

## Alkane C–H Bond Activation in Zeolites: Evidence for Direct Protium Exchange

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**Abstract:** The mechanism of alkane C–H bond activation in heterogeneous acid catalysis is unknown. <sup>1</sup>H solid-state NMR techniques have been used to simultaneously detect the reactivity of both catalyst and alkane reactant protons in a true in-situ experimental design. Specifically, the activation of isobutane C–H bonds by the solid acid zeolite HZSM-5 is directly observed, and the rate of proton transfer between the solid catalyst surface and gaseous isobutane is quantitatively measured using isotopic <sup>1</sup>H/<sup>2</sup>H exchange methods. An observable adsorption complex forms between the isobutane and the primary Bronsted acid site of ZSM-5, which leads to proton exchange between the zeolite surface and the isobutane methyl groups at temperatures (273 K) much lower than previously reported. The secondary acid site in ZSM-5 is less accessible to or less reactive with the isobutane molecule. Simultaneous detection of protium loss from the Bronsted acid site and protium gain by perdeuterated isobutane reveals a common rate constant equal to 4.1–4.6 × 10<sup>-4</sup> s<sup>-1</sup> at 298 K, but at lower temperatures, the transition between this and a much slower rate process is resolved. The measured activation energy for isobutane H/D exchange is 57 kJ/mol. In all experiments, the isobutane reagent was purified to eliminate any unsaturated impurities that might serve as initiators for carbenium-ion mechanisms, and the active catalyst was free of any organic contaminants that might serve as a source of unsaturated initiators. In total, our results are consistent with direct proton exchange between the zeolite surface and the methyl groups of isobutane.

### Introduction

Thermal and heterogeneous catalytic transformations of organic molecules form the cornerstone of the modern petrochemical industry. Even in chemistries whose commercial successes are obvious, the parallel intellectual advances are often noticeably absent. For example, the ability to catalytically convert methanol to hydrocarbons predated the understanding of the operative mechanism by 25 years; it was not until the independent works of Kolboe at Oslo, White and Xu at ExxonMobil, and Haw at the University of Southern California that the importance of “hybrid” catalytic mechanisms in zeolites was discovered in 2000.<sup>1–3</sup> As a result of the new mechanistic information regarding the cocatalytic role of occluded aromatics in methanol-to-olefin chemistry, improved commercial processes were developed.<sup>4</sup> Similarly, the commercial isomerization and alkylation of simple alkanes to useful classes of branched alkanes via heterogeneous methods has preceded a mechanistic understanding of even the most basic reactions steps, notably those involving the activation of C–H bonds by solid acids and hydrogen transfer, by several decades. Stated simply, how does a solid acid catalyst, for example, a zeolite, initiate C–H bond

activation of a completely saturated alkane? Currently, carbenium ion chemistry catalyzed by trace olefinic impurities is considered the most probable route to alkane initiation via hydride transfer, because it is believed that zeolites lack sufficient acid strength to directly protonate an alkane and form a transient pentavalent carbonium ion.<sup>5</sup> However, a sufficient number of recent publications propose this direct protonation step.<sup>6,7</sup> Alternatively, trace amounts of Lewis acid sites, possibly associated with nonframework or terminating aluminum atoms or clusters, may facilitate hydride abstraction from an alkane, thereby generating a reactive carbenium ion.<sup>8,9</sup>

Spectroscopic methods that detect H/D exchange in catalytic systems are obvious tools for elucidating key reaction steps involving hydrogen transfer. Recently, several authors have reported the use of “in-situ” <sup>1</sup>H MAS solids NMR methods to study H/D exchange during the reaction of alkanes with acidic solid catalysts.<sup>10–13</sup> However, in all previously published cases,

