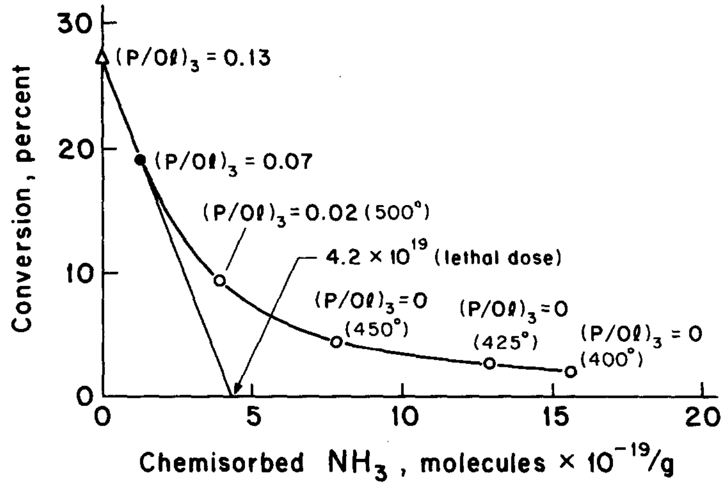

FIG. 5. The effect of preadsorbed ammonia on the cracking activity of H–ZSM-5(35). Reaction conditions and symbols were as in Fig. 4. Catalyst weight was 400 mg; it contained 28 × 10^{19} sites/g.

slightly smaller pore mouths. Hence, if steric effects were important, H–M should be more easily poisoned than H–Y.

H–ZSM-5(35) contained 2.8 × 10^{20} Al/g; therefore, the data (Fig. 5) may also be compared with H–M(27) which has 3.5 × 10^{20} Al/g. The data for the two unpoisoned catalysts (Table 3) show that H–M(27) was more active and more selective to paraffin formation than H–ZSM-5(35). The lethal dose was, however, very similar for the two preparations. Hence, the data suggest that the intensive factor of the mordenite acid sites is much higher than that of H–ZSM-5. Incidently, H–ZSM5(35) is one of those preparations which produced the linear increase in activity for hexane cracking with Al concentration described by Haag *et al.* (*3*). A molecular sieving effect may also have affected adversely the ability of H–ZSM-5 catalysts to undergo H^- transfer reactions.

Water adsorption. The effect of H_2O on the catalytic activity was assayed in two ways. First the He carrier was saturated with H_2O at 0°C (4.6 Torr of H_2O partial pressure). This eliminated most of the activity of all the zeolites tested. Heating these preparations rapidly in dry He to 500°C usually restored most of the original activity and selectivity, but with one catalyst [H–M(7.3)] a 1-h treatment with O_2 followed by another hour in vacuum, both at 500°C, was required to return these properties to the initial conditions.

A second kind of experiment was carried out with H–M(7.3) and H–Y(8.1). With the former, 4.5 × 10^{19} molecules of water reduced the conversion to 74% of that of the unpoisoned catalyst and lowered the paraffin/olefin ratio to 8.8. When this rate was plotted together with those of Fig. 1, the result was consistent. Note that the H_2O, although less basic than NH_3, was nearly as effective in reducing the activity (compare full and open circles with the filled square in Fig. 1). With H–Y(8.1) (Fig. 4) the effect of water added in small amounts was qualitatively similar; again the point fell almost on the curve defined by NH_3.

NMR measurements. When 2-propanol-2-^{13}C was adsorbed on H–M(7.3), the spectrum (Fig. 6A) showed multiple paraffinic CH peaks at ($0 < \delta < 50$ ppm) indicating that a polymerization had occurred. These bands resembled closely those reported by van den Berg *et al.* (*6*) for ethylene adsorbed on H-mordenite. The peak at around 66 ppm corresponded to adsorbed 2-propanol; this could be readily extracted with deuterated chloroform at room temperature and analyzed by high resolution

