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Cyclopentenyl Carbenium Ion Formation in Acidic Zeolites: An in Situ NMR Study of Cyclic Precursors

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Abstract: Previous in situ NMR studies of the reactions of propene and ethylene on zeolites have claimed the formation of small amounts of cyclopentenyl carbenium ions. The present investigation clearly demonstrates the formation of these ions in high yield from cyclic precursors on acidic zeolites. In situ ^{13}C solid-state NMR experiments are reported for the reactions of cyclopentene, cyclopentanol, cyclohexanol, and cyclohexane on a variety of zeolites of differing acid strength. The reaction sequence for the alcohols was dehydration, double-bond migration, oligomerization, C_6 to C_5 ring equilibration, and accumulation of cyclopentenyl ions. In some of the experiments up to one-third of the C_5 ring units of the oligomers were positively charged. A ^{13}C chemical shift anisotropy measurement verified that the downfield signals are due to carbenium ions. Ex situ identification of the neutral extractable oligomers combined with comparison to model carbenium ion shifts permitted a plausible identification of the specific ions formed. The formation of products containing five-membered rings from cyclohexanol was modeled by the cyclohexane–methylcyclopentane skeletal rearrangement reaction. This investigation firmly establishes the formation of cyclopentenyl ions in zeolites and considers their significance in regard to reaction mechanisms. The persistence of these ions in high concentrations in zeolites is shown to be a consequence of the relative acid strength of the zeolite and the acid strength of the carbenium ions. This conclusion has important implications for the spectroscopic detection of reaction intermediates and the establishment of an acidity scale for zeolites.

Introduction

One of the objectives of in situ studies of reactions on catalysts is the identification and characterization of intermediates. In the case of olefins on solid acids, carbenium ions have been sought as intermediate species. A number of stabilized cations have been characterized in superacid solutions at low temperature by NMR[1] or in noncoordinating solvents using transient techniques such as UV–visible pulse radiolysis spectroscopy.[2,3] Although high temperature and steady-state reaction conditions would seem unpromising for spectroscopic detection of carbenium ions on solid catalysts, several observations have been reported. Some of the first studies concerned the extremely stable trityl cation, which readily forms on amorphous oxide catalysts.[4,5] In 1989 this group reported an in situ ^{13}C NMR study of the low-temperature oligomerization of propene on zeolite HY.[6] As the reaction reached completion near room temperature, ^{13}C signals developed at 249 and 156 ppm in a 2:1 intensity ratio. Drawing from chemical shift data and analogies to olefin chemistry in acidic solutions, the authors assigned these resonances to cyclopentenyl carbenium ions with substitution patterns similar to **1**. In a later study of the cracking of the ethylene oligomers on HZSM-5 at 523 K,[7] this group observed ^{13}C NMR signals at 250 and 148 ppm that were assigned to ions with structures like the ion **2**. These observations were intriguing in that Venuto et al.[8] and Poutsma[9] had previously described reaction mechanisms in which such ions had a prominent role as intermediates in cracking reactions.

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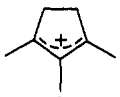

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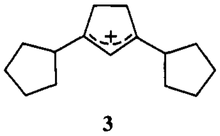
The experience of the authors is that these chemical shift assignments have not been universally accepted, which is not unreasonable given the low intensity for the signals in refs 6 and 7, the dissimilarity of the ions **1** and **2** as to their starting materials, and the central role that carbenium ions play in the standard mechanisms for acid-catalyzed reactions of hydrocarbons. We have therefore undertaken an in situ ^{13}C NMR study of cyclic (C_5 and C_6) olefins and alcohols on zeolites with the hope that these precursors would lead more directly to cyclopentenyl ions in high yield.

Cyclopentene formed simple dimer and trimer species at moderate temperatures, and approximately one-third of the repeat units ionized at 433 K; these persisted indefinitely as charge-balancing species in the zeolites at 298 K. The large ^{13}C chemical shift anisotropy measured for the downfield resonance is consistent with a carbenium ion, and the isotropic shifts are modeled very well by literature values for ions similar to **3**. These structures are similar to the neutral oligomers identified by ex situ analysis.



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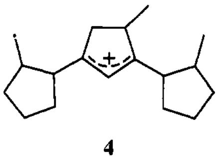

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Ions with structures similar to 4 are proposed to form from cyclohexanol as a result of $C_6 \rightleftharpoons C_5$ skeletal rearrangements and oligomerization. This thermodynamically driven process was modeled with an in situ study of the cyclohexane to methylcyclopentane rearrangement on zeolite HZSM-5.