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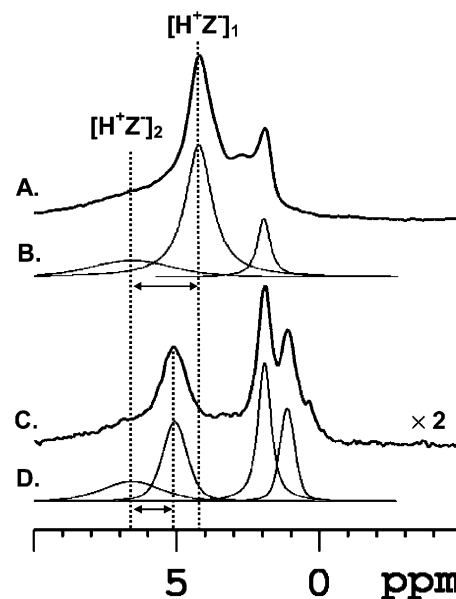
signals were only obtained for the reagent, and not the catalyst. In other words, the fate of the active site in the catalyst was never directly observed, and, in some cases, the system was only analyzed after reaction.<sup>11–13</sup> As we demonstrated many years ago, a true in-situ H/D exchange method must simultaneously detect the fate of both catalyst and reagent during the reaction, not off-line following an extent of reaction.<sup>14</sup> Our recent report of the first detection of a specific adsorption complex between an alkane and the zeolite acid site demonstrates that this distinction is more than a semantic detail.<sup>15</sup> In this contribution, we use a combination of spectroscopic and reactor methods to (1) show that the two types of acid sites known to exist within ZSM-5 have different accessibility/reactivity with isobutane; (2) observe H/D exchange between isobutane and an active zeolite in a true in-situ manner (even at temperatures well below ambient); (3) determine the relevant kinetics for H/D exchange by comparison of both catalyst and isobutane signals; and (4) propose a likely route for C–H bond activation in solid acids involving direct protium exchange between the alkane and the Bronsted acid site.

### Experimental Section

Silica and ZSM-5 (Si:Al = 15) samples were obtained from Grace-Davidson and Zeolyst, respectively. Isobutane (99% purity) was obtained from Aldrich, Inc., isobutane-*d*<sub>10</sub> (99.1% D) was obtained from CDN Isotopes, and isobutane-2-<sup>13</sup>C (99% <sup>13</sup>C) was obtained from Icon Isotopes. Purity of the gaseous samples was verified by GC analysis with a HP 5890 GC (flame ionization detection). Samples free from unsaturated contamination were obtained by treating the as received reagents with D<sub>2</sub> (99.8% D – Isotec) over a supported 0.5% Pt/alumina catalyst obtained from Alfa Aesar. These “cleaned” samples were analyzed by GC to verify the removal of unsaturated impurities.

Calcined and dehydrated zeolite samples were prepared from the ammonium form in a stainless steel reactor body using a gradual, stepwise dry-air calcination up to a final temperature of 450 °C. Samples were sealed under positive pressure and immediately placed in the glovebox to avoid exposure to moisture. Dehydrated silica samples were prepared by using a stepwise temperature increase while maintaining a vacuum of 10<sup>−3</sup> Torr. Complete calcination and dehydration of samples was verified by <sup>1</sup>H NMR prior to any alkane adsorption (Figure 1).

Gas adsorptions were carried out using a CAVERN type apparatus; 7-mm MAS zirconium oxide rotors were loaded with 50–55 mg of the catalyst of interest and placed into the apparatus under dry argon.<sup>16</sup> The assembled apparatus was placed on a vacuum line and evacuated to a pressure of 10<sup>−3</sup> Torr. Stoichiometric samples were prepared by adsorbing one isobutane molecule per Bronsted acid site (1 equivalent = 1 equiv). Exact absorption amounts were determined using a quantitative catalyst acid site density method previously described by us.<sup>17</sup> In addition to the Kel-F spinning cap, a grooved Kel-F plunger/plug was used to seal the rotors, preventing moisture contamination and loss of adsorbate during low temperature experiments. Samples were immediately removed from the vacuum line and placed in the pre-chilled NMR probe to prevent reaction prior to spectral acquisition, in a manner similar to that previously described by Haw.<sup>18</sup>



**Figure 1.** (a) <sup>1</sup>H MAS spectra at 298 K for neat, dehydrated HZSM-5; (b) deconvoluted components from least-squares fit of (a); (c) same as (a), following adsorption of 1 equiv of isobutane-*d*<sub>10</sub> at 298 K; (d) deconvoluted components from least-squares fit of (c). Individual peak assignments, and shift changes (dashed lines/arrows), are discussed in the text. The small peak at 0.5 ppm is a background signal from the probe.