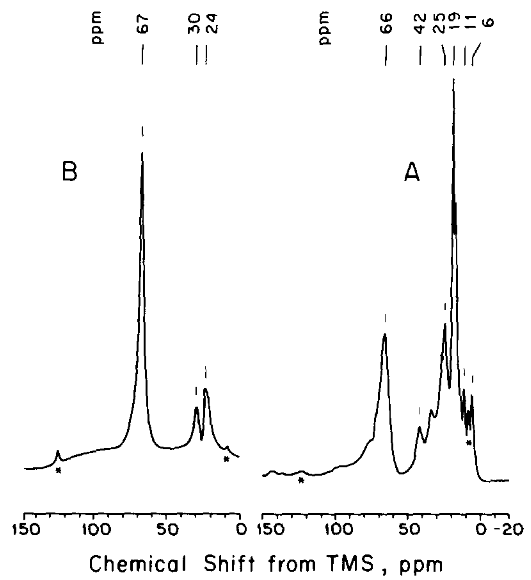

FIG. 6. MASNMR spectra from 2-propanol-2-^{13}C adsorbed on H–M(7.3) at 4000 rpm; (A) on a clean catalyst, (B) on the same preparation with preadsorbed ammonia (0.2 molec. of 2-propanol per Al and 0.5 NH_3 molec. per Al).

NMR (*7*). Such solutions showed the same peak at 64.0 ppm in both the extracted and reference solutions.

Figure 6B shows the spectrum from the same amount of 2-propanol adsorbed on H–M(7.3) after preadsorption of 0.5 NH_3/Al. It is clear that the surface polymerization was dramatically reduced by the NH_3. The dominant peak was now that of the alcohol at 66 ppm with its spinning sidebands. Only two smaller paraffinic CH peaks were now distinguishable in the spectrum.

DISCUSSION

The salient feature of the present work was the effectiveness of relatively small amounts of NH_3 or H_2O for poisoning the catalytic sites of the H-zeolites. The lethal doses reported in Table 3 amounted to about 10% or less of the potential Brønsted sites (counted as lattice Al ions). A number of possible reasons for this may be conceived. These include (a) that the concentration of *strong* acid sites able to crack small paraffins is indeed only a small fraction of the total Brønsted sites, (b) that the most strongly held NH_3 is associated with some special non-Brønsted sites which are critical for the reaction, (c) that formation of NH_4^+ on the Brønsted sites induces long range interactions depressing the activity of all the remaining sites, and (d) that some physical effect is responsible.

In discussing the above possibilities several experimental observations must be considered. First, linear plots of catalytic activity vs lattice Al concentration have been repeatedly reported (*3–5*). Second, positive deviations from this linear behavior may be affected by mild steaming of H–ZSM-5 (*3b*) and negative ones by poisoning H–Y with Na^+ ions (*4, 9a, 10*). However, dealuminated Y-zeolites have been used in constructing such linear plots (*4, 5*), yet convincing evidence has been given (*4*) that the strong acidity exhibited by these hydrothermally dealuminated materials, while directly related to framework aluminum content, depends on a balance between aluminum in the framework and that dislodged from the lattice. Dwyer (*9b*), after recently reviewing the available data, concluded, "The evidence available does not appear to support a simple model in which aluminums in silica-rich zeolites (Si/Al > 7) are always in isolated sites providing sites of constant Brønsted acidity." Third, the effects of the chemisorbed NH_3 resemble closely the poisoning effects of Na^+. Beyerlein *et al.* (*4*) reported that introduction of one Na^+ was equivalent to removal of 3 Al_F from the lattice. A more recent and thorough study by Fritz and Lunsford (*10*) has set the figure at one for about 5 Al_F and the present NH_3 experiments suggest a still higher ratio near one for 10 Al_F. Pine *et al.* (*8*) reported related phenomena that favored the concept of a special subset of strong sites. They suggested that the 0-NNN sites (aluminum T-sites with zero next nearest neighbors) were preferentially neutralized by small amounts of residual Na^+ cations. Alternatively Dwyer and Singh (*9a*) reported that poisoning effects of K^+ were much larger than equivalent amounts of Na^+ for the cracking of *n*-butane over mordenites. This was attributed to differences in cationic radii and electronegativities, implying long-range effects on the intensive factors of the remaining Brønsted sites. Our result that reaction of NH_3 with a Brønsted site to form NH_4^+ is more effective than replacing the same site with Na^+ is in accord with this view. Hildebrandt and Skala (*11*) noted that temperatures of up to 600°C were required to remove NH_3 from the strongest sites of (NH_4)–Y(US). Moreover, it was this fraction which correlated with activity for cracking of light Pennsylvania gas oil. Thus, a number of related observations exist which should have a self-consistent explanation. Unfortunately, so far it has not been possible to discriminate unambiguously between the several possibilities.