Experimental Section

Catalyst Preparation. Zeolite NaX (Si/Al = 1.2) was obtained from Strem Chemicals. Zeolites HZSM-5 (Si/Al = 19) and NH_4Y (Si/Al = 2.5) were obtained from UOP Corp. CsCl and NH_4Cl were obtained from Aldrich. To prepare zeolite CsX, zeolite NaX was first exchanged to the ammonium cationic form to facilitate introduction of the larger Cs cation. The detailed multistep exchange procedure and elemental analysis results were reported previously.[10] Typically, catalysts were activated at 673 K by a procedure described elsewhere[6] and were used within 1 day of activation.

Reagents. Cyclopentanol-*1*-^{13}C (99% ^{13}C), cyclohexane-$^{13}C_1$, and NH_3-^{15}N were obtained from Cambridge Isotopes. Cyclohexanol-*1*-^{13}C (99% ^{13}C) and cyclopentene-$^{13}C_1$ (random position) were obtained from Isotec. Cyclopentanol (99%), cyclohexanol (99%), cyclopentene (99%), and toluene (99%) were obtained from Aldrich.

Sample Preparation for In Situ MAS NMR. The experimental procedure for sample preparation using standard CAVERN devices is described elsewhere.[11] The samples were evacuated to pressures less than 5×10^{-5} Torr. Typically, adsorptions were done at room temperature using loadings of 0.5–1.5 equiv of adsorbate per acid site. This experimental protocol was followed in preparing samples for cyclopentene-$^{13}C_1$ on HZSM-5 and cyclohexane-$^{13}C_1$ on HZSM-5. For cyclopentanol and cyclohexanol, which have low vapor pressures, samples were prepared by first loading 10–15 μL of the compound into a glass bulb using a syringe. The reactant was then purified several times by freeze–pump–thaw cycles. The bulb was sealed, taken into a glovebox, and set on top of a catalyst bed in a zirconia rotor. The rotor was placed in a standard CAVERN device, evacuated, and then capped in a manner that crushed the bulb between the cap and the catalyst bed.[12] This experimental protocol was followed in preparing samples for the following experiments: cyclopentanol-*1*-^{13}C on HZSM-5, HY, and CsX; cyclohexanol-*1*-^{13}C on HZSM-5 and CsX. For the study of ammonia and cyclopentanol-*1*-^{13}C on HZSM-5, ca. 1.5 equiv of ammonia was first adsorbed into the zeolite, and then the rotor was capped while crushing the bulb, which contained 1.2 equiv of cyclopentanol-*1*-^{13}C.

NMR Spectroscopy. In situ ^{13}C solid-state NMR experiments were performed with magic angle spinning (MAS) on a home-built spectrometer operating at 50.06 MHz or on a Chemagnetics CMX-360 spectrometer operating at 90.46 MHz. Hexamethylbenzene (17.4 ppm) was used as an external chemical shift standard, and all chemical shifts are reported relative to TMS. Standard Chemagnetics pencil probes equipped with variable-temperature accessories were used to spin zirconia rotors at 3.5–4 kHz. Spectra were typically acquired over a temperature range of 298–523 K, although low-temperature protocols were occasionally used to permit the reactions of cyclopentene to be studied beginning at 213 K. The following ^{13}C NMR experiments were performed: cross polarization[13] (CP), contact time = 2 ms, pulse delay = 1 s, 400 transients; CP with interrupted decoupling,[14] contact time = 2 ms, pulse delay = 1 s, 400 transients, dipolar dephasing time of 50 μs; and single-pulse excitation with decoupling (Bloch decay), pulse delay = 10–15 s; 200–2000 transients.

Ex Situ Identification. Catalyst (1.0–2.0 g) was activated in vacuo in a Pyrex tube, 2.2 cm in outer diameter by 19 cm in length with a wall thickness of 0.22 cm. Approximately 1.0–3.0 equiv of reactant was loaded into the tube using two different protocols. For cyclopentene, standard vacuum line techniques were used to transfer the reactants. For cyclopentanol and cyclohexanol, the reactant was loaded into the Pyrex tube containing activated catalyst in the nitrogen atmosphere inside the glovebox. The tube was taken out of the glovebox, attached to the vacuum line, and evacuated via several freeze–pump–thaw cycles. The sample was then isolated from the vacuum line, heated to a desired temperature determined by reference to the appropriate in situ ^{13}C NMR study, and maintained at that temperature for 0.5 h. After the sample cooled to room temperature, the glass tube was opened, and the products were extracted using toluene. The extracts were analyzed by GC–MS with a HP-5995 instrument using 70-eV EI ionization and a DB-1 column.