MAS NMR data were collected on a Bruker DSX 300 MHz spectrometer; spinning rates varied from ca. 4–8 kHz. <sup>1</sup>H spectra were obtained using a Carr-Purcell spin-synchronized echo pulse sequence using a wait time,  $\tau$ , equal to one period of the rotor. Recycle delays were 10 s for all <sup>1</sup>H experiments. <sup>13</sup>C spectra were obtained via two methods: a Bloch decay sequence of a simple  $\pi/2$  pulse and acquisition with <sup>1</sup>H decoupling, and MAS cross polarization methods.<sup>19</sup> <sup>1</sup>H spin–lattice relaxation times were measured using saturation-recovery experiments.

Catalytic reactor data were acquired using a home-built pulsed dual-detector microreactor, employing both a thermal conductivity detector (TCD) and an HP 5890 GC with a flame-ionization detector. Catalyst was loaded into a stainless steel reactor body and calcined by maintaining the sample at 450 °C for 12 h while flowing helium through the catalyst. Isobutane conversion data for this plug-flow reactor system were acquired both at 150 and 450 °C. Samples of the product effluent were collected using pneumatically controlled sampling loops (Valco) and analyzed offline.

### Results and Discussion

#### Differential Acid Site Activity/Accessibility in HZSM-5.

Figure 1 shows comparative <sup>1</sup>H MAS spectra for active HZSM-5 catalyst in the absence and presence of 1 equiv of isobutane-*d*<sub>10</sub>. Specifically, Figure 1a and b shows the experimental spectrum for neat catalyst and its deconvoluted fit, respectively, while Figure 1c/d presents the same data for the isobutane/HZSM-5 sample. The unreactive terminal silanol peak at 2 ppm (SiOH) provides a convenient point of reference, in that its position and amplitude do not change, consistent with its well-known nonreactive properties in solid acid catalysis. As we have previously reported, the Bronsted acid site peak at 4.1 ppm (Figure 1b [H<sup>+</sup>Z<sup>−</sup>]<sub>1</sub>) shifts downfield to 5.1 ppm upon adsorption of 1 equiv of isobutane or perdeuterated isobutane; this result, which we previously showed was indicative of an adsorption complex at the acid site, is reproduced in Figure 1c using

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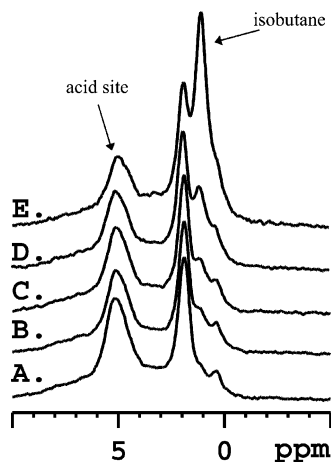
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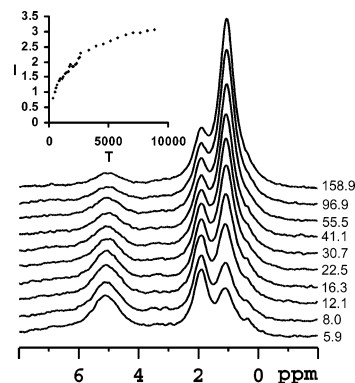
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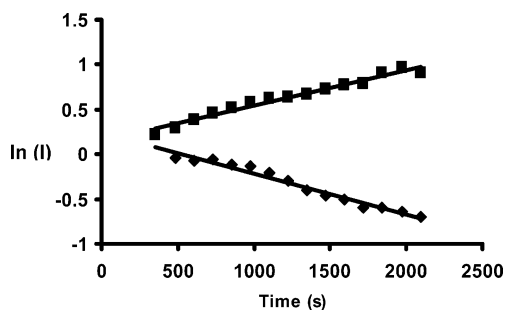
**Figure 2.**  $^1\text{H}$  MAS spectra following adsorption of 1 equiv of isobutane- $d_{10}$ , collected at (a) 230 K, 2 min after adsorption; (b) 270 K, 75 min after adsorption and showing the onset of H/D exchange; (c) 273 K, 85 min after adsorption; (d) 273 K, 135 min after adsorption; and (e) 298 K, 175 min after adsorption. The small peak at 0.5 ppm is a background signal from the probe.