In the cracking of isobutane, a primary reactions occurs (*12–14*) yielding H_2 and CH_4 together with the corresponding olefins or carbenium ions. This serves as the initiation step for carbenium chain reactions which are terminated by olefin formation. Opinion differs as to the nature of the primary process (*13–23*). Brenner and Emmett (*14*) postulated intrinsic dehydrogenation sites; McVicker *et al.* (*13*) suggested that strong electron deficient sites are present which effect a radical decomposition of the substrate, a view accepted by Bizreh and Gates (*17*). Marczewski (*18*) and Beyer (*19*) hold Lewis acid sites responsible. These ideas (*13–15, 17–22*) have one thing in common, viz., that sites other than Brønsted acid are required to initiate the chains. If these were in small number and chemisorb NH_3 very strongly, any of these concepts would afford an explanation for our data.

Others (*3, 21–23*) as well as ourselves (*1, 2, 12, 16, 24*) have favored the idea that Brønsted sites of zeolites cleave C–H and C–C bonds of paraffins as they do in superacid systems (*24*). It has been suggested (*3b, 4*) that the formation of such supersites requires the interaction of aluminum ions expelled from the lattice with Brønsted hydroxyl groups. NH_3 or Na_2O might either poison such sites selectively, or interfere with the Lewis–Brønsted interaction by reacting with the Lewis center. Whatever the cause it now seems clear that the Y-zeolites which provide a linear relationship between activity and lattice aluminum concentration (*4, 5*), do not contain a single kind of identical site. Suppose, for example, that for structural reasons a small constant fraction of the lattice aluminum are Brønsted sites accessible to the gas phase in the supercages and that the remainder have their hydroxyls (or are otherwise bound) inside the sodalite units. The original H–Y zeolite, before it is dehydroxylated, is such a system. Moreover, the extralattice aluminum might also be inside the sodalite cages; it could function as a promoter more easily and perhaps more effectively in this way than by occupying space in the pore system. It could contribute to the hydrothermal stability as well as to the activity by acting much like rare earth ions, forming internal bridges inside the cubo-octahedra. In this way, the concentration of the Brønsted acid sites need not be equivalent to the lattice aluminum concentration.

The possibility that physical effects may play a role in these reactions cannot be overlooked. The catalysts are molecular sieves whose pores are of molecular dimensions. The question germane to the present work, however, is whether the adsorption of NH_3 or the introduction of Na^+ cations could, by physical means, have a critical effect on the reaction rates. This is deemed unlikely for the following reasons. The lethal doses listed in Table 3 did not differ widely for the several different structures. In fact, more NH_3 was required for the mordenites, which have a unidimensional pore system than for the three-dimensional Y-zeolites where pore blocking is more difficult. Similarly, the results for H–ZSM-5(35), where molecular traffic control may be expected, were comparable. Diffusional effects should become more pronounced as the reaction rate is increased, yet the mordenites were many times more active than H–Y(8.1) which had similar activity as H–ZSM-5(35).

The question may be asked whether selective site poisoning occurs at or near the external surfaces of the zeolite particles. We think that with the possible exception of H–M(7.3) the answer is no. Except for this catalyst, the NH_3 appeared to be able to spread uniformly throughout the catalyst bed and presumably throughout the individual particles at 400°C. Moreover, as reported previously (*12*), the reactivity order neopentane > isopentane > isobutane $\gg$ *n*-butane was determined under identical reaction conditions over H–ZSM-5(35) and H–M(7.3). This order is coincident with the electron donor ability of the σ C–C and the σ C–H bonds of these paraffins rather than molecular size. This crude test suggested that transport limitations were not large enough to disguise the activity data even with the smallest pore zeolite. Moreover, if there were preferential adsorption at or near the pore mouths, the number of titrated sites as a percentage of the potential total numbers should decrease in the order H–Y > H–ZSM-5 > H–M. Table 3 shows exactly the opposite trend.