Results

Ex Situ Studies. Cyclopentene, cyclopentanol, and cyclohexanol were reacted on samples of zeolite HZSM-5 and HY, and the reaction products were extracted. This extraction procedure is believed to sample the small oligomeric materials in zeolite HY, but its efficiency for zeolite HZSM-5 is uncertain. GC–MS was used to determine the types of oligomers formed, although specific compound identification was often precluded by the absence of reference spectra in even the largest data bases as well as rearrangements of different isomers to common ions. Cyclopentene formed three dimeric olefins, several trimeric olefins, and cyclopentylcyclopentane. Cyclopentanol yielded three dimeric olefins and dicyclopentyl ether. An analogous study of cyclohexanol identified five dimeric olefins, several trimeric olefins, the ether, and dimeric cycloalkanes.

These ex situ studies suggest that relatively simple oligomers of cyclic units form during these reactions and that dimers and trimers are common. The formation of cycloalkanes is consistent with well-established hydrogen-transfer reactions in acid catalysis.[15] These reactions form a stoichiometric amount of diene, which would be expected to be strongly adsorbed on the zeolite (vide infra). It should be emphasized that the carbenium ions (which are the primary focus of this investigation) cannot be studied ex situ; organic solvents cannot extract them; and acidic solvents would induce other reactions in the charged and neutral organic constituents.

In Situ Studies. Figure 1 compares in situ ^{13}C MAS NMR studies of cyclopentanol and cyclohexanol on the weakly active catalyst CsX. CsX is generally described as weakly basic,[16–21] but the multifunctional nature of this catalyst has also been recognized.[22] Residual weak Bronsted sites due to incomplete ion exchange have previously been implicated in the weak activity for the conversion of acetone to mesityl oxide.[23] The cyclic alcohols eliminated water to form the corresponding olefins at 523 K, but neither double-bond migration nor skeletal isomerization occurred on this zeolite.

Figure 2 shows both cross polarization and Bloch decay spectra from an in situ study of cyclopentanol-*1*-^{13}C on zeolite HY. This catalyst has a faujasite structure similar to CsX, but it is classified as a strong acid. Water was eliminated at moderate temperatures, and cyclopentene was far more reactive than the alcohol (vide infra); thus, Figure 2 shows the conversion of alcohol to oligomers with a steady-state concentration of olefin near the detection limit. Weak but unmistakable signals near 250 and 144 ppm formed and persisted in the temperature range 323–393 K. Their intensities were essentially independent of the mode of excitation (i.e., cross polarization vs Bloch decay). The approximate intensities of the ca. 250 and ca. 150 ppm resonances are reminiscent of the previous study of propene on zeolite HY.[6] Further heating to 433 K resulted in extensive cracking to give a thermodynamic mixture of branched C_4 and C_5 alkanes and aromatics.

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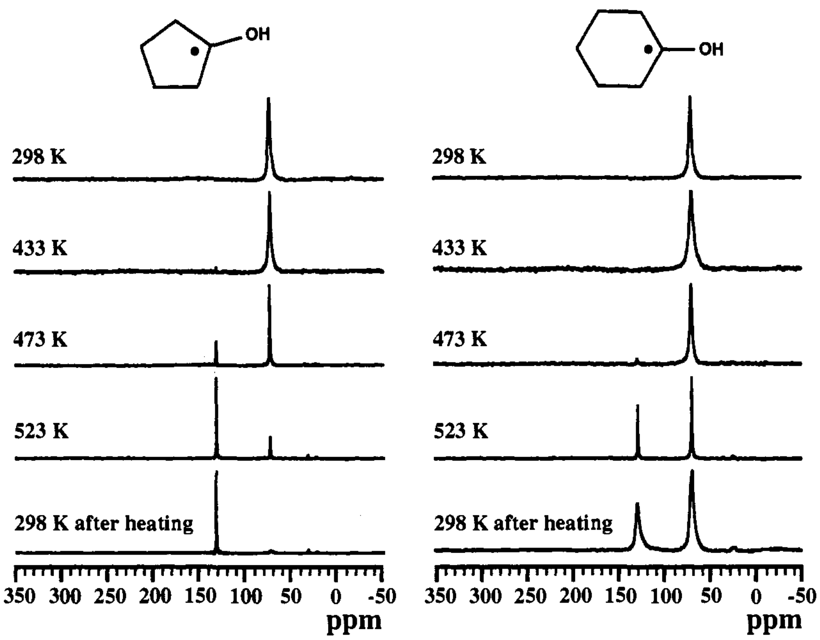

Figure 1. In situ ^{13}C MAS NMR (Bloch decay) studies of the reactions of cyclopentanol-*1*-^{13}*C* and cyclohexanol-*1*-^{13}*C* on zeolite CsX. Cyclopentanol (75 ppm) and cyclohexanol (71 ppm) dehydrated to form cyclopentene (133 ppm) and cyclohexene (130 ppm), respectively.