isobutane- $d_{10}$ . The new peak at 1.1 ppm is from the isobutane  $\text{CH}_3$  groups, which have undergone some H/D exchange with the acid site. Comparing the deconvoluted components in Figure 1b to those in d reveals a subtle but important detail. While the ca. 1 ppm downfield shift of the 4.1 ppm Bronsted acid site proton is obvious upon alkane introduction, the second acid peak at 6.6 ppm appears to be unaffected by adsorption of the isobutane. We follow the previously published assignment of Beck et al., in which the peak at 6.6 ppm (appearing as the broad downfield shoulder in the experimental spectra in Figure 1a/1c; denoted  $[\text{H}^+\text{Z}^-]_2$ ) is assigned to a second type of proton acid site.<sup>20</sup> Subsequent work by Freude et al. confirmed this assignment.<sup>21</sup> Based on the extensive variable temperature work performed by one of us on this same catalyst, and the double-resonance experiments of Beck and co-workers, the deconvoluted peak position of 6.6 ppm at room temperature for this second proton acid site is accurate. In Figure 1b, the two acid site signals are separated by more than 2.5 ppm, versus only 1.5 ppm in Figure 1d. While this second acid peak at 6.6 ppm appears by all published methods to be an acidic proton associated with a proximate Al atom, Figure 1b versus d shows that it is either inaccessible to small molecule reactants or is significantly less reactive on the time scale of our experiment.

**In-Situ Solid–Gas H/D Exchange.** Previous reports of H/D exchange between alkanes and zeolites have been conducted at elevated temperature under conditions that potentially limit important kinetic information. Figure 1c demonstrates that we are able to observe resolved signals for both the isobutane adsorbate and the zeolite active site in our experiments. In this way, the onset of alkane reactivity through C–H bond activation in the H/D exchange process can be experimentally observed via simultaneous assessment of both acid site and isobutane peak areas. Figure 2 shows that the onset of H/D exchange between isobutane and the Bronsted acid site occurs below room temperature (273 K), in contrast to previous reports.<sup>11,12</sup> However, the exchange rate increases significantly when the temperature is increased to 298 K (d vs e). On the basis of the results of Figure 2, we chose 298 K for kinetic evaluation of



**Figure 3.** Series of selected in-situ  $^1\text{H}$  MAS spectra acquired at 298 K following adsorption of isobutane- $d_{10}$ , in which H/D exchange between the Bronsted acid site at 5.1 ppm and the isobutane  $\text{CD}_3$  groups at 1.2 ppm is apparent. The time (in minutes) following adsorption is shown to the right of each spectrum. The top left inset shows the raw data for the  $\text{CH}_3$  peak.



**Figure 4.** Semilogarithmic plot of peak area versus time for the spectra acquired at 298 K, taken at the (■) 1.1 ppm isobutane peak and (◆) 5.1 ppm acid site peak. The exchange rate constants equal  $4.1 \times 10^{-4}$  and  $-4.6 \times 10^{-4} \text{ s}^{-1}$  for the isobutane (■) and acid (◆) signals, respectively. The decaying acid site peak is plotted as  $y = \ln[I(t)/I_0]$ , while the rising isobutane peak is plotted as  $y = -\ln[1 - I(t)/I_\infty]$ .

the H/D exchange process, as the rate was fast enough to obtain a sufficiently large number of data points in a reasonable amount of time, thereby ensuring good fitting statistics.

