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NMR Study of Reactions of Alcohols on Solid Acids

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Contradictory evidence currently exists concerning the stability of small aliphatic carbenium ions on the surfaces of various zeolites. This question has been investigated using triphenylmethanol–^{13}COH, 2-propanol-2-^{13}C and propene-2-^{13}C on a silica–alumina catalyst and H–Y, H–ZSM-5, and H–M (mordenite) zeolites using the ^{13}C MASNMR technique. The stable $(C_6H_5)_3C^+$ cation was used as a calibration standard and a test was devised (bleaching with NH_3 or H_2O) to discriminate between carbenium ions and other nonionic species present. The data indicate that whereas carbenium ions have evidently been formed from 2-propanol and propene, they are not stabilized on these materials. Instead they react with olefin released from other sites to produce polymeric residues, some of which may be ionic.

INTRODUCTION

It has long been known that small aliphatic carbenium ions can be stabilized in liquid superacids (*1*). Such species can undergo only intramolecular transformations because free olefin is not present with which to react. On the other hand an enormous volume of literature exists on heterogeneous acid catalysis where the data conform to the involvement of *metastable* carbenium ion intermediates. Indeed in many cases, it has been supposed that the activation energy for the transformation corresponds to the energy requirement to reach this metastable state. It was therefore with considerable interest that we read the claim of Grady and Gorte (*2*) that isopropyl and *t*-butyl cations could be stabilized in H–ZSM-5 zeolites and that this might be expected on energetic grounds (*3*). Indeed this possibility could not be dismissed lightly since we demonstrated many years ago (*4*) that the $(C_6H_5)_3C^+$, $(C_6H_5)_2C^+CH_3$, and $C_6H_5C^+(CH_3)_2$ cations are indeed stable on the surfaces of silica–alumina catalysts (as is verified once again in the present work). Hence, the stabilization of the isobutyl cation, $(CH_3)_3C^+$ in H–ZSM-5, if not on silica–alumina (*5*), seemed conceivable. If this were the case, the zeolite could then be termed a solid superacid.

Zardkoohi *et al.* (*6*) reported recently that the isopropyl cation could be characterized by ^{13}C MASNMR on addition of propene-2-^{13}C to an H–Y zeolite. A peak which appeared at about 250 ppm downfield from TMS was attributed to this ion partially shielded by an oxygen of the lattice. [In magic acid (*1*) the referenced peak appeared at 330 ppm.] On the other hand, van den Berg *et al.* (*7*) reported that they were unable to detect any peaks which might be attributable to a carbenium ion when C_2H_4, C_3H_6, or other heavier olefins were adsorbed on H–ZSM-5 or H–M zeolites.

The ability to form metastable pentacoor-

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dinated carbonium ions by protonation of paraffin molecules is another characteristic of superacids. Haag and Dessau (*8*) invoked this species to explain their *n*-hexane cracking data over H–ZSM-5 and most recently we (*9*) have added some convincing evidence that the formation of such carbonium ions is the primary reaction step in the decomposition of neopentane and isobutane over H zeolites, silica–alumina, and even $AlCl_3/Al_2O_3$. Giannetto *et al.* (*10*) reached similar conclusions, but stressed the importance of site density.

McVicker *et al.* (*11*) reported that ultrastable Y zeolite showed the characteristics of a superacid in studies of the decomposition of isobutane whereas less acidic catalysts did not. Thus, in view of all of the above it is conceivable that aliphatic carbenium ions could be stabilized at a low temperature in an H zeolite where they could be formed without desorption of the corresponding olefin, i.e., if one stable ion were formed on each site. Gorte *et al.* (*2, 3, 12*) have attempted to do this by reactions of alcohols with the Brønsted sites of H–ZSM-5. Reportedly, they were able to achieve one chemisorbed alcohol per site, but their TPD data showed that H_2O and the resulting olefin desorbed at nearly the same temperature. Thus, some oligomerization was inevitable.

Interestingly, the same *t*-butyl cation which is formed during alcohol dehydration is also the primary intermediate in the decomposition of neopentane (*9*). These data not only demonstrated olefin desorption at temperatures as low as 473 K but also showed that the lifetime of the ion was sufficiently long to facilitate secondary reactions requiring the simultaneous presence of this ion and its conjugate olefin.