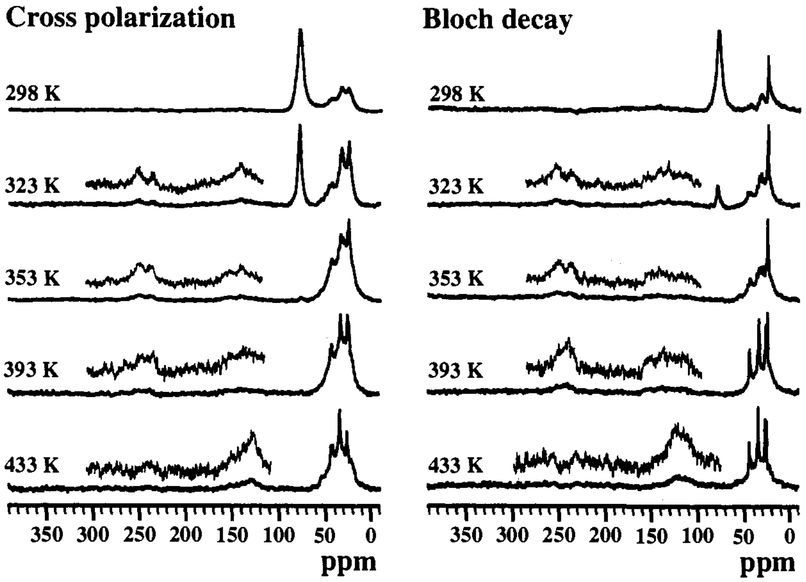

Figure 2. In situ ^{13}C MAS NMR study of the reactions of cyclopentanol-*1*-^{13}*C* on zeolite HY. Signals associated with cyclopentenyl ions were observed at ca. 250 and 144 ppm in both cross polarization and Bloch decay spectra.

It seems reasonable to expect a greater relative degree of carbenium ion formation on a more strongly acidic zeolite. Figure 3 shows the reactions of cyclopentanol on zeolite HZSM-5. Appreciable carbenium ion signals formed in the 373–433 K temperature range and indefinitely persisted at 298 K after heating. A small amount of cyclopentene-^{13}*C*$_1$ was available for this investigation. Figure 4 shows that this olefin oligomerized on HZSM-5 near room temperature and formed abundant signals at 250 and 144 ppm at 433 K and that these ions persisted indefinitely at 298 K.

Drawing from literature reports of ^{13}C chemical shifts for cyclopentenyl carbenium ions with diverse substitution patterns[24-32] and the neutral products identified by ex situ analysis, the simplest specific assignment for the downfield chemical shifts is ion 3, although similar ions of higher oligomerized structures would have identical chemical shifts. The interrupted decoupling response of the signals confirmed that the 250 ppm peak was due to a quaternary carbon, while the 144 ppm peak corresponded to a tertiary carbon.

The 250 ppm signal was also characterized with sideband analysis of slow spinning speed spectra (not shown). Herzfeld–Berger analysis[33] of the sideband intensities revealed that the principal components of the shielding tensor were $\delta_{11} = 375$ ppm, $\delta_{22} = 290$ ppm, and $\delta_{33} = 86$ ppm. The large anisotropy implied

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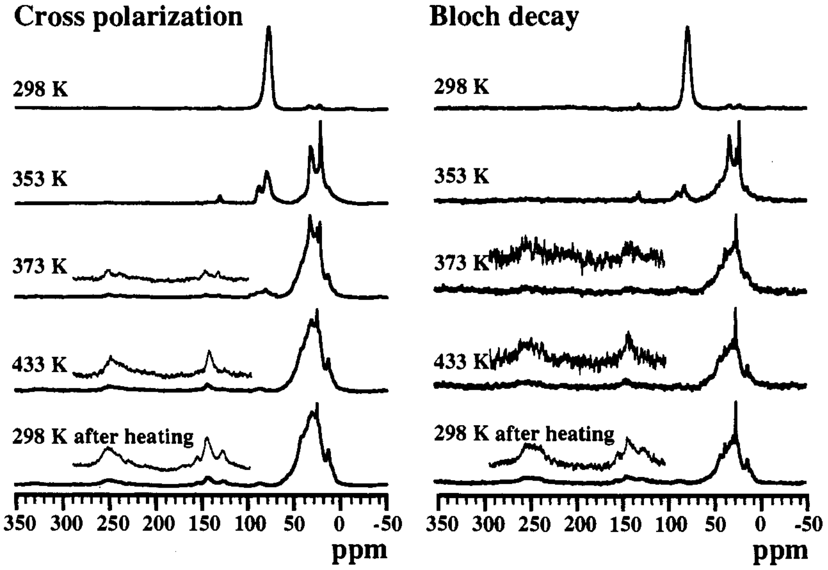

