Physical Organic Chemistry of Solid Acids: Lessons from in Situ NMR and Theoretical Chemistry

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The acid−base reaction is the most general in chemistry, and solid acids such as zeolites and metal halides are among the most important catalysts. Until recently, some commonly-held interpretations of reactions on solid acids were oversimplified, due both to the limitations of experimental studies of the solid state and to incorrect analogies to solution chemistry. For example, zeolites were most often classified as superacids, the solid equivalent of magic acid. Thus, reactive intermediates such as five-coordinate carbonium ions, primary carbenium ions, and other very unstable species, capable of transient existence in liquid superacids,[1] were also assumed to be central to zeolite reaction mechanisms. Herein we summarize recent studies that clarify the strength of solid acids and better define reaction mechanisms in zeolites.

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Starting in 1987, we developed a variable temperature solid state NMR approach for the in situ study of complex reactions on solids. Since then, we have applied in situ NMR to the study of over 80 reactants or probe molecules on various solid acids. We demonstrate here that the acid strength of zeolites is well below the threshold of superacidity (100% H_2SO_4), and that the zeolite framework is more than a passive system for delivery of a proton. We also demonstrate how our recent progress in solid acid chemistry was aided by the coupling of high-level quantum chemical calculations with the design and evaluation of in situ spectroscopic experiments. Simple proton transfer and donor−acceptor equilibria in the gas phase can be measured with great accuracy, and gas-phase reactions are the easiest to treat with theoretical methods. However, many important reactions occur in the liquid (homogenous) or solid (heterogeneous) state, where the effects of the media can be large. For example, solvation has a profound effect on acid−base properties, and one can cite pairs of compounds whose relative basicities in aqueous solution are the reverse of their gas phase proton affinities. There are also suggestions that solid systems can "solvate" reactions through the influence of dielectric effects, the electric field, and polarization. The bridge between the gas and condensed phases is slowly being crossed by experimental studies of gas phase clusters, and *ab initio* studies that explicitly treat solution and solid phase systems. In this Account, we

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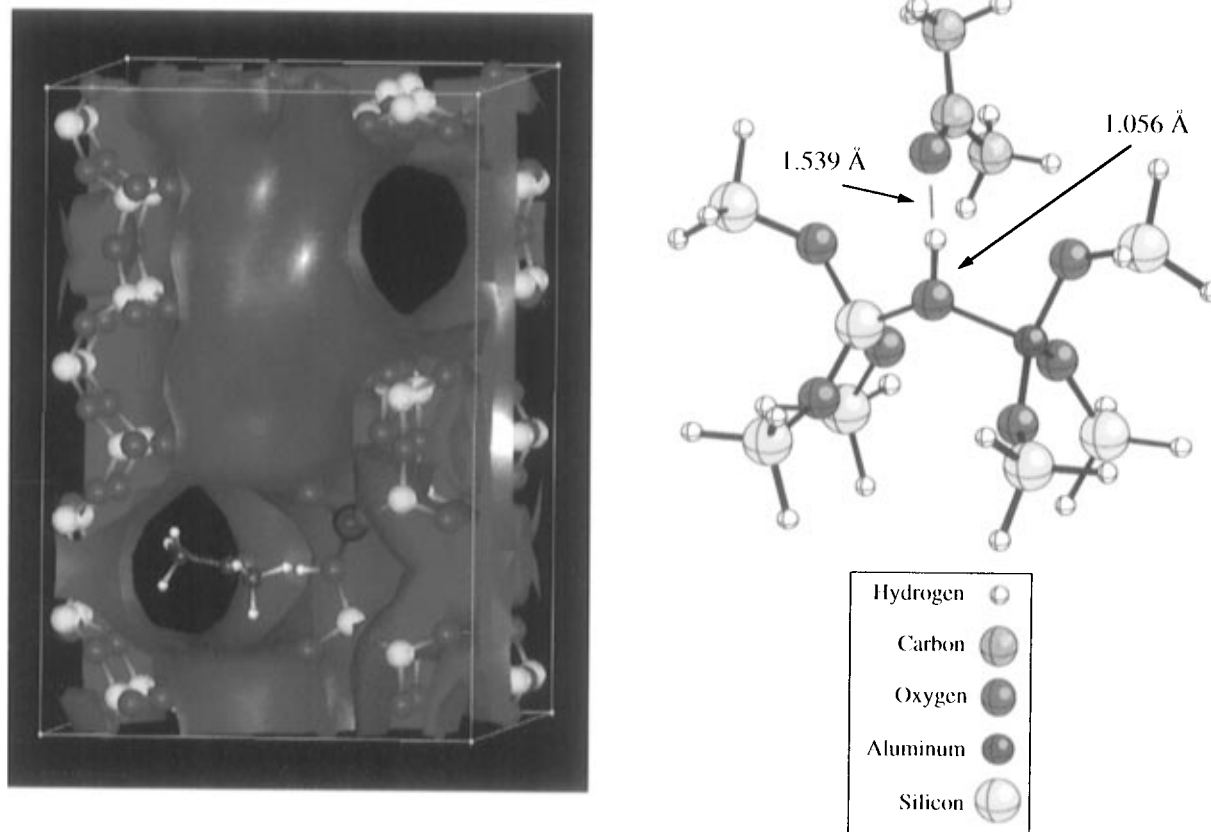† Texas A&M University.
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Figure 1. Left: Approximate van der Waals surface of the internal pore structure of zeolite HZSM-5, showing acetone coordinated to a Brønsted site. The view is down a zigzag channel. Right: Optimized geometry of acetone and a cluster model of the Brønsted site. The calculation was done at the BLYP level of density functional theory using the program DMol.