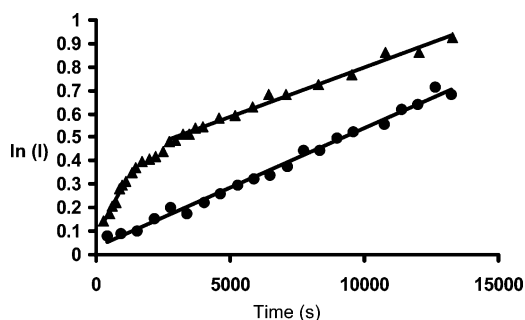
Figure 3 shows 10 selected spectra from a total of 75 acquired at 298 K, following adsorption of 1 equiv of isobutane- $d_{10}$  on HZSM-5. The first and last spectra shown in Figure 3 correspond to the actual first and last data points in time; clearly, some H/D exchange has taken place during the 6 min required to collect the first spectrum following isobutane adsorption (consistent with the separate experimental data in Figure 2), as indicated by the isobutane  $\text{CH}_3$  intensity at 1.1 ppm.

In agreement with previous reports, we do not observe H/D exchange involving the isobutane CH group, which would lead to a signal at 1.8 ppm.<sup>11</sup> Quantitative initial rate analyses of the first 14 points of the 75 total that were collected are shown in Figure 4, in which both the acid site and the isobutane peak areas are plotted versus time.

At 298 K, the absolute exchange rate constants as measured from either the 5.1 ppm acid site or 1.1 ppm  $\text{CH}_3$  signal are equal within error, at  $4.6$  and  $4.1 \times 10^{-4} \text{ s}^{-1}$ , respectively. Figure 4 is the first data showing that the rate of proton transfer is the same for an alkane reagent and the zeolite acid site in a process involving C–H bond activation. Some exchange has already occurred by the time the first data point is collected, and the regression lines do not extrapolate to zero. However, as suggested previously by Figure 2, the exchange rate is much

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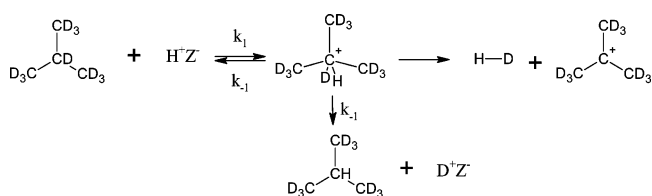


**Figure 5.** Rate plot for the H/D exchange experiment between isobutane- $d_{10}$  and HZSM-5 at 273 K (●) and 285 K (▲), extracted from the isobutane  $\text{CH}_3$  signal in real time. The single-exponential process at 273 K has a rate constant of  $5.0 \times 10^{-5} \text{ s}^{-1}$ . At 285 K, the initial rate constant equals  $2.2 \times 10^{-4} \text{ s}^{-1}$ , while the second component observed at longer times equals  $4.2 \times 10^{-5} \text{ s}^{-1}$ . Linear regression results are shown.

lower at 273 K, and analysis of similar experimental data acquired at that temperature did result in a zero intercept as shown in Figure 5. Indeed, Figure 5 indicates that the exchange process is more complicated than the single rate in the room-temperature data of Figure 4. Comparison of the 273 and 285 K data in Figure 5 shows that, in addition to the zero-intercept behavior captured at the lowest temperature, a second process with a larger rate becomes operative at 285 K (for clarity, only the  $\text{CH}_3$  peak intensities are shown). Clearly, the 285 K data are characterized by two components: a large initial rate equal to  $2.2 \times 10^{-4}$ , and a lower long-time component equal to  $4.2 \times 10^{-5}$ . The quadrupling of the initial rate constants from 273 to 285 K indicates a change in the operative protium exchange pathway; comparison of the initial rates at 273 K shows that it is equal, within error, to the long-time rate constant at 285 K (ca.  $4\text{--}5 \times 10^{-5} \text{ s}^{-1}$ ). Comparison of the 285 K initial rate to that obtained at 298 K (Figure 4) shows the expected doubling at  $2.0 \times 10^{-4}$  and  $4.1 \times 10^{-4} \text{ s}^{-1}$ , respectively. Finally, the long-time rate constant at 285 K in Figure 5, equal to  $4.2 \times 10^{-5} \text{ s}^{-1}$ , increases by slightly more than a factor of 2 when the temperature is raised to 298 K (to  $9.0 \times 10^{-5} \text{ s}^{-1}$ ; data not shown). Again, this is expected for the ca.  $10^\circ\text{C}$  change in temperature if there is no change in the reaction pathway for H/D exchange between the active site and isobutane.

