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Density Functional Theoretical and NMR Study of Hammett Bases in Acidic Zeolites

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The quantification of the strength of solid acids is a long-standing problem that has most frequently been attempted using the Hammett acidity function, H_0.[1,2] In principle, the H_0 of an acid is given by

$$H_0 = \mathrm{p}K_{\mathrm{BH}^+} - \log\{[\mathrm{BH}^+]/[\mathrm{B}]\}$$

requiring a measurement of the degree of protonation of a weak base with conjugate acid strength H_{BH^+} adsorbed on the solid. Accurate spectrophotometric determination of $[\mathrm{BH}^+]$ and [B] in microporous media is problematic, and many reports are based on visual observation of color changes. Furthermore, the equation is overly simplistic; for example, it does not explicitly treat complex formation between the conjugate acid and conjugate base. We demonstrate here that theoretical calculations using density functional theory (DFT) accurately model proton transfer reactions between Brønsted sites in zeolites (the archetypal solid acids) and Hammett bases. The validity of the theoretical results is verified by NMR measurements of key nuclei of the same Hammett bases in zeolites HZSM-5 (MFI) and HY (FAU), the first such experiments.

The Hammett indicators selected for the theoretical and NMR studies were *p*-fluoronitrobenzene ($H_{\mathrm{BH}^+} = -12.4$), *p*-fluoroaniline ($H_{\mathrm{BH}^+}$ = ca. +2.4), *p*-nitrotoluene ($H_{\mathrm{BH}^+} = -11.4$), and *p*-nitroaniline ($H_{\mathrm{BH}^+} = +0.99$). The matched pairs of indicators have similar structures, but their H_0 values are above and below the zeolite acid strengths (≈ -7) we estimated in our recent studies of mesityl oxide[3] and carbenium ions[4] in zeolites. The use of two pairs of indicators allows us to investigate protonation by both ^{19}F and ^{15}N NMR. All of the indicators chosen are compact enough to easily reach the Brønsted sites in zeolites HZSM-5 and HY.

Similar to other theoretical studies of proton transfer reactions in zeolites,[5] our study modeled the adsorption of Hammett bases on a cluster taken from the HZSM-5 (MFI) crystal structure[6] and performed the calculations with the DFT program Dmol[7] using both the SVWN[8] and BLYP[9,10] exchange-correlation functionals and a double numerical polarized (DNP) basis set.[11] Our zeolite model has a calculated proton affinity of 280 kcal/mol, close to the experimental value[12] of 284 for the most acidic protons in zeolite HZSM-5. All optimizations allowed full relaxation except that the terminal silyl groups of the zeolite model were held fixed. The results shown here were obtained at the higher BLYP/DNP level, although the SVWN/DNP results were similar. For brevity, Figure 1 shows only the results for the fluorine-containing bases, but the results obtained for other pair of bases were essentially identical. In Figure 1a we show the optimized geometry for *p*-fluoronitrobenzene adsorbed on the zeolite model. To bias the calculations against the experimental results, we started the optimization with the protonated indicator at hydrogen-bonding distance from the deprotonated zeolite. The optimized configuration shows very clearly that the proton was transferred back to the zeolite, and both the zeolite and the bases are perturbed little by the hydrogen-bonding interactions. The charge on the F is only $0.006|e|$ less than the value in the isolated neutral molecule, the C−F bond is only 0.005 Å longer, the O−H bond of the bridging hydroxyl group on the zeolite is only 0.021 Å longer, and the bridging hydrogen is 1.88 Å away from the nearest adsorbate oxygen. In contrast, the optimized geometries of the aniline derivatives clearly show proton transfer to the amino group, but even so, completely free ions are not the result. The multidentate coordination of the aniline derivatives with the zeolite (Figure 1b) agrees with previous calculations of ammonia adsorption.[13]

Suitable quantum chemical calculations can be performed on structures like those in Figure 1 to predict spectroscopic observables and thus provide a check of the agreement between theory and experiment. Predictions of the ^{19}F chemical shifts were obtained using the GAIO method[14] as implemented in Turbomole.[15,16] NMR calculations were done at the RHF/6-31G* level[17] using the DFT optimized geometries. Our experience with this level of theory is that it generally provides reasonable agreement with experiment for neutral molecules but can overestimate shift changes due to protonation to form carbenium ions and related species. For the isolated neutral *p*-fluoronitrobenzene, we obtain a theoretical ^{19}F chemical shift of −97.6 ppm. For the adsorbate in the complex (Figure 1a), the shift is −95.0 ppm, and for the isolated protonated base, the calculated shift is −44.2 ppm.