At the suggestion of a referee, adsorption isotherms were determined at 26°C for H–Y(8.1), H–M(7.3), and H–ZSM-5(35) using isobutane and neopentane as adsorbates.[4] In all cases, the pore volumes, calculated using the liquid densities, were from 10 to 50% lower than those determined using N_2 or O_2 and lower using neopentane than isobutane. These observations simply reflect the fact that the packing of these molecules in pores not much larger in size cannot be as efficient as in much larger vessels. Most noticeable was the difference between the isotherms for isobutane and neopentane on H–ZSM-5, the latter being less than half the former. Significantly, however, the changes effected by adsorption of NH_3 were much smaller varying from no detectable change for H–Y to a small but significant decrease with H–ZSM-5. Similarly the time required to reach equilibrium varied from instantaneous to a matter of minutes, respectively, for these two materials. Thus, although diffusion may affect the overall rates, it affords no apparent explanation for the poisoning results.

A comparison of the data from the several catalysts is made in Table 3 where the unpoisoned activities, the estimates of the lethal doses, and the paraffin to olefin ratios in the principal products are listed for identical experiments carried out at 400°C. With the three H–M catalysts the percentage conversion was roughly linear in the Al concentration, as has been observed previously with *n*-hexane cracking over H–ZSM-5 and H–Y zeolites (*3–5*). The product selectivities also changed favoring increased paraffin/olefin ratios and i-C_5/n-C_5 ratios moving toward equilibrium (2.6 at 400°) with increasing conversion. These data suggest that the strength of the individual sites is the dominating factor.

In the cracking of *n*-hexane (*3*) and isobutane (*4, 12, 15, 16*) two mechanisms have been recognized, viz., the primary protolysis and secondary carbenium ion reactions. With neopentane the primary reaction yields CH_4 and the *t*-butyl cation. The latter can isomerize into the *n*-butyl cation, but neither of these ions can undergo β-scission. Moreover, hydride transfer from neopentane to either may be assumed to be difficult (only primary C–H) and probably does not occur to any significant extent. Only minor amounts of C_5 products are produced (*1*), whereas if direct H-transfer occurred from either neopentane or from isopentane (which conceivably might be formed by paraffin isomerization), some evidence of the resulting isopentyl ion should appear in the products. Hence, the formation of C_4 olefins would appear to be inevitable. These could either appear as products [as with H–ZSM-5(35)] or undergo oligomerization with the coexisting

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[4] We are indebted to Dr. Jozsef Engelhardt for making these measurements.

C_4-cations. The key question then is how do the products become so rich in paraffins? Evidently the answer must be that olefins do not desorb readily from the H–M and H–Y zeolites studied, whereas paraffins do. [H–ZSM-5(35) is clean because olefin desorption is dominant.] Since the olefins formed do not escape the surface, they must oligomerize and the oligomeric ions produced must rearrange, disproportionate, crack (releasing paraffins), and undergo hydrogen transfer producing surface residue (precoke). A possible description of this kind of reaction network is shown in Scheme 1. That chemistry of this sort occurs has been previously demonstrated (2) by mass balance calculations which show that the high H/C ratios found in the gaseous products are compensated by a stoichiometric low ratio in the carbonaceous residue left on the catalyst.

If carbenium ion chain reactions cannot be established with neopentane, then at least one CH_4 should appear in the products for every molecule reacted, as usually observed (Table 2). On this basis, the rate of decomposition of neopentane should equal the rate of the primary reaction, viz., protonolysis to yield CH_4 and the *t*-butyl ion; every molecule reacted undergoes this process. Clearly, the NH_3 chemisorption has interfered with this step.

The data of Tables 2 and 3 show vast differences in the activity and selectivity of H–M and H–Y zeolites of similar composition. This may be taken as a reflection of the increased stability of the intermediate carbenium ions on the former relative to the latter. Both the conversion rate and the paraffin to olefin ratios over the mordenites decrease with increasing (Si/Al) ratio. However, reducing the rate by NH_3 poisoning (presumably also decreasing the extensive factor) led to the same result. Hence, not unexpectedly, these effects are inseparably related.