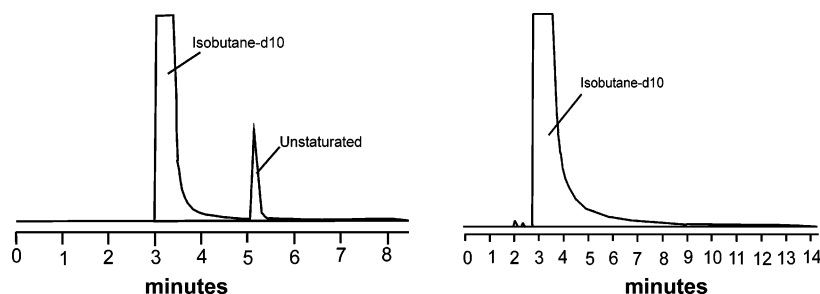
**Alkane C–H Bond Activation by Defect or Contaminant Catalysis.** The possible role of trace amounts of unsaturated impurities, for example, olefins or aromatics, has been considered. The isobutane- $d_{10}$  used in the experiments described above was hydrogenated by exposure to a supported Pt catalyst in a large overpressure of  $\text{D}_2$ , as described in the Experimental Section. The GC chromatogram on the resulting deuterated

**Scheme 1**



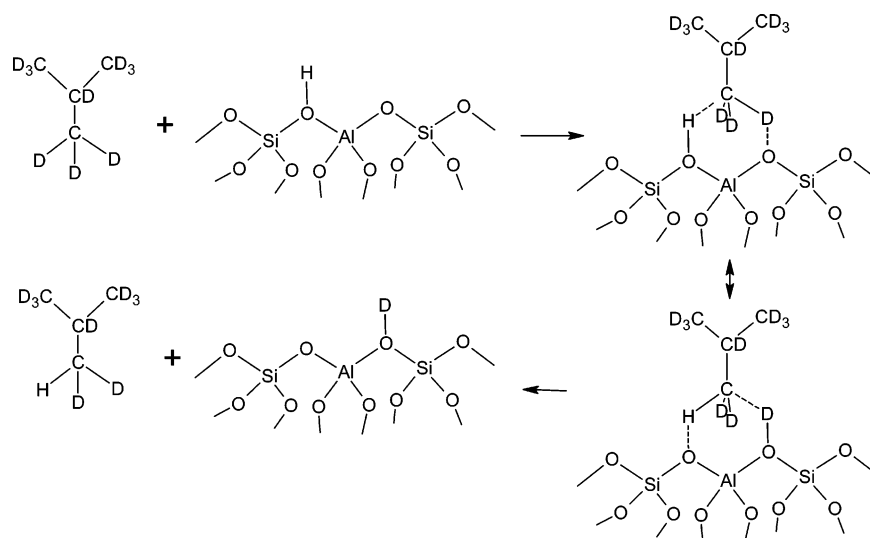
material showed only one peak for isobutane; no other volatile species were detected as shown in Figure 6.

