

Communication

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between an Alkane and Zeolite Active Sites**

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## Identification of an Adsorption Complex between an Alkane and Zeolite Active Sites

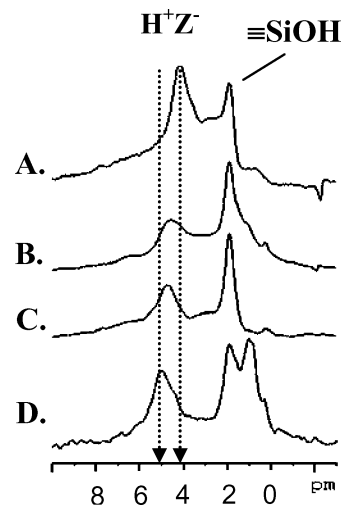
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Mechanistic steps for the initiation and conversion of saturated hydrocarbons over solid acids are ambiguous relative to analogous reactions involving alkenes or oxygenates.<sup>1,2</sup> Currently, carbenium ion chemistry catalyzed by trace olefinic impurities is considered the most probable route to alkane initiation via hydride transfer, since it is believed that zeolites lack sufficient acid strength to directly protonate an alkane and form a pentavalent carbonium ion.<sup>3</sup> However, a sufficient number of recent publications still propose this direct protonation step.<sup>4,5</sup> Alternatively, trace amounts of Lewis acid sites, possibly associated with nonframework aluminum atoms or clusters, can facilitate hydride abstraction from an alkane, thereby generating a reactive carbenium ion.<sup>6,7</sup> Given recent key discoveries regarding cocatalytic roles played by trace amounts of “impurities” and residual organic species in heterogeneous catalysis of oxygenates, it is clear that a molecular-level experimental understanding is needed to identify the most probable route for alkane initiation and reaction in solid acids.<sup>8–10</sup> As a particular example, the synthesis of clean-burning alkylate fuels (branched hydrocarbons) from isobutane, using heterogeneous catalytic processes, has not been realized due in part to these fundamental mechanistic questions.<sup>11,12</sup> Consequently, as a part of our larger interests in alkylate synthesis, we have sought to identify routes to alkane initiation by direct spectroscopic observation of reactive catalytic systems.

Figure 1 shows *in situ* <sup>1</sup>H magic-angle spinning (MAS) spectra of zeolite HZSM-5 obtained at 298 K following the low-temperature adsorption (at 77 K using the CAVERN method)<sup>13</sup> of isobutane-*d*<sub>10</sub>. The Brønsted acid site chemical shift, which is 4.2 ppm in the pure zeolite, shifts downfield to 5.1 ppm upon adsorption of ≥1 equiv of isobutane (Figure 1D), with fractional shifts for fractional loadings of isobutane. As has previously been demonstrated, perturbations in the local electronic environment of the Brønsted acid site resulting from quantitative molecular titration experiments indicate the formation of an adsorption complex.<sup>14</sup> The results in Figure 1 have been reproduced tens of times (see Table of Contents Graphic for another example), using both deuterated and hydrogenated isobutane, and are suggestive of one of two possibilities: (1) the isobutane interacts specifically with the Brønsted acid site, or (2) isobutane contains trace amounts of olefinic species, which preferentially adsorb due to specific interactions between the active site and the π electrons of the olefin. While the magnitude of the observed shift in Figure 1D suggests the latter case, the fact that the entire acid peak shifts is consistent with complete stoichiometric coverage of each acid site afforded by the isobutane loadings of ≥1 equiv (no further shift was observed at 2 or 3 equiv loadings). Moreover, the loading-dependent results at <1 equiv are an even stronger indicator of a specific complex (and not simple physical adsorption), since complete saturation of the zeolite void volume at high loadings might be expected to lead to susceptibility perturbations of the Brønsted proton shift, even in the absence of an energetically favored adsorption complex. The observed downfield shift is consistent with what has previously been observed for hydrogen-bonded complexes in zeolites, i.e., a weakening of