restrict our discussion to solid acids important in catalysis.[2−5]

Zeolite Solid Acids

A particularly well-characterized solid Brønsted acid is zeolite HZSM-5, the microporous crystalline material shown in Figure 1. ZSM-5 is composed of tetrahedral SiO_4 units that form intersecting straight and zigzag channels, each nearly circular with diameters of ca. 0.55 nm. One can get a sense of this pore system from Figure 1 which shows a view down the zigzag channels. The topology of the pore system has a profound effect on the diffusion of reactants and products, and can also influence reactions through steric constraints on transition states. In other zeolites such as HY, the tetrahedral building units are combined differently to yield other framework structures, but explicit consideration of only the HZSM-5 structure is sufficient for the purposes of this Account. Also in Figure 1 is the optimized geometry of a Brønsted site in the vicinity of the channel intersection with an acetone molecule complexed to the acidic proton. The Brønsted site is created by the substitution of AlO_4^- for one SiO_4 in the framework. The resulting negative charge is balanced by a proton bonded to a bridging oxygen.

The high-temperature phase of purely siliceous ZSM-5 has 12 crystallographically unique tetrahedral

sites, so a distribution of Brønsted site structures will exist if aluminum is substituted randomly for silicon. Theoretical studies suggest that several crystallographic sites are preferentially substituted, and electrostatics preclude substitution of aluminum in adjacent sites. Temperature-programmed desorption and calorimetric studies of amine titrations show that the acid strengths of all of the sites are approximately equivalent in strength. The framework Si/Al ratio in HZSM-5 is typically 20 or much greater, and the acid−base reaction of any of these isolated sites is reasonably independent of reaction at other sites. A variety of NMR experiments are applicable to zeolites even in the absence of reactants.[6,7] ^{29}Si and ^{27}Al magic-angle spinning (MAS) NMR is a routine method of zeolite characterization, and ^{1}H MAS NMR is used to examine Brønsted sites in carefully dehydrated materials.[8] In the case of HZSM-5, ^{1}H spectra obtained at room temperature were previously interpreted to claim that there is only one type of Brønsted site, but using spectra acquired over a range of temperatures and experiments probing dipolar coupling to nearby ^{27}Al, we demonstrated that there are at least two distinct Brønsted environments.[9]

In Situ NMR

NMR has proven to be an exquisite tool for the study of reactions on solid acids. The oscillating magnetic

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(2) Corma, A. *Chem. Rev.* **1995**, *95*, 559−614.
(3) van Santen, R. A.; Kramer, G. J. *Chem. Rev.* **1995**, *95*, 637−660.
(4) Farneth, W. E.; Gorte, R. J. *Chem. Rev.* **1995**, *95*, 615−635.
(5) Davis, M. E. *Acc. Chem. Res.* **1993**, *26*, 111−115.

(6) *NMR Techniques in Catalysis*, Bell, A., Pines, A., Eds.; Marcel Dekker: New York, 1994.
(7) Fyfe, C. A.; Feng, Y.; Grondey, H.; Kokotailo, G. T.; Gies, H. *Chem. Rev.* **1991**, *91*, 1525−1543.
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(9) Beck, L. W.; White, J. L.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 9657−9661.

field used to elicit an NMR signal penetrates nonconductive matter to a considerable depth. This would normally be anathema to surface selectivity, but the isotope specific nature of an NMR experiment guarantees complete surface selectivity if the chemistry of the system is such that the isotope under study is confined to the surface. ^{13}C MAS NMR has detected intermediates at ca. 0.01 monolayer coverage on a metal oxide with a surface area of less than 10 m^2/g.[10] Zeolites have much higher surface areas, and up to 500 m^2 of surface is detected with complete selectivity for a typical 0.5 g sample. *Thus, the sensitivity of surface NMR experiments on real catalysts under reaction conditions may exceed that of UHV surface science measurements on model catalysts with unrealistic conditions!*

Yannoni and co-workers achieved early success with low-temperature MAS.[11,12] We found that routine operation over a wide range of temperatures required the solution of a number of material constraints, and reliable temperature measurement required the development of solid state chemical shift thermometers.[13] By 1987 we could routinely carry out MAS studies on chemical systems at temperatures between 77 and 473 K (later 623 K). A collaboration with the Lunsford group gave preliminary results on the complex mixture of intermediates and products that form when propene-2-^{13}C is adsorbed on the solid acid zeolite HY at room temperature.[14] We imagined an experiment in which one of the three ^{13}C isotopomers of propene was adsorbed onto zeolite at cryogenic temperature. The sample would then be sealed in an MAS rotor and transferred to the probe without warming. Acquisition of ^{13}C MAS spectra as the temperature was incrementally raised would track the fate of the label through intermediates and products, and three identical experiments with the different ^{13}C isotopomers would give a detailed reaction mechanism for oligomerization and skeletal isomerization. We imagined that we would see the isopropyl cation as the first species in such a study. However, the ^{13}C spectrum of the isopropyl cation on a solid acid was not measured until 1995, and then not on a zeolite. In 1989 we published experimental evidence that simple carbenium ions were not stable within the zeolite channels.[15]