However, total carbon analysis on the calcined ZSM-5 catalyst prior to isobutane exposure (provided by Galbraith Laboratories and based on combustion to form detectable  $\text{CO}_2$  gas) indicated that less than 0.1 wt % carbon was present in the catalyst following preparation. Assuming 0.1 wt % as an upper limit, this corresponds to 1 part per thousand, or 1000 ppm of residual carbon, trapped in the catalyst following calcination. One may assume that at least some of this carbon remains near the Bronsted active site, because the organic template molecule ultimately generates the site. However, if one calculates the number of carbon atoms per acid site for this level of contamination, and recalling that the HZSM-5 used here has at most 1.04 mmol of acid sites per g of catalyst (from Al concentration), the result is 0.08 C/acid site. The smallest reactive unit would require at least two carbons, for example, ethylene, thereby reducing this value to 0.04 molecules/acid site. Clearly, this amount is insufficient to promote stoichiometric isotopic exchange. Moreover, it is unlikely ethylene would survive the calcination process, and an aromatic structure would reduce this number by at least a factor of 6. Even if one further assumes that this residual carbon takes the form of polynuclear aromatics with C/H ratios of one or less, then it is unreasonable to expect that the protons from the catalyst would preferentially exchange with isobutane deuterons in the presence of aromatic molecules. Zeolite protons would simply exchange with the aromatic rings, which are not deuterated, and therefore no loss of Bronsted acid site intensity would be detected in our experiments. Clearly, this is not the case. Stated differently, if the residual carbon left over from calcination serves as an initiation pathway for H/D in a concerted mechanism between isobutane and the acid site, then it must be proximate to the Bronsted site. The presence of a polynuclear aromatic would sterically preclude the isobutane from reacting with the acid proton. Conversely, if the unsaturated species were small enough to allow steric access, for example, a benzene ring or olefinic oligomer, then protium exchange would preferentially involve the lower energy benzene/acid site complex.<sup>14</sup> Finally, there is no evidence of any type of induction period in any of the rate



**Figure 6.** GC data on (a) 99.99% purity isobutane- $d_{10}$  versus (b) the same sample after treatment over a dispersed Pt hydrogenation catalyst and deuterium gas. The isobutane peak is deliberately shown off scale. In (b), the vertical scale is expanded by a factor of 2 relative to (a).

## Scheme 2



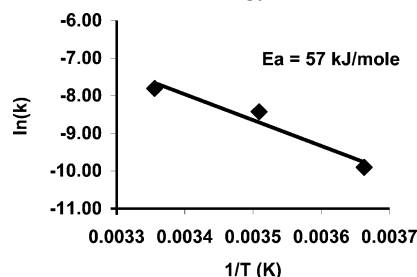
data we have obtained, as would be expected for participation of a “mediating” species. In-situ  $^{13}\text{C}$  NMR experiments on labeled isobutane (in the methine position) showed that no skeletal rearrangement occurred until 150 °C, consistent with the microreactor data. In total, there is no evidence to support a role for unsaturated contaminants in the H/D exchange process between isobutane and the zeolite surface.

**Mechanistic Implications.** The experimental results described above, in which (1) a stoichiometric adsorption complex forms at the active site, (2) no olefinic impurities exist in the reactive system, (3) insufficient amounts of total organic carbon, other than isobutane itself, exist, which could act as a proton/hydride transfer agent, and (4) the agreement of all kinetic data for isotopic exchange indicates that proton transfer/exchange occurs directly between the isobutane reagent and the zeolite active site at the relatively low temperatures where data were obtained. We do not observe any H/D exchange at the isobutane CH position; only  $\text{CH}_3$  groups are involved. This regioselectivity is in agreement with Sommers work.<sup>11,13</sup> Traditional liquid superacid chemistry would anticipate protonation at the CH position, to form a pentavalent carbonium ion, followed by loss of hydrogen to form the more stable tertiary *tert*-butyl carbenium ion. Clearly, this mechanism cannot be operative inside a zeolite, because we would observe some H/D exchange at the CH position due to the equilibrium of the first step, that is, protonation/deprotonation, as shown below in Scheme 1.