Figure 3. In situ ^{13}C MAS NMR study of the reactions of cyclopentanol-*1*-^{13}C on zeolite HZSM-5. Cyclopentanol reacted to form cyclopentyl ether (89 ppm) and cyclopentene (131 ppm), and the latter further reacted to form cyclopentenyl ions.

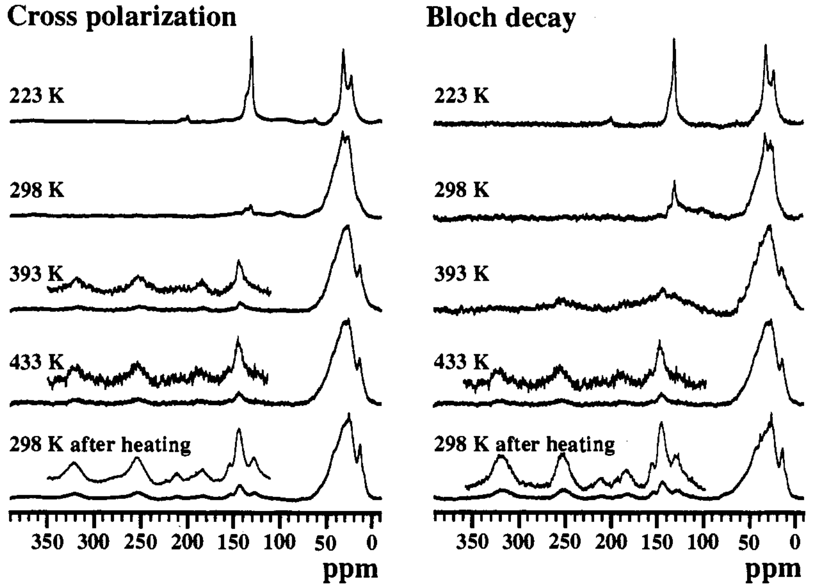

Figure 4. In situ ^{13}C MAS NMR study of the reactions of cyclopentene-C_1 (random position) on zeolite HZSM-5. Oligomerization of cyclopentene (130 ppm) was nearly complete at 393 K, and cyclopentenyl ions (250 and 144 ppm) began forming at that temperature. The quantitative Bloch decay spectrum at 298 K after heating showed that ca. one-third of all the rings were charged.

by these numbers and the large isotropic shift are best explained by a resonance-stabilized carbenium ion.[34]

The integrated signal intensities of the Bloch decay spectra obtained at 298 K after heating were used to estimate the fraction of cyclopentyl rings present as cyclopentenyl carbenium ions. The assumption that the high-field region contains signals from all five carbons of neutral units and two carbons of the charged units allows this calculation to be performed. The 250 ppm peak and its associated sidebands sum to an intensity that is 18% of the integrated intensity of the upfield signal (8–55 ppm), and one obtains an estimate that 35% of the cyclopentyl rings are present as cyclic carbenium ions. This works out to 42% of the framework sites in ZSM-5 being charge compensated with carbocations, as the loading of cyclopentene was 1.2 equiv in this experiment.

Figure 5 reports an in situ study of cyclohexanol on HZSM-5. The alcohol equilibrated with the ether (79 ppm) prior to forming the olefin (127 ppm). The latter oligomerized at 353 K and formed persistent carbenium ions at 373 K. These ions had ^{13}C chemical shifts at 252, 239, and 145 ppm, and interrupted decoupling showed that the 145 ppm peak corresponded to a tertiary carbon. These signals cannot be reconciled with cyclohexenyl ions because of chemical shift discrepancies,[24-28,35] but they are in close agreement with cyclopentenyl structures like **4**. Further heating resulted in carbenium ion signals indistinguishable from those derived from cyclopentanol and cyclopentene.

The suggested conversion of six-membered rings to methyl-substituted five-membered rings on an acidic catalyst at high temperature is a thoroughly established skeletal rearrangement reaction.[15,36] Figure 6 reports an in situ study of the reaction of cyclohexane (28 ppm) on HZSM-5. A small amount of methylcyclopentane (35, 27, and 20 ppm) began forming at 473 K, and at 523 K the ratio of methylcyclopentane to cyclohexane was approximately 1:1. Prolonged heating at 523 K produced aliphatic and aromatic cracking products as well as a low-intensity signal near 240 ppm.