Figure 2 shows one of our current sample preparation devices[16] for low-temperature in situ NMR experiments, a great improvement over our original design.[15] A thin layer of catalyst is supported on a glass trapdoor, and the device is evacuated. A furnace is clamped in place, and the catalyst is heated to remove water and convert the ammonium zeolite to the acidic hydrogen zeolite. After removing the furnace, the catalyst is cooled with a cryogen bath, and a controlled amount of adsorbate is introduced from the vacuum line. The trapdoor is raised, the loaded catalyst falls
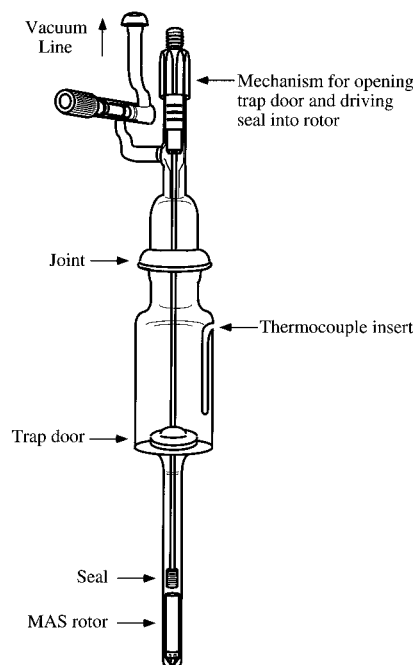

Figure 2. Line drawing of a CAVERN device used for preparing samples of solid acids and reactants for in situ NMR study. A shallow bed of solid acid is spread over the trap door, and the device is assembled and attached to the vacuum line. After evacuating and heating to generate the active form of the acid, cryogen is brought up to the level of the catalyst and a controlled amount of reactant is adsorbed. Rotation of the shaft first raises the trap door, dropping the sample into the MAS rotor, and then drives the seal into place.
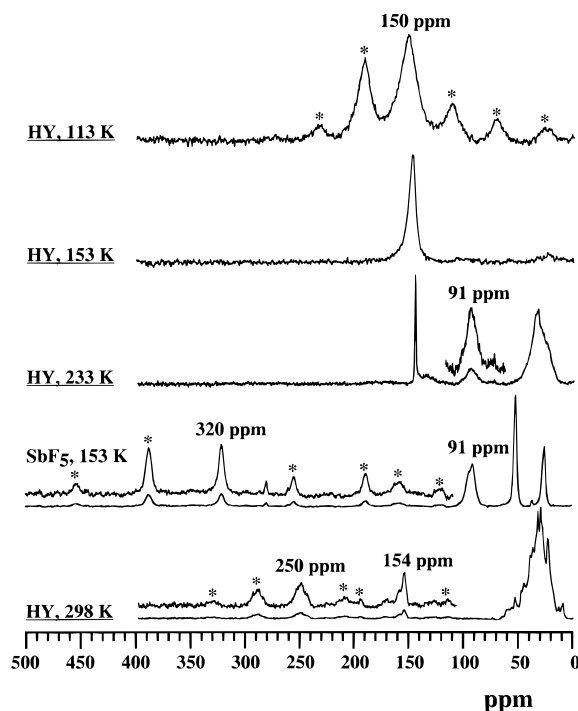

Figure 3. ^{13}C MAS NMR spectra from in situ studies of propene-2-^{13}C on zeolite HY and 2-bromopropane-2-^{13}C on SbF$_5$. The text describes the reaction chemistry and dynamics.

(10) Kheir, A. A.; Howard, T.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 10839−10840.

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into the MAS rotor, and the seal is driven into place. Finally the cold, sealed rotor is manually transferred into the cold MAS probe.

Carbenium Ions in Zeolites. Figure 3 reports recent ^{13}C MAS spectra of propene-2-^{13}C on zeolite HY that both reproduce and expand upon our 1989 report. At 113 K, the adsorbed propene is a π complex on the

Brønsted site (**1**). The static nature of this complex is apparent from the spinning sideband pattern due to the appreciable orientation dependence of the chemical shift. Numerical analysis of the side band intensities yields the three principal components of the ^{13}C chemical shift tensor: $\delta_{11} = 214$ ppm, $\delta_{22} = 188$ ppm, and $\delta_{33} = 49$ ppm. The average of these quantities is the isotropic chemical shift, 150 ppm, which is 17 ppm downfield of propene in solution! Even at 113 K, the π complex undergoes reversible dissociation on the millisecond time scale as reflected in the exchange contribution to the line widths. At 153 K the exchange life time is much shorter than the MAS rotational period (333 μs), and there is a single resonance that narrows with further increase in temperature but remains downfield of the solution chemical shift. Upon raising the temperature to 233 K, propene is protonated to form not a free isopropyl cation but rather the framework alkoxyl species **2**, which has an isotropic ^{13}C shift of 91 ppm. The alkoxyl species may be a strong alkylating agent, but it is very different from a free secondary carbenium ion. It is important to note that the oligomerization of propene at low temperatures initially proceeds without scrambling of the ^{13}C label from the 2-position to the methyl carbons.
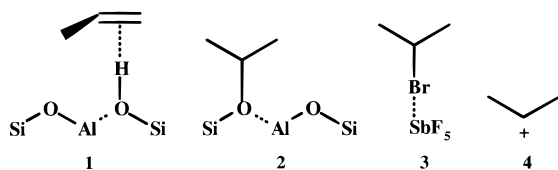

It is instructive to contrast propene on the solid Brønsted acid HY with 2-bromopropane-2-^{13}C on the very strong solid Lewis acid, frozen SbF_5. The first species formed is the donor–acceptor complex **3**, which (somewhat coincidentally) has the same isotropic ^{13}C shift (91 ppm) as the framework alkoxyl species. Indeed, the framework alkoxyl species can also be regarded as a donor–acceptor complex formed in lieu of a carbenium ion. In sharp contrast to propene on the zeolite, 2-bromopropane on SbF_5 yields the isopropyl cation **4**, which is assigned unambiguously by its large isotropic chemical shift of 320 ppm (identical to the magic acid solution value), its huge chemical shift anisotropy, and its response to spectral editing experiments. Furthermore, ^{13}C label scrambling readily occurs in the free cation at low temperature as demonstrated by the methyl signal of **4** at 52 ppm. This is a characteristic reaction of **4** in superacid solution; it is believed to occur through a transient, protonated cyclopropane intermediate. *This low-temperature scrambling reaction does not occur for propene on zeolites, proving that **4** is not in equilibrium with the π complex **1** or alkoxyl species **2** in the zeolite!*