Consider the pseudo-equilibrium which must be established when CH_4 is released from neopentane with the concomitant formation of the *t*-butyl cation, i.e.,

$$(CH_3)_2C{=}CH_2 + SiAlOH \overset{K}{\rightleftharpoons} (CH_3)_3C^+ + SiAlO^- . \qquad (1)$$

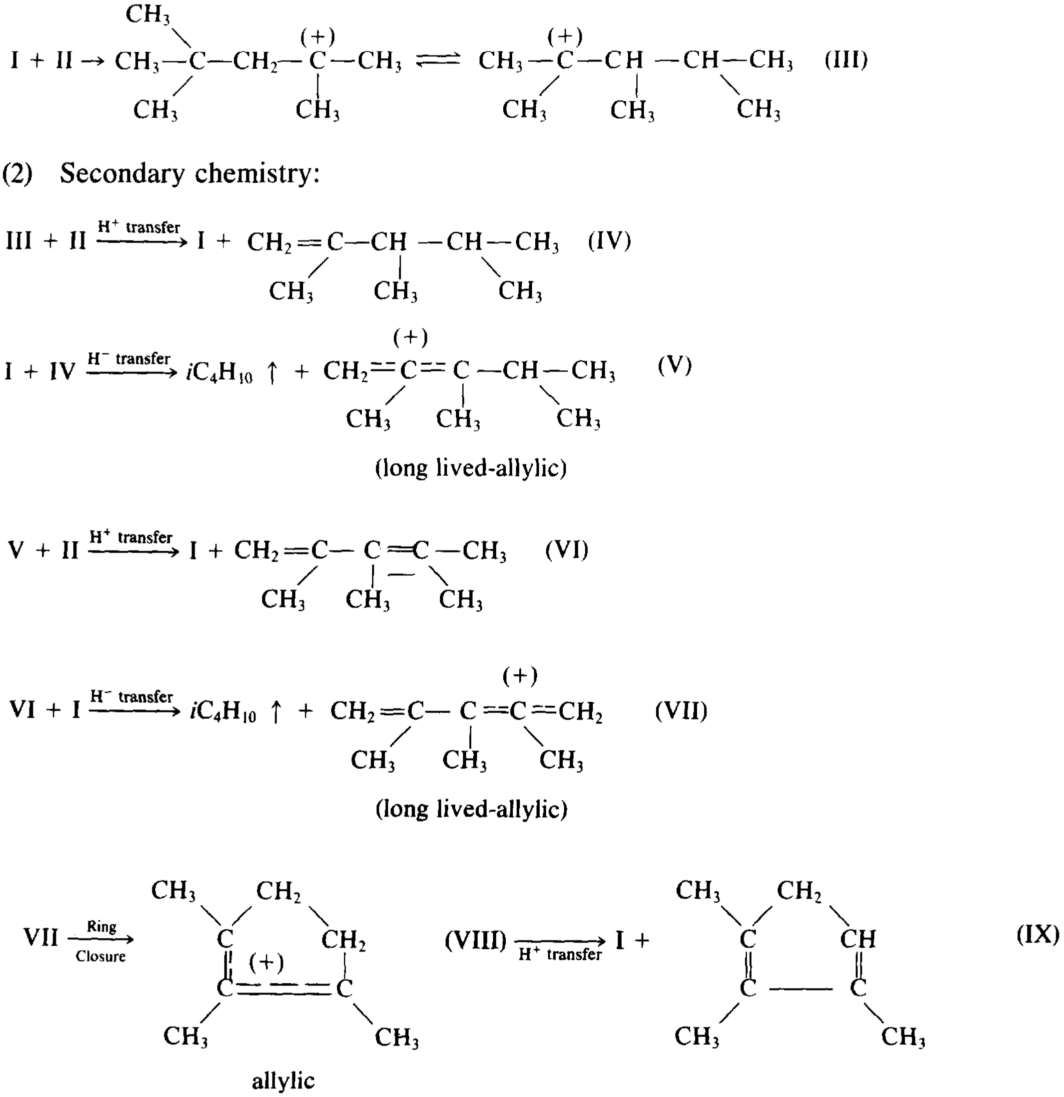
Other things being equal, an increase in the concentration of Brønsted sites (SiAlOH) would be expected to move this reaction to the right effectively increasing the average lifetime of the carbenium ion and hence the propensity for undergoing secondary reactions. On the other hand, an increase in the intensive factor (an increase in K) would have the same effect. The observed changes in selectivity must be thought of in these terms.