The present work was undertaken specifically to determine whether or not aliphatic carbenium ions can be stabilized in zeolites and to further define the nature of the reactions that occur on solid acids. Spectra from ^{13}C-labeled compounds were obtained using MASNMR. To establish the ability of this technique to detect carbocations on solid acids, $(C_6H_5)_3{}^{13}COH$ was adsorbed on a silica–alumina catalyst where it was known (*4, 13*) that the triphenylcarbenium ion can be readily formed in concentrations of about 1.5×10^{19}/g ($5 \times 10^{12}/cm^2$). We were also able to employ this reagent with H–Y, but the molecule was evidently too large to enter the pore systems of the remaining zeolites. The smaller 2-propanol-2-^{13}C molecule was free of this limitation and its reactions were studied on all of these materials following closely the procedures used in Gorte's experiments (*2, 3*). It was found that although 2-propanol is reacted at room temperature on these solid acids, the carbenium ion intermediate is unstable. Reaction occurs between these ions and the olefins they release to form stable products. Also, propene-2-^{13}C was used to check the observations of Zardkoohi *et al.* (*6*).

EXPERIMENTAL

Zeolites and their pretreatment. The preparations studied are listed in Table 1 where their physical properties and chemical compositions are summarized. The cat-

TABLE 1

Chemical Composition and Pore Volume of the Catalysts

Catalyst[a]	Al atoms ($g \times 10^{-20}$)[b]	Pore volume[c]
Na–Y(2.5)	27.0 (26)	(0.30)
H–Y(8.1)	11.0 (7.9)	0.28 (0.30)
H–ZSM-5(35)	2.8 (2.8)	0.20 (0.18)
H–M(27)	3.5	0.21 (0.20)
H–M(17)	5.7	0.21 (0.20)
H–M(7.3)	11.9	0.21 (0.20)
Silica–alumina	5.9	—

[a] Si/Al ratios are given in parentheses; these values are based on chemical analysis.

[b] Based on chemical analysis. Figures shown in parentheses are framework aluminum obtained by NMR (H–Y) or from the base exchange capacity.

[c] Filling factors obtained from N_2 condensation at 0.5 relative pressure at 78 K. Structural pore volumes estimated from crystal structure are given in parentheses.

alysts were pretreated in flowing dry O_2 for 1 h at 773 K followed by evacuation to less than 10^{-5} Torr for another hour.

Reactants. Triphenylmethanol-2-^{13}C (ICN Biomedicals Inc.), 2-propanol-2-^{13}C (ICON), and propene-2-^{13}C (Merck, Sharpe and Dohme) had stated isotopic purities of 99, 98, and 99%, respectively (but see later).

NMR experiments. The spectra were obtained at room temperature, except as noted, using a Brüker MSL-300 instrument equipped with a MAS probe. Samples were spun at rates between 3 and 5 kHz. Bloch decay, both with and without proton decoupling, and cross-polarization measurements were made as required. In many cases spectra from the same sample were determined using two of the acquisition techniques.

The pretreated catalysts were cooled to room temperature, and the reagent of interest was adsorbed on the solid. The technique was varied as required by the substrate. Triphenylmethanol, a solid, was dissolved in benzene and then poured under vacuum into the vessel in which the solid acid had been pretreated. The amount of solution was sufficient to fill the pore system of the solid acid (incipient wetness). After 1 h of contact time (longer times did not modify the spectra), the solvent was distilled back into a cold finger maintained at 78 K and the solid further evacuated to $<10^{-5}$ Torr. The amount of alcohol used was adjusted to one molecule per aluminum in the solid.

The 2-propanol to be adsorbed was measured in the standard BET system at room temperature. The liquid alcohol was cooled to 283 K to lower its equilibrium vapor pressure. The measured gas was all adsorbed.

Following Zardkoohi *et al.* (*6*), an excess propylene [>1 molecule of olefin per Al atom in the solid] was measured in the BET system and then contacted with the solid.

In all cases, the MAS rotors were loaded and sealed in a glove bag under a dry N_2 atmosphere to minimize the contact with atmospheric air (principally H_2O). In blank tests performed with several catalysts, the rotors were stored in a desiccator and the spectra recorded a second time. No significant changes were observed between the spectra taken 2 weeks apart. On the other hand, brief contact with air bleached the $(C_6H_5)_3C^+$ spectrum.