The absence of NMR signals consistent with the isopropyl cation on zeolites in no way implies that NMR is incapable of detecting such species; carbenium ions do indeed form at higher temperatures and loadings of propene, but these are not simple carbenium ions acting as intermediates in olefin oligomerization. The alkyl-substituted cyclopentenyl cations **5** are well known in solution acid chemistry; their acid strength is equivalent to ca. 35% sulfuric acid, and they are obtained in appreciable yield from their diene

Scheme 1
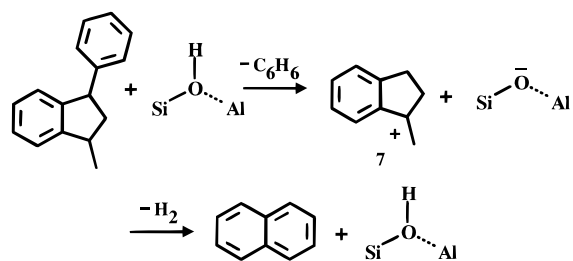
precursors in weak acids.[17] The formation of cyclopentenyl cations from the reaction of olefins in acid solutions is part of the process of "conjunct polymerization" described by Herman Pines.[18] This process could be a previously unsuspected mechanism of zeolite deactivation that operates by exchanging protons for stable carbenium ions like **5**. We have recently reported the rational synthesis of cyclopentenyl cations in zeolites from cyclic precursors.[19]
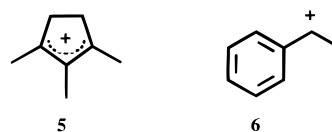
The 1989 propene study concluded that since "no simple secondary or tertiary carbenium ions were detected by NMR, the role of the zeolite framework in stabilizing alkoxyl intermediates should be considered".[15] A number of different alkoxyl species have been characterized on acidic zeolites including studies of the *tert*-butyl alkoxyl[20,21] and a species derived from acetylene.[22] In an early example of the application of theoretical approaches to reactions on solid acids, Kazansky predicted that ethylene would not protonate to make the ethyl cation, but instead a framework alkoxyl.[23] Similar species also form from the reactions of alkyl halides on metal-exchanged zeolites as demonstrated by the papers of Murray[24,25] and Bosácek.[26] The experimental and theoretical evidence for alkoxyl formation was an early sign that zeolites are not superacids like magic acid and that the zeolite framework is important for stabilizing electrophilic intermediates.

Although the cyclopentenyl cations demonstrate that some carbenium ions can form as *products* in zeolites, their roles as *intermediates*, if any, are in secondary reactions such as the formation of aromatics. Scheme 1 shows an example of a free carbenium ion as a persistent free intermediate in a zeolite-catalyzed reaction. This is the only case of which we are aware of this being demonstrated by direct spec-

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(24) Murray, D. K.; Chang, J.-W.; Haw, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 4731−4741.

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(26) Bosácek, V. *J. Phys. Chem.* **1993**, *97*, 10732−10737.

troscopic characterization.[27] Styrene-α-^{13}C was adsorbed onto HZSM-5 at low temperature. Progressive heating to 373 K cracked the styrene dimers on the zeolite to form an appreciable amount of the methylindanyl cation **7**. Evidence for this assignment includes the isotropic shift of 251 ppm for this well-characterized solution species as well as the appreciable chemical shift anisotropy and nonzero asymmetry parameter.

Further heating of **7** on the zeolite converted the carbenium ion intermediate quantitatively to naphthalene. Although Scheme 1 demonstrates intermediacy of a carbenium ion, the indanyl cations are again exceptional species, well known in the early history of solution carbenium ion chemistry.[28] As with cation **5**, the five-membered ring of **7** and other indanyl cations maximizes resonance stabilization, and although one might naively expect **7** to be no more stable than the dimethylphenylcarbenium ion **8**, the former is observed in 78% sulfuric acid while the latter required 30% oleum (SO₃/H₂SO₄).[29] Adsorption of α-methylstyrene onto HZSM-5 did not yield a detectable amount of **8**. While the very stable methylindanyl cation is clearly a persistent intermediate in the above reaction, the styryl cation **6** was not observed. The NMR experiment by itself does not preclude a *transient* styryl cation, but if a resonance-stabilized secondary cation will not persist in a zeolite, how can we believe mechanisms that require far less stable primary cations?
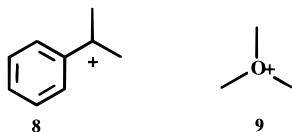
Reactions of Oxygenates in Zeolites. A number of other electrophilic species which are formally heteroatom-substituted carbenium ions or analogs of carbenium ions have been observed through in situ NMR studies of the reactions of organic precursors containing oxygen or other chalcoginides. When an excess of dimethyl ether is adsorbed on HZSM-5, some of it disproportionates on an acid site to make the trimethyloxonium ion **9** and a stoichiometric quantity of methanol.[30] The analogous trimethylsulfonium and trimethylselenonium ions are more stable in zeolites, which was explained in terms of hard−soft acid−base theory. The observation of both the ^{13}C and ^{77}Se resonances of the trimethylselenonium ion at their characteristic solution shifts was indisputable evidence of onium ion formation in zeolites.[31]