^{15}N or ^{19}F NMR spectra of the four indicators were determined in solvents including either 25% "Magic Acid" $\mathrm{FSO_3H/SbF_5}$, $H_0 = -16$, or strong mineral acid. The four indicators were individually adsorbed into zeolites HY and HZSM-5 at loadings no higher than 0.25 equivs and typically much lower. Representative ^{19}F MAS spectra are collected in Figure 2, and Figure 3 reports the corresponding ^{15}N MAS spectra. Solution shifts are transcribed onto these figures as markers. Figures 2 and 3 show no protonation of the weakly basic indicators and extensive protonation of the more strongly basic anilines. No protonation of *p*-nitrotoluene was seen, even at 473 K. These experiments directly prove that the zeolites studied are not

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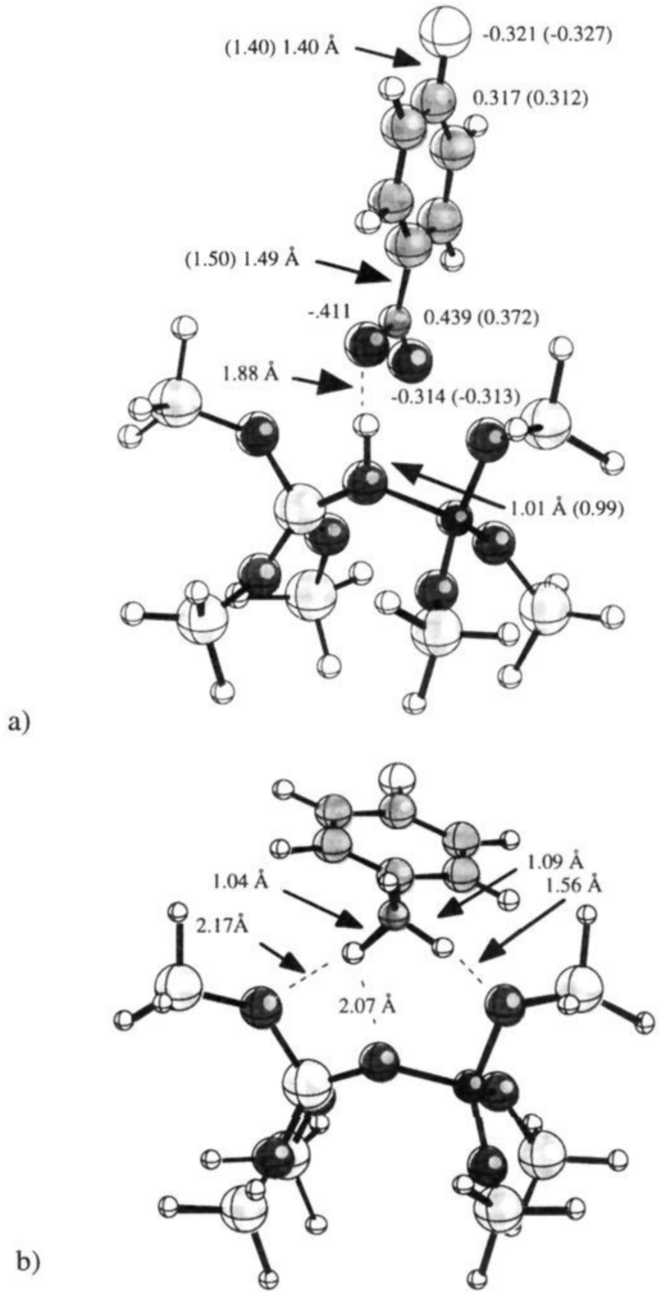

Figure 1. Representative theoretical results. (a) Selected internal coordinates and partial charges for *p*-fluoronitrobenzene adsorbed on the zeolite model. *p*-Fluoronitrobenzene is weakly hydrogen bonded to the zeolite, but not protonated. Values in parentheses are those of an isolated, neutral *p*-fluoronitrobenzene molecule. (b) Optimized geometry for *p*-fluoroaniline adsorbed onto the zeolite. In this case we started with the proton on the zeolite; the optimization resulted in protonation of the adsorbate.