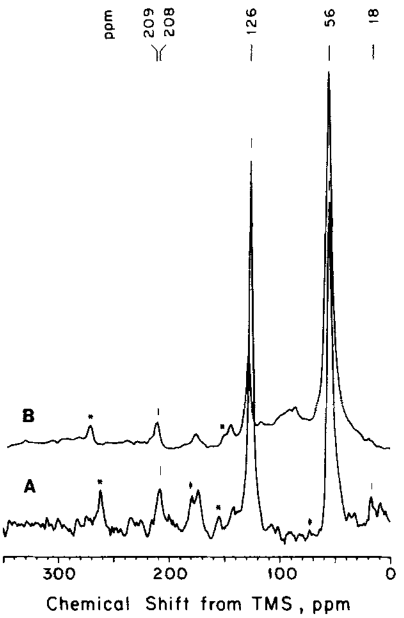

FIG. 1. The interaction of triphenylmethanol-^{13}COH with H–Y (A) and silica–alumina (B). Spinning sidebands are designated *. Band assignments (see text): 56 ppm, triphenylmethane; 81 ppm, triphenylmethanol; 127 ppm, benzene ring carbon; 208 ppm, triphenylcarbenium ion. Spectrum B was obtained using Bloch decay 90° pulses without proton decoupling. Cross polarization was used for Spectrum A. The differences in relative signal intensities noted for the two spectra can be attributed to the use of two different acquisition procedures.

RESULTS

Triphenylmethanol adsorption. When $(C_6H_5)_3{}^{13}COH$ was dissolved in benzene and adsorbed on either silica–alumina or H–Y zeolite, the solids instantaneously developed the characteristic yellow color of the triphenylcarbenium ion. Figure 1B shows the characteristic band at 208 ppm from this species on the silica–alumina catalyst. This value is identical to that reported by Maciel (*13*) and for this carbocation in the liquid phase in superacid media (*1*). Spinning sidebands were identified as peaks which shifted with spinning rate; they are labeled with asterisks. The spectrum also shows the benzene ring carbons at ~127 ppm; there are 18 of these per molecule plus those from any residual benzene solvent. Only small traces of residual alcohol were observed at 81 ppm. These bands did not appear until larger amounts of alcohol were adsorbed. The large band at 56 ppm had no immediate explanation, (but see below). Most of the peaks shown in Fig. 1B also appeared in Fig. 1A from the H–Y zeolite.

The appearance of the large band at 56 ppm in both spectra puzzled us very much. Maciel (*13*) also showed this band in his spectrum, but made no comment about it. In an attempt to identify it, the catalyst was washed with $DCCl_3$ and the decanted liquid analyzed using high-resolution NMR techniques (Brüker/IBM-300). By comparison of the ^1H-coupled and the decoupled spectra, the 56.91-ppm peak could be unambiguously assigned to triphenylmethane. A brief mass spectral study of the 99% $(C_6H_5)_3{}^{13}COH$, taken as a small aliquot of the solid, revealed a large impurity, possibly $(C_6H_5)_3{}^{13}COC_2H_5$. Thus, although we know the origin of the 56-ppm band, we cannot at this time explain why or how it could be present in such large amounts. Benzene, when adsorbed on H–Y, showed only the characteristic 127-ppm peak.

The triphenylmethyl cation is formed by reaction of the triphenylmethanol with the Brønsted sites of acid catalysts, i.e.,

$$(C_6H_5)_3COH + HB \rightleftharpoons (C_6H_5)_3C^+ + B^- + H_2O, \quad (1)$$

where B^- is the conjugate base of the acid site. To check on the reversibility of this reaction, triphenylmethanol was adsorbed on H–Y and the spectra were recorded before (A) and after (B) exposure to air (Fig. 2). When the rotor was opened to ambient air and the powder poured onto a weighing paper, it was striking to see the color change from yellow to white in a period of a couple of minutes. Thus, as previously described (*4*), the reaction of the cation with H_2O could be visually observed. When this powder was again packed into the rotor and the spectrum re-recorded, the 208-ppm peak was missing and the peak corresponding to alcohol at 81 ppm appeared strongly (Fig. 2B). A similar effect was observed when NH_3 was used instead of water except that the $(C_6H_5)_3COH$ peak at 81 ppm did not reappear; instead a signal at about 201 ppm was generated. Thus, these simple tests are available to distinguish between cationic and neutral species. The respective intensities of the alcohol and the carbenium ion signals do not appear to correspond in the spectra because the cross-polarization techniques used for the acquisition of the