We carried out detailed studies of aldol reactions in zeolites beginning with the early 1993 report of the synthesis of crotonaldehyde from acetaldehyde in HZSM-5[32] and continuing through investigations of acetone,[33] cyclopentanone,[33] and propanal.[34] The ex-

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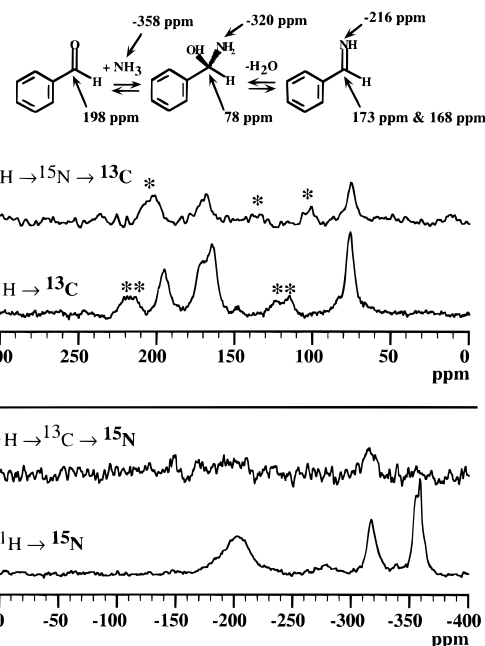
Figure 4. ^{13}C and ^{15}N MAS spectra of benzaldehyde-α-^{13}C reacting with ammonia-^{15}N in zeolite HY to form an imine by way of a tetrahedral intermediate. Spectral editing by means of "double cross polarization" affords unambiguous assignment of the intermediate's spectra. The imine ^{15}N has a short $T_{1\rho}$ and is absent from the ^{1}H → ^{13}C → ^{15}N spectrum.

perience of in situ NMR studies of cyclopentanone on various zeolites was used to design a multigram synthesis of the dimeric α,β-unsaturated ketone. The formation of mesityl oxide **10**, from the dimerization of acetone followed by the dehydration of diacetone alcohol, was a fortunate occurrence, because Farcasiu had recently proposed the use of the ^{13}C shifts of this molecule as a measure of liquid acid strength. Farcasiu made exacting measurements of the ^{13}C shifts in various concentrations of H₂SO₄, HClO₄, and other solution acids.[35] In solution, the ^{13}C shifts of **10** reflect the protonation equilibrium and the contributions of the resonance structures for the protonated ketone **11**. In the acidic zeolites, acetone-2-^{13}C exhibits a downfield shift (that is, not nearly as large as that seen in 100% H₂SO₄ solution), and **10** gives shifts that can be interpreted with Farcasiu's solution measurements to suggest that HZSM-5 has an effect on mesityl oxide that is similar to the effect of ca. 70% H₂SO₄.
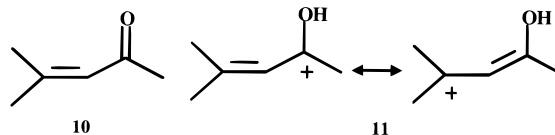
The primacy of the carbonyl group in organic synthesis is also reflected in its facile transformation in zeolites. Benzaldehyde reacts with ammonia in zeolite HY to form a surprisingly stable *gem*-aminohydroxy tetrahedral intermediate which dehydrates upon mild heating to form the imine.[36] Figure 4 shows ^{1}H → ^{13}C and ^{1}H → ^{15}N cross polarization, and ^{1}H →

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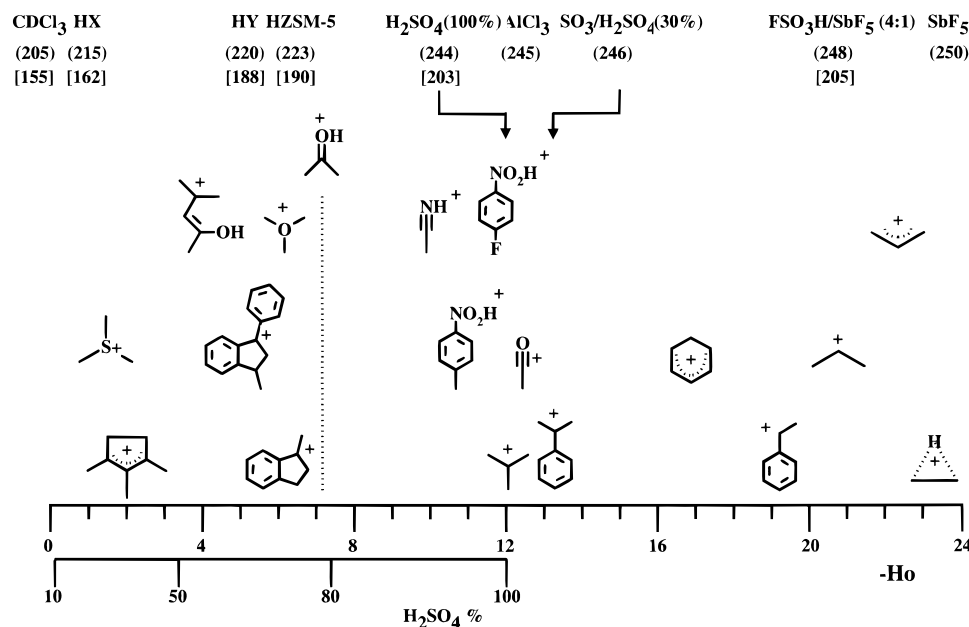
Figure 5. A summary of the work thus far on carbenium ions, related electrophilic species, and protonated weak bases on various solid acids. The position of each species reflects its acid strength and is somewhat speculative for poorly characterized species such as the ethyl cation. The chemical shifts of acetone-2-^{13}C (in parentheses) and mesityl oxide-β-^{13}C (in square brackets) are suggestive of the ordering of acid strength based on our observations of solvent-free materials. The dashed line is the limit of acid strength for Brønsted sites in zeolites. Anyone wishing to move this line significantly to the right would need to demonstrate, for example, a persistent *tert*-butyl cation in a zeolite. Approximate Hammett acidity and percent H_2SO_4 scales are shown to facilitate analogy with solution chemistry. Their application to solid acids is not rigorous.