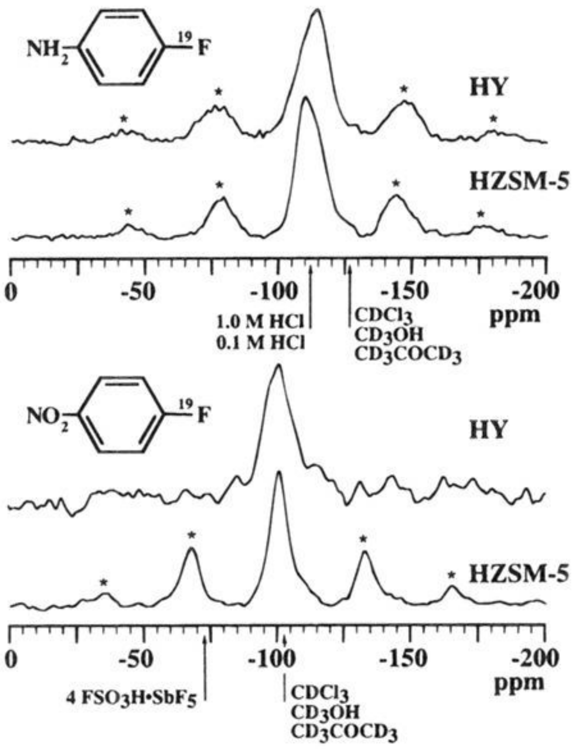

Figure 2. Representative 188-MHz ^{19}F NMR spectra of *p*-fluoroaniline (top) and *p*-fluoronitrobenzene (bottom) obtained in zeolites HY and HZSM-5. Spinning sidebands are denoted by asterisks (*). Spectra were acquired (several thousand scans) using magic angle spinning (4-mm rotors), cross polarization (2 ms), and proton dipolar decoupling.

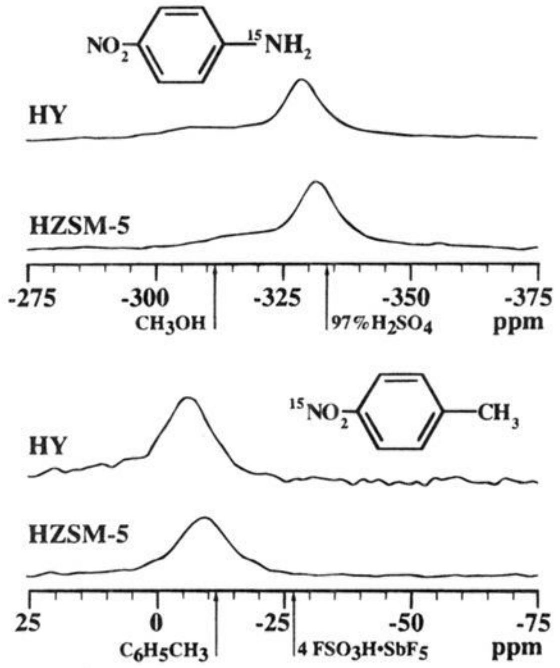

Figure 3. Representative 36-MHz ^{15}N NMR spectra of *p*-nitroaniline-$^{15}NH_2$ (top) and *p*-nitrotoluene-^{15}N (bottom) obtained in zeolites HY and HZSM-5. The spectra of the adsorbates showed no obvious temperature dependence over a wide range; those shown here were obtained at 298 K. Spectra were acquired (1024 scans) with cross polarization (2 ms), magic angle spinning (7.5-mm rotors), and proton dipolar decoupling.

Hammett superacids ($-H_0 > 12.3$). This conclusion is consistent with other recent NMR work on stable carbenium ions,[4] oxonium ions,[18] and other probes in zeolites including methanol,[3,19] but the experimental work reported here is definitive.

The accuracy of the predictions of the DFT calculations for the HZSM-5 zeolite model suggests that they may be extended to other zeolite cluster models, including those which have not yet been realized experimentally and hence are not available for NMR study. One synthetic objective is to prepare new zeolites with greater Si−O−Al bond angles in the hope[5a,20,21] that such might have greater acid strength, even possibly superacidity. We optimized the adsorbate−zeolite complexes with this angle constrained to larger values; to our surprise, the SVWN/DNP calculations resulted in the proton being transferred from *p*-fluoronitrobenzene back to the zeolite, even if the Si−O−Al angle was held fixed at 180°. Further tests at higher levels of theory are in progress.

This investigation used a choice of indicators that necessarily resulted in wide limits on zeolite acid strength, but the theoretical and experimental methodologies have been established. Ongoing calculations will seek to refine these results by considering larger clusters, further geometry relaxation, and explicit inclusion of long-range electrostatic interactions, which have been found to be important in some cases.[14] We will also use our experimental−theoretical approach to measure the strength of other solid acids.

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