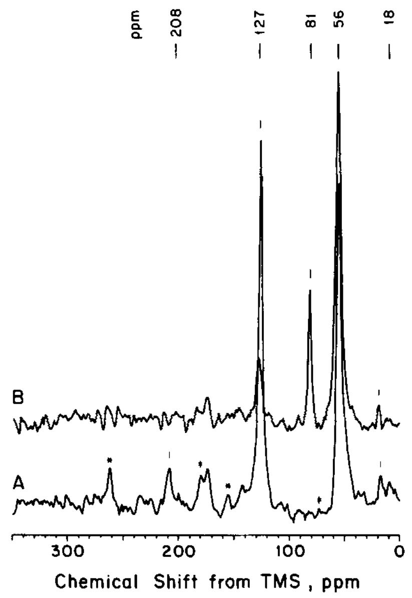

FIG. 2. ^{13}C CPMAS spectra showing the effect of water on the triphenylcarbenium ion adsorbed on H–Y. Spectrum A was recorded as prepared in the absence of water; Spectrum B was recorded from the same sample after exposing it to ambient humidity. The 81-ppm band shown prominently in B corresponds to displaced $(C_6H_5)_3COH$. The other assignments can be taken from Fig. 1.

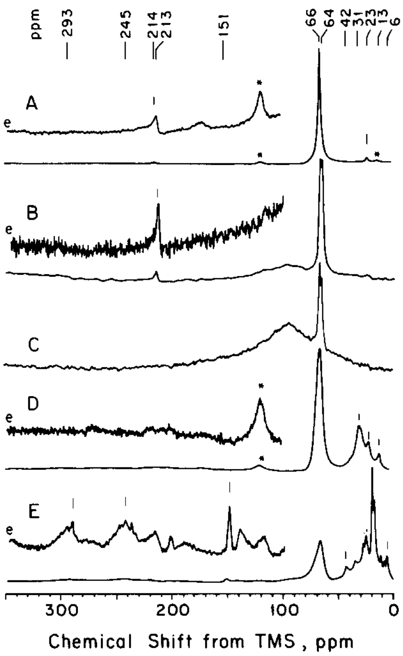

FIG. 3. The adsorption of 2-propanol-2-^{13}C on several solid acids. Spectra A, B, C, D, and E were obtained using silica–alumina, H–Y, Na–Y, H-ZSM-5 and H–M, respectively, as adsorbents. In some cases the scale was expanded, e, to emphasize the weak peaks. Band assignments (see text): 6–42 ppm paraffinic CH_x groups, 64 and 66 ppm C–OH of adsorbed alcohol, 213 and 214 ppm C═O of acetone, peaks above 245 ppm found with H–M could be attributed to polymeric carbenium ions. Acquisition procedures were as follows: A and E, MAS Bloch decay with high-power proton decoupling; B and C, MAS Bloch decay without proton decoupling; cross polarization (CPMAS) was used for D.

spectra effected an enhancement of the alcohol signal in Fig. 2B.

Repeated attempts to extend these experiments to the H–M system failed because triphenylmethanol would not enter the pore system. Hence, the characteristic yellow color of the triphenylmethyl cation did not appear and only the peaks corresponding to unreacted substrate were observed in the NMR spectra.

2-Propanol-2-^{13}C adsorption. The isopropyl carbenium ion is much less stable than the triphenylcarbenium ion (330 vs 208 ppm in liquid superacid). The focus of this investigation was to establish whether or not it can be stabilized on solid acid zeolites as claimed in earlier related studies (*2*, *3*, *6*). This information is vital to the interpretation of studies of the cracking of small paraffins such as isobutane and neopentane (*9–11*).

The MASNMR spectra from 2-propanol adsorbed on several solid acids and on a Na–Y zeolite are shown in Fig. 3. On silica–alumina (A) the 66-ppm peak was by far the largest. In addition to its sidebands at 13 and 119 ppm, only a small peak at 23 ppm corresponding to the methyl group and a tiny bump at 214 ppm appeared in this spectrum. The latter can be seen on scale expansion in Spectrum Ae. The ^{13}C–OH peak of liquid 2-propanol has been reported (*14*) to be at 63.4 ppm. To be sure that the 66-ppm signal corresponded to adsorbed alcohol, the solid was washed with $DCCl_3$ at room temperature. The extract was analyzed using the high-resolution ^{13}C NMR spectrometer. The spectrum showed a peak of 2-propanol at 64.0 ppm, and the peak of acetone at 207 ppm, vide infra.