$^{15}N \rightarrow {}^{13}C$ and $^1H \rightarrow {}^{13}C \rightarrow {}^{15}N$ double cross polarization spectra of the intermediate in the zeolite. With a modest improvement in sensitivity, triple-resonance, 2D HETCOR experiments on reactive intermediates in zeolites will be feasible.

True Solid Superacids. By 1994 we had accumulated a lot of observations about the strength of zeolite solid acids. Some of the more compelling evidence was the *negative observation* of carbenium ions such as **4** and **8** on zeolites, despite their persistence in liquid superacids at low temperature. This resulted in objections that in situ NMR experiments are somehow incapable of detecting carbenium ions on solid acids. Furthermore, misinterpretation of the spectroscopic results by some researchers led to claims of stable carbenium ions in zeolites that have never been observed in superacid solution!

In order to strengthen the evidence that simple carbenium ions cannot persist on zeolite solid acids, it was necessary to carry out otherwise identical in situ NMR experiments on true solid superacids, and demonstrate NMR detection of such cations. Yannoni had done this previously in frozen SbF_5,[37,38] but this excellent work is overlooked by the catalyst community because frozen SbF_5 is not a familiar material. Synthetic chemistry provided our answer. The Friedel−Crafts alkylation and acylation reactions, first reported in 1877, are among the most important in chemistry.[39,40] These reactions proceed on a variety of Lewis acid catalysts; the most familiar is $AlCl_3$, but other metal halides are sometimes more active or

selective. Using devices similar to that in Figure 2 and procedures identical to the zeolite studies, we immediately observed simple carbenium ions on metal halide solid acids.[41] The acylium ion **12** forms quantitatively when acetyl chloride is adsorbed on $AlCl_3$ powder, and the *tert*-butyl cation **13** is indefinitely persistent on $AlBr_3$ at and slightly above room temperature, as it is in magic acid. Acetone forms donor−acceptor complexes **14** on metal halide powders. More elaborate salt systems including hydrogen halides adsorbed on metal halides and supported metal halides have Brønsted or combined Brønsted−Lewis strengths that exceed those of typical zeolites.
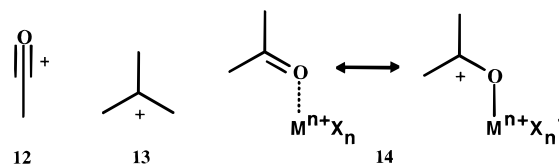
Solid Acid Strength. The Message of the Carbenium Ions

When viewed in total, the positive and negative evidence for the production of stable carbenium ions on zeolites and other solid acids presents a striking picture of the true acid strength of these catalysts. Figure 5 organizes the results reviewed above and other important measurements through the summer of 1995 into a ranking of solid acids based on the acid strengths of the carbenium ions and other electrophilic species sustained on those media. This method of ranking is appropriate since the stabilization of transition states with electrophilic character is the object of acid catalysis. Several acidity scales are indicated or implied in this figure. Since pH is not defined for

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solid acids, the Hammett acidity function,[42] H_0, was developed as an extended acidity scale. Hammett acidity is determined by evaluating the extent of protonation of one or more of a series of weak bases.[43] The application of the Hammett formalism or the thermodynamic acidity related to solid acids is not strictly valid. However, it is insightful to determine whether or not a given weak base is protonated on a given solid acid.

The Hammett acidity of 100% sulfuric acid is −12.3, and a superacid is defined as one with a more negative value. Thus, the traditional view of zeolite acidity requires a Hammett acidity greater (more negative) than −12.3. Figure 5 includes three Hammett indicators that readily fit into zeolites, *p*-nitrotoluene ($pK_{BH^+} = -11.4$), *p*-fluoronitrobenzene ($pK_{BH^+} = -12.4$), and *p*-nitroaniline ($pK_{BH^+} = +0.99$). ^{19}F and ^{15}N NMR studies demonstrate that while *p*-nitroaniline is protonated by HZSM-5 and HY, the weaker bases are not.[44] In a similar fashion, NMR and theoretical work have shown that acetonitrile ($pK_{BH^+} = 10.3$) is also not protonated by the zeolites.[45] Also shown is percent H_2SO_4, which is calibrated against the Hammett scale as well as Farcasiu's mesityl oxide scale. Many of the carbenium ions in Figure 5 have had their acid strength determined explicitly, or enough is known about the media in which they form or do not form to hazard an informed guess of their acid strength. The positions of the acidic zeolites HZSM-5 and HY and weakly acidic HX are established on the basis of the relation of their mesityl oxide shifts to those of H_2SO_4.[33] Beneath the symbol for each solid acid is the isotropic shift of acetone-2-^{13}C in that medium. This ordering is reasonably predictive of the success or failure of observing the carbenium ions in the figure.