In the above analysis the steady state concentration of the *t*-butyl cation has been taken as a measure of its "lifetime" and this parameter has been described as dependent on the intensive factor of the acidity (Eq. 1). However, another property should also be considered as part of the intensive factor; viz., how well the extra negative charge which is put on the lattice when the $(CH_3)_3C^+$ is formed, can be delocalized. This stabilization (or ion solvation) controls the lifetime and, hence, the extent of the secondary processes.

The present data suggest that only a small percentage of the sites are able to crack paraffins. Even so, these vary in the intensive factor of their acidity. Note in Fig. 1 the different effect observed when small pulses of ammonia were introduced at the reaction temperature as compared with those obtained when an excess of NH_3 was adsorbed and then desorbed first from the less strongly held sites. The change in the intensive factor could be clearly seen when these observations were compared with those from the more extensively dealuminated samples H–M(17) and H–M(27) (Figs. 2 and 3). In these cases the way in which ammonia was adsorbed made essentially no difference because with these weaker acids it was less strongly bound and was able to equilibrate at 400°C with all the sites.

The MASNMR experiments of adsorbed 2-propanol-$2^{13}C$ also demonstrated the sharp difference in activity and selectivity

(1) The primary reaction creates a flux of $(CH_3)_3C^+$ (I) and $(CH_3)_2C{=}CH_2$ (II):



III and other higher polymeric carbenium ions may undergo β-scission forming C_3 and C_5 products which ultimately become paraffins further complicating the reaction network.

SCHEME 1. Paraffin formation from neopentane cracking.

which developed on H–M(7.3) on addition of NH_3. This comparison is made in Figs. 6A and 6B. Without NH_3 the residual unreacted alcohol was small and extensive formation of surface polymer was evidenced by the appearance of strong multiple bands from paraffinic ^{13}C in the 0 to 50 ppm range. Evidently a chemical reaction has occurred and undoubtedly this was a simple surface polymerization of the type previously described (*6, 25, 26*). Clark and Finch (*26*) reported many years ago that the formation of surface polymer on a silica–alumina catalyst exposed to butenes was strongly inhibited by NH_3. The inferences to be drawn here have been discussed previously (*7*); most of the added alcohol was first dehydrated; then the olefin formed underwent oligomerization and subsequent isomerization. Carbenium ions were formed, but only as transient intermediates; ionic species were detected, but not the simple isopropyl cation. More likely these were more stable ions, e.g., as in Scheme 1. Hence, alcohol dehydration occurred at room temperature, but the simple carbenium ions formed concomitantly were not *stable* (*27a*); they acted as intermediates for surface polymerization or formed alkoxides.

Gorte and co-workers have made extensive studies of the interaction of alcohols and amines with the acid sites of several zeolites. They have reported (*27b*) that one molecule of base per framework Al was strongly chemisorbed, independent of zeolite structure or the Al concentration. When a series of different molecules with varying carbenium ion stabilities were examined, no evidence was obtained for the situation suggested by the present results, viz., about 10% strong sites and 90% too weak to effect carbenium ion catalysis. Finally, the same behavior was characterized (*27c*) for H–ZSM-5, H–ZSM-12, and H–mordenite; the results were indistinguishable. Molecules which did not react in one zeolite in TPD did not react in the others. Molecules which did react, reacted at the same temperature in each case. These results led the authors to conclude that all sites were identical. However, these alcohols and amines are strong bases relative to neopentane and evidently cannot discriminate between the weak and strong acid sites as can cracking of neopentane or isobutane. Nevertheless, Gorte's ideas are consistent with the interpretation given previously (*3–5, 29*) for the linear dependence of reaction rates on aluminum concentration of H–ZSM-5 and H–Y zeolites, respectively, and with the more recent report (*3c*) that these two materials have about the same turnover frequency (per Al) when tested under identical conditions. Interestingly, neopentane is about the same size as *t*-butanol, one of the alcohols studied by Gorte, and, if anything, should be less sterically hindered in its interactions with the lattice; yet Gorte has reported the one *t*-butanol per lattice Al relationship held even with H–ZSM-5. The same *t*-butyl carbenium ion may be formed from both reagents. Evidently, these molecules can and do readily penetrate this small pore system. Although diffusion may be a factor in limiting the rate, we have no basis to think that the pronounced effects of NH_3 can be explained in this way.