The H–Y (8.1) spectrum (Fig. 3B) showed two important differences when compared with Fig. 3A. On the one hand, the 213-ppm peak was now clearly evident and two main alcohol peaks at 64 and 66 ppm were resolved in the spectrum. This doublet was not due to ^1H coupling since the splitting was retained when proton decoupling was employed. On extraction with $DCCl_3$, the resulting liquid showed a single peak at 64 ppm. Hence, the doublet probably corresponds to isopropanol adsorbed in two different modes (or sites) on the Y zeolite framework because a similar doublet was observed in the spectrum obtained from Na–Y (Fig. 3C). Bronnimann and Maciel (*15*) reported a similar doublet located at 51–56 ppm when they adsorbed methanol on H–Y. The $DDCl_3$ solution spectrum also showed a small peak at 207 ppm which matches well the 206.2-ppm value given in the literature (*14*) for acetone in chloroform. Evidently the 213-ppm signals in the H–Y spectrum may be assigned to chemisorbed acetone. However, to be sure that this peak did not arise from a cationic species, ammonia ($1NH_3/Al$) was adsorbed on the sample. This produced no significant change in the spectrum.

The broad hump centered near 90 ppm in Fig. 3C (and less evident in Fig. 3B) was due to the probe background. It was most evident in spectra obtained using the simple Bloch decay technique. This signal was also enhanced when the amount of alcohol adsorbed was small because higher amplitude expansion must be used; e.g., the amount of alcohol retained by Na–Y was much smaller than that retained by the H–Y zeolite; hence, the hump is more evident (3B vs 3C).

The spectrum (Fig. 3D) obtained from 2-propanol-2-^{13}C adsorbed on H–ZSM-5 (*35*) was distinctly different from the previous ones. In addition to the 66-ppm peak corresponding to the adsorbed alcohol, the band intensities from the CH_x paraffinic carbons upfield in the 12–24 ppm range have become relatively important. Three bands were resolved (in order of decreasing intensity) at 31, 23, and 13 ppm. According to van den Berg *et al.* (*7*), these data would be attributable to linear oligomers of propene several units long. On the other hand, downfield from the 66-ppm peak, the base line was entirely flat (between 100 and 350 ppm) as shown in expanded Spectrum De. No ionic or oxidized species were detectable.

The H–M spectrum (Fig. 3E) suggested that the extent of polymerization together with chain branching was higher with this catalyst than with H–ZSM-5. Not less than nine overlapping peaks in the paraffinic CH_x region are evident. This spectrum in this region resembles that published by van den Berg *et al.* (*7*) for adsorbed propene. Moreover, spectra from polypropylene (*16*) showed that resonances at 45, 39, 28, 23, 21, and 9 ppm indicate the presence of branched hydrocarbons in the oligomer. This would be expected from the acid-catalyzed oligomerization given sufficient space in the pore system. An additional small signal appeared at 151 ppm which may be assigned to an olefinic carbon. Downfield from the alcohol (66 ppm), two much weaker signals were detected at 245 and 293 ppm. These are more clearly seen in expanded Spectrum Ee. These could stem from polymeric carbenium ions.

Propene-2-^{13}C adsorption. The spectrum obtained following adsorption of about 2 molecules/Al on H–Y is shown in Fig. 4A. Paraffinic $^{13}CH_x$ species appeared in the 20 to 30 ppm range and olefinic carbons near 155 ppm. These fingerprints are very similar to those found in the spectra of van den Berg *et al.* (*7*) for the adsorption of olefins such as C_2H_4 and C_3H_6 on H–ZSM-5 and H–M. The broad signal centered at ~90 ppm was again due to probe background. Peaks observed at 252 and 155 ppm compared favorably with those reported by Zardkoohi *et al.* (*6*) at 250 and 160 ppm. The former was attributed by them to the isopropyl cation in strong ionic interaction