A final experiment reported here concerns the reactions of

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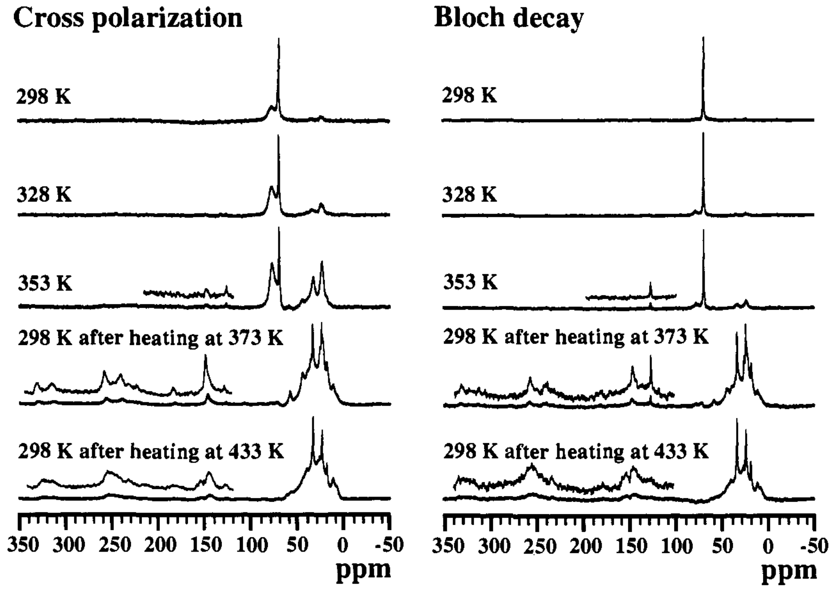

Figure 5. In situ ^{13}C MAS NMR study of the reactions of cyclohexanol-*1*-^{13}C on zeolite HZSM-5. Cyclohexanol (71 ppm) reacted to form cyclohexyl ether (79 ppm) and cyclohexene (127 ppm), and the latter rearranged and oligomerized. Signals at 252, 239, and 145 ppm were assigned to cyclopentenyl ions like **4** (see text for explanation).

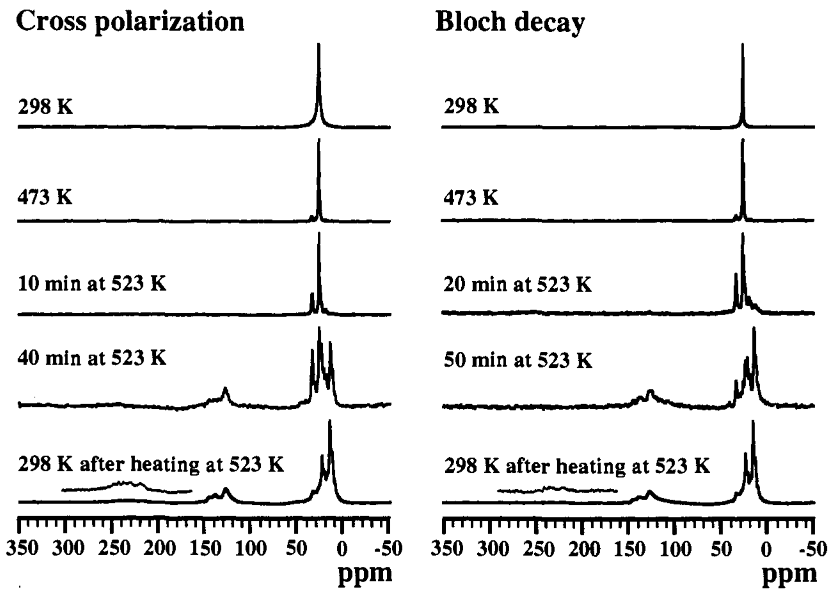

Figure 6. In situ ^{13}C MAS NMR study of the reactions of cyclohexane-C_1 on zeolite HZSM-5. Cyclohexane (28 ppm) began rearranging to form methylcyclopentane (35, 27, and 20 ppm) at 473 K. Prolonged heating at 523 K produced aliphatics (ca. 10–45 ppm) and aromatics (ca. 120–145 ppm) as well as a low-intensity signal near 240 ppm.

cyclopentanol on a sample of zeolite HZSM-5 that was loaded with an excess of NH_3 prior to adsorbing the alcohol. As Figure 7 shows, cyclopentene formed at high temperature as well as cyclopentylamine (56 ppm). Interconversion of the olefin and amine led to label scrambling. Carbenium ions did not form in detectable concentrations in this experiment.