When NH_3 reacts with a Brønsted site, a *stable* NH_4^+ ion is produced together with its conjugate $SiAlO^-$ ion. Introduction of Na^+ accomplishes the same result. The effect of this is to drive Eq. (1) to the left, reducing the steady state concentration (lifetime) of metastable carbenium ions and the overall activity of the catalyst. Since this system may be viewed as analogous to an electrical capacitor, the non-linear and non-stoichiometric poisoning effects can be readily understood as can the markedly different behavior of simple aliphatic alcohols. The latter react to form *metastable* ions which neutralize the site by reverting to alkoxide species. Thus no real contradiction exists between the present results and those of Gorte *et al.* (*3, 5, 27, 29*).

Very recently Abbott and Wojciechowski (*21*) reached some of the same conclusions presented herein. They studied the cracking of 2-methylbutane and 2,2,4-trimethylpentane in steady state flow experiments over H–Y. Molecular H_2 was formed as an initial product from the former, but not the latter nor did it appear in the cracking of *n*-hexane or of cyclopentane. We have found it to be a primary product with isobutane (*6, 8*), but not with neopentane (*1, 2,* and this paper). Thus, we agree that H_2 can be formed as a primary product only when the structure of the feed molecule contains a tertiary C–H bond (except when it is highly shielded by multiple branching), and that in this respect reactions of paraffins on solid acid catalysts are analogous to those in liquid superacids (*24*). Interestingly, this same chemistry occurs on relatively weak acids such as silica–alumina, albeit at much higher temperatures. We concur that the tendency to liberate H_2 increases with temperature in the primary reaction steps. These workers (*21*) also found comparable amounts of isobutane and isobutene as the principal hydrocarbon products from 2,2,4-trimethylpentane, and of propane and propene from 2-methylpentane. This would be predicted for protonolysis of the central C–C bond to yield a paraffin and the most stable carbenium ion in the primary reaction step. Their observations on the formation of an unsaturated coke deposit and the absence of volatile aromatic species also matches ours. The two pieces of work nicely complement each other. We think, however, that a primary protonolysis must always occur in the cracking of *pure* paraffins. This is the initiation step required to maintain the carbenium ion chain reactions involving H^- transfer, even when the latter become dominant (*28*).

ACKNOWLEDGMENTS

The authors are grateful to the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Research, for support of this work under Grant DE-FG02-87ER13774A000. Thanks are also due to Air Products and Chemicals Company for their continued interest in this work and to Dr. Werner Haag for helpful discussion.

REFERENCES

1. Lombardo, E. A., Gaffney, T. R., and Hall, W. K., *in* "Proceedings, 9th Int. Congr. on Catalysis, Calgary, Canada" (M. J. Phillips and M. Ternan, Eds.), Vol. I, p. 412. CIC Publishers.

2. Lombardo, E. A., Pierantozzi, R., and Hall, W. K., *J. Cat.* **110,** 171 (1988).

3. (*a*) Haag, W. O., Lago, R. M., and Weisz, P. B., *Nature* (*London*) **309,** 589 (1984); Haag, W. O., and Dessau, R. M., *in* "Proceedings, 8th Int. Congr. on Catalysis, Berlin, 1984," Vol. II, p. 305. Dechema, Frankfurt-am-Main; (*b*) Lago, R. M., and Haag, W. O., *in* "Proceedings, 7th Int. Conf. on Zeolites, Tokyo, 1986," p. 677ff; Haag, W. O., and Chen, N. Y., *in* "Catalyst Design: Progress and Perspectives" (L. L. Hegedus, Ed.), p. 181ff. Wiley, New York, 1987.