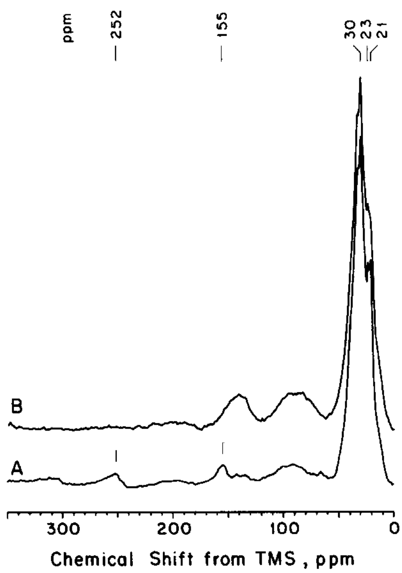

FIG. 4. ^{13}C MASNMR spectra obtained without ^1H decoupling showing the interaction of propylene-2-^{13}C with H–Y. (A) On a clean zeolite; (B) after exposing the previous sample to a partial pressure of ammonia of 5 Torr. Band assignments: ca. 20–30 ppm paraffinic CH_x groups; 155 ppm olefinic CH_x groups; and the 252-ppm peak is from an ionic species.

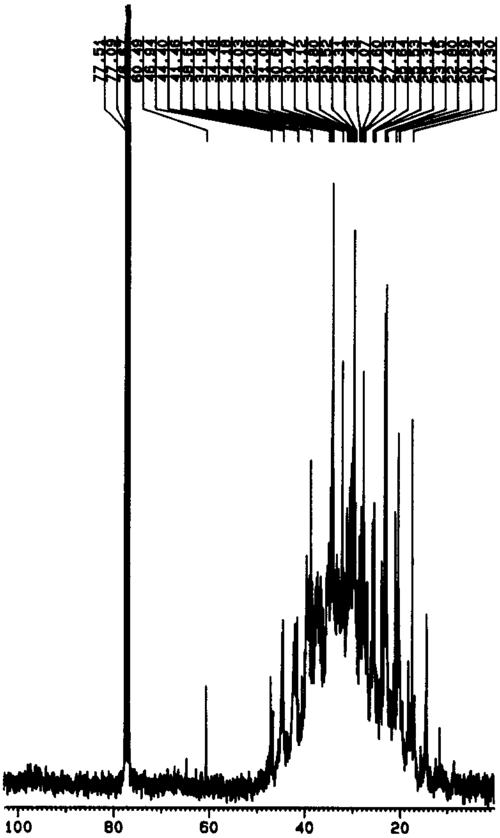

FIG. 5. The ^{1}H-decoupled ^{13}C spectrum from extract from H–Y zeolite after recording Fig. 4B. Paraffinic species are responsible for the banks shifted <50 ppm from TMS; the sharp bands at about 77 ppm stem from CCl_3D.

with a structural oxygen of the zeolite lattice and the latter was assigned to an averaging of polymeric ions undergoing rapid degenerate exchange by intramolecular H^- transfer, e.g., the ethylisopropylcarbenium ion with the methylisobutylcarbenium ion.

Although throughout these experiments the reactor was cooled in ice water to minimize secondary processes, an instantaneous exothermic reaction nevertheless occurred when propene was allowed to contact clean H–Y. The catalyst became orange colored suggesting that conjugated unsaturation, and perhaps conjunct polymerization, had developed. This, together with the strong peaks below 50 ppm stemming from paraffinic oligomers, suggested that a disproportionation reaction must have occurred. Support for this idea was obtained by washing the catalyst with $DCCl_3$ and recording the ^{1}H-decoupled ^{13}C MASNMR spectrum of the extract. This is shown in Fig. 5. Over 50 bands appeared in the paraffinic region below 50 ppm demonstrating the great variety of environments of the ^{13}C atom.

For conformation of the assignment of the 252- and 155-ppm signals, the sample was exposed to excess NH_3 (final pressure ~5 Torr). The color changed from orange to the original snow white of the clean zeolite. Figure 4B was now recorded. Note that the same CH_x bands appeared in the spectrum, but the base line downfield beyond 170 ppm no longer contained the 252-ppm signal or any trace of charged carbon species. A large broad peak centered at ca. 140 ppm was generated when NH_3 was added, possibly from nitrogen-containing compounds. It may also include the olefin signal previously noted at 155 ppm.