Discussion

The observation of cyclopentenyl carbenium ions at near-stoichiometric levels raises the question as to why these ions are so readily formed in zeolites. Simple secondary or tertiary carbenium ions were not observed in this investigation even though standard reaction mechanisms would predict their formation during olefin oligomerization. A separate but related question concerns the ease with which cyclopentenyl ions formed from structural precursors such as ethylene and propene. In order for cyclopentenyl carbenium ions to be common intermediates or products in complex olefin reactions in acidic zeolites, there must be a general mechanism by which diverse olefins can reach similar ions.

The Stability of Cyclopentenyl Carbenium Ions in Zeolites. Much of our insight into the mechanisms of acid catalysis comes from spectroscopic studies of carbenium ions in superacid solution such as FSO_3H/SbF_5.[1] Such solutions are much stronger acids than 100% H_2SO_4, and simple tertiary or sometimes secondary ions (i.e., those without resonance stabilization or other special properties) can be generated stoichiometrically at low temperature to prevent oligomerization. In order for a carbenium ion to form in appreciable amounts in a conventional acid such as sulfuric acid, it must be further stabilized; simple tertiary and secondary ions may form in low steady-state concentrations as transient intermediates, but they do not persist in near-stoichiometric quantities. In order for a carbenium ion to persist at a high concentration in a zeolite, the zeolite must be a stronger acid than the carbenium ion. Thus, we should consider two related

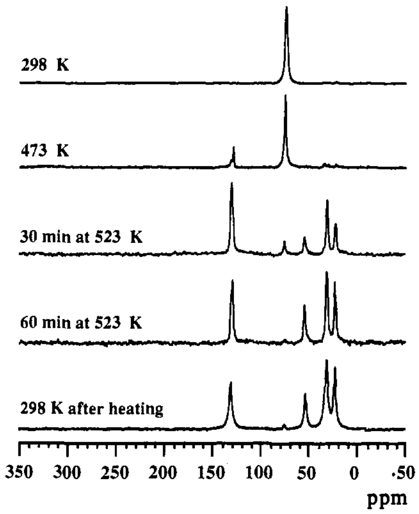

Figure 7. In situ MAS NMR (Bloch decay) study of the reactions of NH_3 and cyclopentanol-*1*-^{13}C on zeolite HZSM-5. Cyclopentene (130, 33, and 24 ppm) and cyclopentylamine (56 ppm) formed at high temperatures. Label scrambling was also observed.

questions: what is the strength of the acid sites in zeolites, and what are the acid strengths of various carbenium ions? The precise answers to these questions are a little difficult to quantify, the prevalent views on zeolite acidity are in flux, and the Hammett acidity scale[37] has several limitations. Fortunately, the relative stabilities of carbenium ions do not appear to be strongly dependent on solvation,[9] and Fărcaşiu and co-workers[38,39] have recently proposed an alternate scheme for quantifying acid strength that has an obvious connection to carbenium ion formation.

Zeolites are commonly believed to be superacids on the basis of their ability to catalyze *at high temperatures* reactions of alkanes that might require five-coordinate carbonium ion intermediates. But Kramer et al.[40] have recently shown that zeolite framework oxygens play an important role in H/D exchange reactions, suggesting that the acid function of zeolites is complex. Several NMR studies[23,41,42] have demonstrated that the extent of proton transfer from the zeolite to various weak bases, as measured by ^{13}C isotropic chemical shifts, is less complete than for the same molecules in 100% sulfuric acid. These comparisons are made between stoichiometric adsorption complexes in zeolites and dynamic exchange equilibration in solutions, but the comparison is still suggestive. In one of the more quantitative studies,[23] the authors measured ^{13}C shifts of mesityl oxide (an α,β-unsaturated ketone) in various zeolites and applied the method proposed by Fărcaşiu et al.[38] to measure acid strength. That study showed that chemical shift changes for mesityl oxide in zeolite HZSM-5 were equivalent to those reported in 70% sulfuric acid solution.[23] On the basis of these measurements of proton transfer to organic adsorbates, it seems unrealistic to expect a particular carbenium ion to persist at high concentration in a zeolite unless this same ion forms to a significant extent in a sulfuric acid solution of comparable strength.