We do not claim that Figure 5 is the last word on the strength of solid acids, but it organizes a large body of different measurements into a single picture. The zeolites we have studied appear to be no stronger than 80% H_2SO_4, and the dashed line in the figure is the wall we have never crossed by preparing a more strongly acidic electrophilic species at high concentration in a zeolite. This figure clearly demonstrates why a free isopropyl cation is not observed in a zeolite, and why the claim of a stable allyl cation[46] was quickly challenged[47,48] and disproved.[34] The allyl cation has never been prepared in solution, although it has been reported in frozen SbF$_5$.[47] The free ethyl cation has never been prepared in condensed media. High-level *ab initio* calculations show that it is not a classical ion as it is commonly drawn, but rather the C_{2v} structure shown,[49] and it has a three-center, two-

electron bond.[50] While a remarkable number of papers continue to assume primary carbenium ion intermediates in zeolites, the formation of these species in condensed media of any sort remains a great synthetic challenge.

Theoretical and Experimental Approaches Working Together

NMR experiments cannot characterize transition states, and although transient intermediates can sometimes be inferred by label scrambling[51] or measurements of dynamics, NMR evidence of their detailed structure is necessarily weak. In addition, while NMR is a powerful technique for determination of the structures of persistent species, its weakness is that chemical shift spectra cannot be directly "inverted" to yield unique structures. Rather, they must be interpreted, and one's skill at interpretation is challenged by the spectra of exotic surface species.

To move beyond the limits of experiment alone, we have recently coupled our experimental work with theoretical calculations.[44,52] We found the synergy between the two approaches greatly increases the range of problems we can treat, the amount of information we can obtain about any given solid acid, and the confidence we have in the interpretation of results. In particular, theoretical quantum chemistry alleviates the problems in structural interpretation discussed above by providing a direct link between structure and spectra.

In practice, we generally approach a problem in the following manner: we first use NMR experiments to obtain a qualitative model of a catalytic process. Since theoretical calculations require an atomic level description of the system under study, we must construct a reasonable model of the active site, often using a variety of experimental evidence to suggest geometry and stoichiometry, and then hypothesize reaction pathways. We perform calculations on the model system, and calculate any data that can be reliably obtained by suitable experiments, typically interatomic distances, chemical shift tensors, vibrational frequencies, and reaction barriers. Agreement between the values of a variety of data, determined by both theoretical and experimental means, provides powerful verification of our interpretation of the catalytic process. Further theoretical calculations can then be done to obtain information that experiment cannot provide, such as the structure of transition states, and to suggest how modification of the structure may change its properties.

The comparison between theoretical and experimental results must consider the physical aspects of the system under study. Experiments typically measure the behavior of a huge number of molecules at particular temperatures and pressures over some length of time. In contrast, quantum mechanical methods are typically limited to static calculations of one or a few molecules with some approximation of temperature effects. In addition, we must consider whether the theoretical method adequately represents

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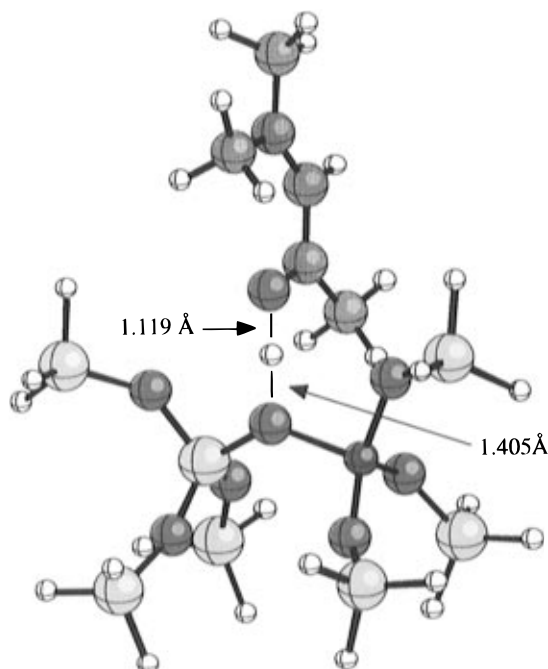
Figure 6. Optimized geometry (BLYP/DNP) for mesityl oxide interacting with a model of HZSM-5.

the dominant interactions within the system. For chemisorption studies in zeolites, cluster models of appropriate size have been used to elucidate a wide range of zeolite chemistry.[53-55] In some cases, long-range electrostatic interactions may need to be included in the Hamiltonian, and recent advances in methodology make the full periodic treatment of crystalline catalytic systems possible.[56]

There are also many considerations that critically affect the *intrinsic* accuracy of a quantum mechanical calculation, the most obvious of which are the degree to which the atomic coordinates of the theoretical model relate to the experimentally observed compound, the flexibility of the basis set, and the extent to which electron correlation is accounted for.[50] Since charge separation is important in many chemisorption processes, large basis sets treating polarization and incorporating diffuse functions are often required. In addition, electron correlation is critical for the treatment of transition state structures, hydrogen bonding, and proton transfer reactions. The perturbation theory of Møller and Plesset is the most straightforward way of improving a Hartree–Fock calculation; such treatments truncated at second order (MP2) usually provide much of the correlation effect at a reasonable computational cost.