DISCUSSION

The results presented herein lead to some important conclusions. First, the stable triphenylcarbenium ion can be readily detected even on the weakest solid acid of this series. Moreover, it appeared with almost the same chemical shift as that reported for magic acid (*1*). By analogy, it can be concluded that the 2-propyl ion was not stabilized on reaction of 2-propanol with H–ZSM-5 or H–Y, contrary to the original idea expressed by Grady and Gorte (*2*), since this ion would have appeared at 320 ppm as in magic acid (*1*). In the reaction of propene with H–Y, Zardkoohi *et al.* (*6*) attributed the band at 252 pm to the 2-propyl ion screened by a lattice oxygen. We cannot refute this assignment with absolute certainty, but from our observations we regard it as unlikely. We think that the reactions of olefins at 273 K are simply too fast and exothermic to avoid polymerization. The color change observed on exposure of H–Y to propene, together with the appear-

TABLE 2

The Cracking of Neopentane and the 2-Propanol Reactions on Solid Acids[a]

Catalysts	Neopentane[b] conversion (%)	$(P/Ol)_4$[c]	n-C_5/i-C_5[d]	Peak area ratio $^{13}CH_x$/^{13}C-OH[e]
Na–Y	0	—	—	0
SiO_2–Al_2O_3	0.8	0	—	very small
H–Y(8.1)	4.3	2.5	0.0	<0.1
H-ZSM-5(35)	4.5	0.3	—	0.1
H–M(27)	25.0	7.8	0.10	0.1
H–M(17)	37.1	11.8	0.16	0.2
H–M(7.3)	98.1	23.0	0.27	5

[a] Catalytic data taken from our earlier work (*9*).

[b] The reaction temperature was 673 K; pulse experiments were made using 1.54×10^{19} molecules of C_5H_{12} per pulse and 400 mg of catalyst. The He flow rate was 90 cm^3/min.

[c] The paraffin-to-olefin ratios in the C_4 fraction.

[d] The equilibrium ratio at 673 K is 0.38.

[e] Adsorbed at room temperature (297 K) was 0.3 molecule of propanol-2-^{13}C per aluminum.

ance of a multiplicity of paraffinic peaks below 50 ppm, indicates that carbenium ions have formed at room temperature, but have undergone oligomerization with excess olefin, followed by disproportionation and the formation of conjunct polymers. With isopropanol, on the other hand, the primary formation of the alkoxide might be expected (*2*) but here too the evidence suggests that oligomerization occurred followed by secondary disproportionation reactions which produce the paraffinic bands.

The absence of the free 2-propyl carbenium ion is not surprising in view of its high reactivity and low stability. When released by decomposition of the alcohol, it will readily desorb as propene as demonstrated by Gorte and co-workers (*2, 3, 12*). This propene is then available to react with other newly formed ions. The H_2O released concomitantly on decomposition of the adsorbed alcohol will assist in olefin desorption.

It is interesting to note that the $(C_6H_5)_3C^+$ is formed with almost identical characteristics on both silica–alumina and H–Y, two catalysts which differ greatly in activity. This suggests that the triphenylmethanol is not able to discriminate between their acidity, e.g., by means of changes in the chemical shift.

The adsorption of 2-propanol yielded some very interesting information about the processes which occur on the surface of these different solids. The interrelationships among the cracking activity, product distribution, and the ^{13}C-OH/CH_x intensity ratios are evident in the data of Table 2. The figures in the last column give a measure of the reactivity of the surfaces for the conversion of the alcohol into surface polymeric residues. They show an increasing propensity for formation of paraffins and this property correlates with the extent of secondary reactions as measured (*9*) by the C_4 paraffin/olefin ratio and both of these increase with the extent of conversion (Column 2). Note also that the C_5 isomer ratio approached equilibrium as the conversion increased from 4.3% for H–Y (8.1) to 98% for H–M (7.3). This is also diagnostic of increasing acidity from top to bottom.

An apparent inconsistency becomes apparent when H–ZSM-5 is compared with the remaining data. Here the secondary reactions from neopentane cracking are less important than those for H–Y and are, in fact, much closer to those of silica–alumina. On the other hand, the CH_x signal is much more important (Fig. 3) than that for either of the above. The reason for this may be that the smaller pore size of the ZSM-5 structure greatly impairs bimolecular reactions such as hydride transfer and hence residue formation. This may not be as important with smaller olefins such as propene as it is with neopentane which must form isobutene in the primary reaction.

In conclusion, Gorte's observations that the low-molecular-weight alcohols (with the possible exception of methanol) can be adsorbed on H–ZSM-5 in excess, and then desorbed to about one molecule per Brønsted site, remain important. However, it now seems clear that when the alcohol is decomposed, both H_2O and olefin are released and the latter forms polymeric residue which remains on the sites. It may still be possible to make use of this and related systems as preformed reaction systems for the study of reaction mechanisms.

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