Deno and co-workers performed extensive measurements of the equilibrium constants for protonation of dienes as well as other properties of allylic cations.[43-46] It is informative to consider some representative conclusions of their work on the cations **2**, **5**, and **6**. One of the figures of merit for stability determined by Deno[43] was the percentage of H_2SO_4 required for the concentration of the ion to equal that of the diene(s) in equilibrium. For the ion **2**, 35% H_2SO_4 (a relatively weak acid) sufficed, but the noncyclic ion **5** required a much stronger acid (73% H_2SO_4). The figure of merit for the cyclohexenyl ion **6** was 50% H_2SO_4. Indeed, cyclohexanol derivatives rearrange to form cyclopentenyl cations even in 96% sulfuric acid.[47]

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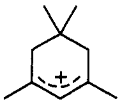

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Our previous study of mesityl oxide in zeolites,[23] in combination with the work of Fărcaşiu[38] and Deno,[43] provides a compelling explanation for the special stability of cyclopentenyl carbenium ions in zeolites. Ions with structures similar to **2** (e.g., **3** and **4**) can form nearly quantitatively in acidic media comparable to ca. 70% H_2SO_4 in strength, but noncyclic allylic cations without special stability will form and persist at lower concentrations. Deno has explained the difference in stability between **2** and **5** in terms of steric inhibition of resonance for **5**.[43] The cyclopentenyl cation **2** is locked into a planar structure that maximizes resonance.

One would not expect to see appreciable formation of simple carbenium ions in 70% H_2SO_4, and it is no wonder that simple carbenium ions have not been seen in in situ NMR studies of olefin reactions in zeolites. Such ions could be transient intermediates in zeolite-catalyzed reactions as they are proposed to be in solution, but their spectroscopic characterization by any means in a zeolite or elsewhere must deal with short lifetimes and vanishing steady-state concentrations.

The Formation of Cyclopentenyl Carbenium Ions from Diverse Precursors. The reactions of olefins in acidic solutions were reviewed by Pines.[15] The process of oligomerization, isomerization, cyclization, and hydrogen transfer is called conjunct polymerization. Hydrogen transfer forms alkanes and dienes; the latter cyclize, lose more hydrogen, and form cyclopentadienes in equilibrium with cyclopentenyl cations, which, as we have seen, are particularly stable.

Venuto et al.[8] and Poutsma[9] have proposed reaction schemes in which cyclopentenyl ions have a prominent role. For example, propene dimerizes or trimerizes and then disproportionates in hydrogen-transfer reactions. An electrocyclic reaction converts linear dienylic cations to six-membered ring allylic ions. The latter isomerize to cyclopentenyl isomers, which are favored at equilibrium.[48-51] Thus, aromatization must involve the minor component(s) of the mixture of allyl cations.

It therefore seems reasonable that cyclopentenyl cations would form from a variety of olefinic precursors and that these species are in fact true intermediates in the formation of aromatics, albeit relatively stable intermediates. On a working catalyst with reagent flow, hydrogen-transfer reactions are more facile than with batch reactor conditions in which the hydrogen inventory is fixed, and the cyclopentenyl ions are more readily converted to aromatics and coke. Cyclopentenyl ions may also influence catalyst activity since their formation consumes a stoichiometric number of acid sites.

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Implications for the Spectroscopic Detection of Intermediates. As suggested earlier, the detection of unstable, simple carbenium ions in zeolites by NMR or other spectroscopic means may be an unpromising quest. The recognition that the acidity of zeolites is less strong (at least at moderate temperatures) and certainly "different" from superacid solutions allows a proper focus on the more subtle interactions of weak bases with zeolitic acid sites rather than forcing the analogy to the superacid solution literature. The ready formation and persistence of cyclopentenyl ions argue strongly for the transient formation of less stable ions as intermediates, but primary and secondary species may exist as framework-bonded intermediates rather than free ions. The fine line between the stability limits of free vs bonded species may ultimately be drawn by theorists.[52]

Cyclopentenyl carbenium ions have the requisite stability to persist as free ions in zeolite HZSM-5 as well as other relatively strong zeolites with moderate to high Si:Al ratios. Consideration of the stability of other common ion types suggests other possibilities for persistent carbenium ions in zeolites.

Chemistry of Cyclic Alcohols in Zeolites. The reactions of simple organic molecules in zeolites are of interest because of the use of these catalysts in the synthesis of fine chemicals[53–56] and the possibility of replacing conventional acids with environmentally sound alternatives. In situ NMR studies of small alcohols have been reported in the context of hydrocarbon synthesis,[57–61] but this is the first study of alcohols large enough to be regarded as synthetic building blocks. The reaction pattern observed here, dehydration, oligomerization, etc., is similar to solution chemistry. The formation of cyclopentyl amine from NH_3 and cyclopentanol is more interesting. The importance of nitrogen-containing functional groups in fine chemicals and pharmaceuticals would suggest further investigation of this chemistry.

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