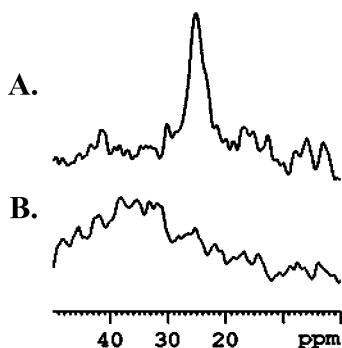


**Figure 1.** Comparison of Brønsted acid site peak chemical shift in (A) neat, dehydrated and activated HZSM-5 vs HZSM-5 with (B) 0.25 equiv of isobutane-*d*<sub>10</sub>, (C) 0.5 equiv of isobutane-*d*<sub>10</sub>, and (D) 1 equiv of isobutane-*d*<sub>10</sub>. The peak at 0.9 ppm, particularly visible in D, is protonated isobutane (methyl signal) resulting from H/D exchange with the acid site H<sup>+</sup>Z<sup>-</sup>. In D, note the reduced Brønsted acid site intensity and the loss of the broad downfield shoulder seen in A, following the small amount of H/D exchange. The Brønsted acid site concentration was 0.50 mmol/g of catalyst. 300 MHz <sup>1</sup>H spectra were acquired at 298 K using a spin-echo with 32 scans, 10 s recycle delay, and 65 kHz rf field strength.

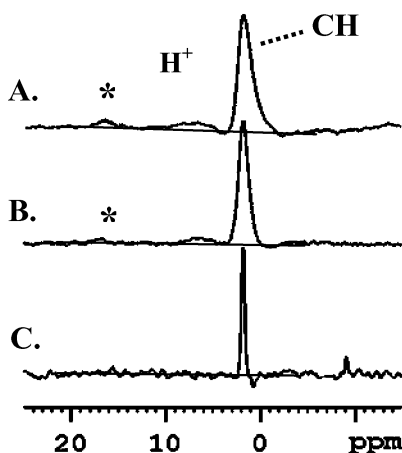
the Brønsted acid site O–H bond due to formation of the adsorption complex.<sup>14</sup> A resolved two-peak slow-exchange spectrum was not achieved at 200 K, the lowest temperature currently accessible in our probe. In addition, contributions from susceptibility anisotropy are also important, but less so for the tetrahedral isobutane molecule relative to linear molecules previously reported.<sup>14</sup> Finally, we note that the ca. 1.0 ppm shift in Figure 1D is the largest shift reported following adsorption of a saturated alkane on an active zeolite.

Intermolecular polarization transfer via static dipole–dipole couplings indicates that the involved species are proximate. Figure 2 shows the results of a *natural abundance* <sup>1</sup>H → <sup>13</sup>C CP/MAS experiment following adsorption of 1 equiv of isobutane-*d*<sub>10</sub> on HZSM-5. The only source of <sup>1</sup>H magnetization for the isobutane carbons is the Brønsted acid site, since a direct <sup>1</sup>H excitation control experiment (collected *after* the data in Figure 2) confirmed that no H/D exchange had occurred between the perdeuterated isobutane and the zeolite. No isobutane <sup>13</sup>C signal is observed in the absence of the <sup>1</sup>H excitation pulse in the cross-polarization sequence. These data are consistent with the formation of an adsorption complex. Again, the overall sensitivity is reduced due to the fact that the isobutane loading is very low (25 μmol), is at natural abundance, and that polarization transfer is not completely efficient at 210 K.

To unequivocally prove that the isobutane <sup>13</sup>C signals in Figure 2 arise exclusively from the Brønsted acid site proton, reverse CP/MAS (<sup>13</sup>C → <sup>1</sup>H) experiments on similar samples were completed. However, in contrast to the sample used in Figure 2, the isobutane



**Figure 2.** Results from in situ CP/MAS experiment at 210 K following low-temperature CAVERN adsorption of 1 equiv of isobutane- $d_{10}$  on (A) HZSM-5 and (B) dehydrated silica. The observed (natural abundance)  $^{13}\text{C}$  signal at 25 ppm in A is due to polarization transfer from the Brønsted acid site proton to the isobutane carbons. A  $^1\text{H}$  MAS control experiment (not shown) on the sample in A showed no isobutane proton signal, which might result from H/D exchange. In A and B, 4000 scans were acquired using a 5 s recycle delay, 1 ms cross-polarization time, and 4.2 kHz spinning.