As an alternate means of including electron correlation, density functional theory (DFT) methods have been demonstrated to give results comparable to high-level post-Hartree–Fock calculations with considerably less computational cost.[57-59] Recent studies have validated the DFT approach in the computation of
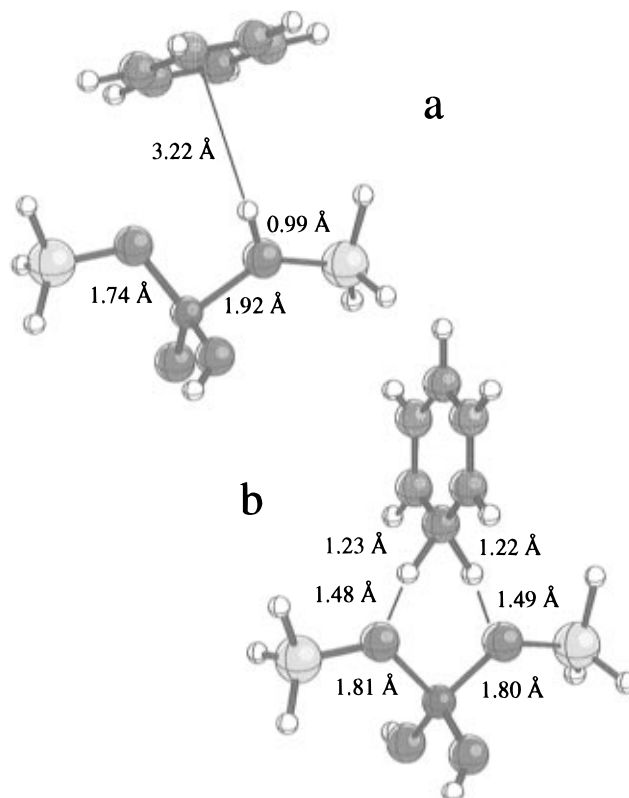

Figure 7. Optimized DFT structures of benzene on a zeolite cluster calculated using DFT at the BLYP/DNP level: (a) π complex; (b) transition state for H/D exchange.

geometries, vibrational frequencies, energetics, and other molecular properties. More important to catalytic applications, DFT has also been shown to give good results for reaction barriers and transition state geometries in proton transfer reactions.[60]

Figure 6 demonstrates the application of DFT to calculation of the equilibrium conformation of mesityl oxide in an acidic zeolite. The calculated (BLYP/DNP) deprotonation energy of this cluster is 280 kcal/mol, close to the experimental proton affinity[61] of 284 for the most acidic protons in zeolite HZSM-5. For comparison, the calculated deprotonation energies of acetone and mesityl oxide are 198.8 and 217.3 kcal/mol, respectively. A close inspection of Figure 1 reveals that when the zeolite Brønsted site complexes with acetone, the proton remains bonded to the bridging oxygen, although the bond is slightly elongated. In the case of the zeolite complex with mesityl oxide (Figure 6), the proton is more fully transferred to the base molecule.

In order for us to directly relate theoretical structures and experimental NMR spectra, we must obtain theoretical NMR spectra. Such calculations are now possible using a variety of methods.[62-65] Recently, Gauss presented the GIAO-MBPT(2) NMR equations,[66] allowing the assessment of the effect of elec-

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tron correlation on shieldings—a very significant contribution for carbenium ions and molecules with multiple bonds.[67] Chemical shift calculations are fundamentally changing the practice of interpreting NMR spectra of reactive intermediates and other controversial species, and such calculations should be attempted whenever an accurate model is available. Also, the emergence of a large body of reliable chemical shift tensors (as opposed to isotropic shifts alone), obtained by experiment and calculation, is a fundamental advance in the practice of correlating structures and spectra.[68]

Theoretical chemistry is also essential for the characterization of transition states. In 1992 we reported in situ NMR observation of H/D exchange for benzene-d_6 on zeolite HZSM-5.[69] We have since refined these measurements and performed careful rate measurements on various zeolites over a range of temperatures and also obtained preliminary measurements for substituted benzenes. In Figure 7 we show the calculated π complex and transition state for the H/D exchange reaction on a model of zeolite Y.[52] Although the transition state resembles a benzenonium cation, the charge on C_6H_7 is only 0.56 |e|. In addition, the bond lengths between the exchanging hydrons and the carbon are $\sim$0.1 Å longer than in a free benzenonium cation. More importantly, the transition state collapses to the π complex with no barrier; thus, no stable benzenonium is involved. The energy barrier for H/D exchange, taken as the difference in total energy between the π complex and transition state geometries, is within the error bars for the experimental reaction barrier on zeolite Y. The synergy between experiment and theory is also apparent in the work of Kramer and van Santen, who have shown that CH_5^+ is not the intermediate in H/D exchange of methane on zeolites.[70,71] Rather, there is a carbonium ion-like *transition state* stabilized by the zeolite framework by interaction with two oxygens. One oxygen donates a proton as the other removes one, and the difference in proton affinity between these adjacent oxygens contributes to the rate of the reaction.

Conclusions

We have described direct characterization of the reaction mechanisms of organic molecules on solid acids. Just as solution state NMR was central to progress in solution acid—base chemistry, solid state NMR is a powerful method for the direct study of solid reaction media and mechanism. Moreover, the effectiveness of our in situ spectroscopy is greatly enhanced by the integration of theoretical calculations into the design and interpretation of experiments.

A physical organic chemistry of zeolites and other solid acids is now being developed. This new science benefits considerably from previous work in solution media, but we have shown that analogies between solution and solid acid catalysis must be made with caution, and must carefully consider the unique properties of solid acids. In particular, traditional views of acid catalysis overestimate the strength of zeolite acids, assume carbenium and carbonium ion mechanisms that require superacids, and ignore the role of the framework in stabilizing transition states. Zeolites are not superacids; they are smart and subtle acids that find shortcuts past high-energy intermediates and the even higher energy transition states that must lead to them.

The work described here has primarily been curiosity driven, but it has practical application. The rational design of improved solid acid catalysts is an important objective, and rational design presupposes knowledge of reaction mechanisms.

AR950105K

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