4. Beyerlein, R. A., McVicker, G. B., Yacullo, L. N., and Zemiak, J. J., *J. Phys. Chem.* **92,** 1967 (1988).

5. Sohn, J. R., DeCanio, S. J., Fritz, P. O., and Lunsford, J. H., *J. Phys. Chem.* **90,** 4847 (1986); *J. Catal.* **101,** 132 (1986); *Zeolites* **6,** 225 (1986).

6. van den Berg, J. P., Wolthuizen, J. P., Clague, A. D. H., Hays, G. R., Huis, R., and van Hooff, J. H. C., *J. Catal.* **80,** 130 (1983).

7. Lombardo, E. A., Dereppe, J. M., Marcelin, G., and Hall, W. K., *J. Catal.* **114,** 167 (1988).

8. Pine, L. A., Maher, P. J., and Wachter, W. A., *J. Catal.* **85,** 466 (1984).

9. (*a*) Dwyer, A., and Singh, A. P., *Zeolites* **8,** 242 (1988); (*b*) Dwyer, A., *in* "Motivations in Zeolite Materials Science" (P. J. Grobet *et al.*, Eds.), p. 333ff. Elsevier, Amsterdam, 1988.

10. Fritz, P. O., and Lunsford, J. H., *J. Catal.* **118,** 85 (1989).

11. Hildebrandt, R. A., and Skala, H., *J. Catal.* **12,** 61 (1968).

12. Lombardo, E. A., and Hall, W. K., *J. Catal.* **112,** 565 (1988).

13. McVicker, G. B., Kramer, G. M., and Ziemiak, J. J., *J. Catal.* **83,** 286 (1983).

14. Brenner, A., and Emmett, P. H., *J. Catal.* **75,** 410 (1982).

15. Kramer, G. M., and McVicker, G. B., *J. Catal.* **115,** 608 (1989).

16. Hall, W. K., Lombardo, E. A., and Engelhardt, J., *J. Catal.* **115,** 611 (1989).

17. Bizreh, Y. W., and Gates, B. C., *J. Catal.* **88,** 240 (1984).

18. Marczewski, M., *J. Chem. Soc. Faraday Trans. I* **82,** 1687 (1986).

19. Zholobenko, V. L., Kustov, L. M., Borovkov, V. Y., and Kazansky, V. B., *Kinet. Katal.* **28,** 965 (1987).

20. Beyer, H. K., Horvath, J., and Reti, F., *React. Kinet. Catal. Lett.* **14,** 395 (1980).

21. Abbot, J., and Wojciechowski, B. W., *J. Cat.* **113,** 353 (1988) and earlier references cited therein.

22. Giannetto, G., Sansare, S., and Guisnet, M., *J. Chem. Soc. Chem. Commun.*, 1302 (1986); Hilaireau, P., Bearez, C., Chevalier, F., Perot, G., and Guisnet, M., *Zeolites* **2,** 69 (1982).

23. Corma, A., Planelles, J., and Tomas, F., *J. Catal.* **93,** 30 (1985); **94,** 445 (1985).

24. Olah, G. A., Halpern, Y., Shen, J., and Mo, Y. K., *J. Amer. Chem. Soc.* **95,** 4960 (1973).

25. Hirshler, A. E., Preprints Petrol. Div., ACS, Vol. 15 (No. 3), A-87. Chicago, 1970.

26. Clark, A., and Finch, J. N., *in* "Proceedings, 4th Int. Congr. on Catalysis, Moscow, 1968," Paper 75. Adler, New York, 1968.

27. (*a*) Grady, M. C., and Gorte, R. J., *J. Phys. Chem.* **89,** 1305 (1985); Aronson, M. T., Gorte, R. J., and Farneth, W. E., *J. Catal.* **98,** 434 (1986); (*b*) Kofke, T. J. G., Gorte, R. J., and Farneth, W. E., *J. Catal.* **114,** 34 (1988); (*c*) Kofke, T. J. G., Gorte, R. J., Kokotailo, G. T., and Farneth, W. E., *J. Catal.* **115,** 265 (1989).

28. Hall, W. K., Engelhardt, J., and Sill, G. A., *in* "Proceedings, 8th Int. Symp. on Zeolites, Amsterdam, 1989," p. 1253ff.

29. Mirodatos, C., and Barthomeuf, D., *J. Catal.* **114,** 121 (1988) and earlier references cited therein.