**Figure 3.** Spectra from in situ reverse ( $^{13}\text{C} \rightarrow ^1\text{H}$ ) CP/MAS experiment following CAVERN adsorption of 1 equiv of labeled  $^{13}\text{CH}(\text{CH}_3)_3$  on HZSM-5, obtained at (A) 220 K; (B) same sample as in A, obtained at 298 K; (C) 220 K spectrum following a sample preparation similar to that of A, except replacing the HZSM-5 with dehydrated silica gel. Note the intensity in the shaded region from ca. 4–7 ppm in A and B, which is absent in C, and which was absent in control experiments lacking either a  $^{13}\text{C}$   $\pi/2$  excitation or spin-lock pulse. For A and B, 400 scans were obtained, while 1000 scans were used in C. Asterisks denote spinning sidebands (4.2 kHz), and the baselines are drawn as guides to the eye. The peak labeled CH, at 1.7 ppm, is the methine hydrogen of isobutane.

was  $^{13}\text{C}$ -labeled at the methine carbon to improve sensitivity. Figures 3A and 3B show that  $^1\text{H}$  signal intensity is observed in the Brønsted acid site region following polarization transfer, with the expected reduction in signal intensity relative to the direct excitation results in Figure 1. The fact that the observed signal is broad (4–7 ppm region) in 3A is not inconsistent with what is known about acid sites in ZSM-5, since a second signal at 5–7 ppm has been previously observed and assigned as an acid site.<sup>15,16</sup> A more intense acid signal would be expected at lower temperatures.<sup>14</sup> No signal is observed in this region when the  $^{13}\text{C}$  excitation pulse is removed from the cross-polarization sequence (not shown) or when isobutane is adsorbed on dehydrated silica gel (Figure 3c). While the 1.7 ppm shift for the isobutane CH signal is near the 2.0 ppm shift for the nonacidic hydroxyl groups, expansion and deconvolution of the CH peaks in Figure 3, and 3C in particular, show no hint of polarization transfer to this nonacidic Si–OH proton. We note that the static dipolar coupling between the labeled methine carbon and the surface Brønsted sites is stronger than the intramolecular interaction with

methyl groups, since little  $\text{CH}_3$  proton signal (in the 1 ppm region) is observed in Figure 3.

From the data in Figures 1–3, we have the following evidence that isobutane does not simply undergo physical adsorption with the zeolite but rather forms a specific adsorption complex with the Brønsted acid site proton: (1) Loading-dependent chemical shift changes are observed for the Brønsted acid site proton, which reach a maximum at 1 equiv loading of isobutane. (2) The shifts are independent of whether deuterated or protiated isobutane is adsorbed. (3) No Si–OH  $^1\text{H}$  signals were observed in Figures 3A and 3B. Further, since the concentration of Si–OH hydroxyl groups used for the control experiments in Figures 2B and 3C exceeds by a factor of 2 the Brønsted acid site concentration in the zeolites, if simple physical adsorption at any hydroxyl site occurred, signals should have been observed in Figures 2B and 3C.

Sommer and co-workers have shown that H/D exchange takes place between isobutane and HZSM-5, and in their work, the exchange required temperatures significantly greater than room temperature.<sup>17</sup> While we have observed H/D exchange in situ at room temperature for our ZSM-5 catalysts (complete results not shown, but see Figure 1D), we believe that the adsorption complex detected here is the route by which isobutane C–H bonds are activated. Whether or not this adsorption complex enables complete proton transfer to form a carbenium ion and hydrogen via an isobutonium cation is not clear, but it does show the propensity of isobutane to associate with an electropositive species like the acid site or such as might occur in the concerted reaction between a carbenium ion derived from protonation of an olefin by the Brønsted site. Subsequent hydride transfer from isobutane would then incorporate isobutane into the catalytic cycle. However, we have preliminary data that shows that H/D exchange between isobutane and the surface takes place at temperatures slightly below 298 K for low coverages (<1 equiv), suggesting a direct reaction between isobutane and the Brønsted site. The fact that the conversion of isobutane to alkylates (branched hydrocarbons) occurs with highest efficiency and lifetime on catalysts with very high Brønsted acid site densities is consistent with the activation of isobutane molecules via the specific adsorption complex described here.<sup>11,18</sup>

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