Moreover, it is not reasonable to expect a bulky reagent like isobutane to sterically accommodate protonation at the methine position by an inflexible, solid acid catalyst. Indeed, recent calculations show that alkoxy species derived from the protonation of isobutene inside a zeolite cannot form due to steric constraints, but, rather, carbenium ions stabilized by the lattice are formed by protonation of the olefinic  $\text{CH}_2$  group.<sup>24</sup> If the steric barriers are too large for formation of an alkoxy intermediate from isobutene, then a carbonium ion transition state derived from protonation of the isobutane CH carbon is also not expected to occur. One should note that as compared

to other previous publications where H/D exchange is observed for several carbons in an alkane, for example, ref 10b in which propane undergoes H/D exchange at both methylene and methyl positions on HZSM-5, the data we report here are in all cases at least 220 K lower in temperature. Scrambling mechanisms involving skeletal isomerization may be excluded, as we verified that C–C bonds are not broken for isobutane on HZSM-5 at these temperatures using both in-situ  $^{13}\text{C}$  NMR (with  $^{13}\text{C}$ -labeled isobutane in the methine position) and pulsed microreactor experiments. In other words, at high temperatures the first steps in C–H bond activation become difficult to separate from skeletal isomerization contributions. Our true in-situ experiments, at room temperature and below, avoid these complications.

Additional evidence against proposals represented by Scheme 1, and their variants, involves consideration of activation energies. Figure 7 shows the calculated activation energy of 57 kJ/mol obtained from our in-situ experimental data for isobutane H/D exchange on HZSM-5. This value is 4 times less than published theoretical values for an isobutane dehydrogenation step of the type represented by the first step in Scheme 1 (222.6 kJ/mol) or related isobutane oxidation schemes.<sup>26</sup> In addition, published values for olefin protonation by a Bronsted site range from 30 to 45 kJ/mol; such a step would necessarily follow any isobutane dehydrogenation based mechanism.<sup>27,28</sup> Indeed, at the temperatures used in this work, any  $\text{C}_3$  or  $\text{C}_4$  olefin would react too rapidly to follow in situ by the methods employed here.<sup>29,30</sup> Therefore, we must seek an alternative explanation for how the isobutane  $\text{CH}_3$  groups undergo direct isotopic exchange with the zeolite at the low temperatures used in this work, and with an activation energy of 57 kJ/mol.



**Figure 7.** Activation energy for H/D exchange of isobutane on HZSM-5 calculated from the data in Figures 4 and 5.

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Scheme 2 shows one proposed mechanism by which direct, but regiospecific, H/D exchange can occur between isobutane and the catalyst surface, and in the absence of unsaturated proton carriers.

In this mechanism, the adsorption complex involves weak hydrogen bonds between the methyl groups and the immediate zeolite surface surrounding the Bronsted acid site. A resonance-stabilized 5-center/4-electron bond allows formation of a six-membered ring transition state, enabling regiospecific H/D exchange between Bronsted acid sites and the isobutane CH<sub>3</sub> groups. The "partial protonation" at the isobutane methyl carbon position is sterically much less demanding than the classical carbonium ion proton addition at the methine carbon, and we note that calculations show only 2.5 kcal/mol difference in protonation of isobutane, followed by loss of hydrogen versus methane.<sup>5</sup> Because such calculations cannot model the steric and solvation effects associated with the entire zeolite channel segment in which adsorption occurs, either must be considered as possible. Our proposed mechanism is consistent with the emerging discoveries surrounding weak, nonclassical hydrogen bonds,<sup>25</sup> and the solvation contributions from the excess oxygen electron density that exists in the zeolite channels. Currently, we are pursuing detailed calculations of this, and other, reaction pathways that are consistent with the data, using both DFT and SCF/correlated-electron level calculations.

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## Conclusions

The mechanism of saturated alkane activation on solid acid catalysts was investigated by monitoring H/D exchange between a perdeuterated alkane adsorbed on a zeolitic catalyst using <sup>1</sup>H MAS NMR. Exchange was observed well below previously reported temperatures, and kinetic data were obtained for both the reactant peak as well as the product peak. This was possible only as a result of reaction monitoring by true in-situ MAS NMR methods. The kinetic data obtained from both "sides" of the reaction were in close agreement. At lower temperatures, a more complicated rate than the apparent single rate in the room temperature was observed, suggesting a change in the operative mechanism of exchange. The absence of unsaturated impurities in the reagent gas, as well as the absence of necessary quantities of residual carbon in the catalyst, eliminates mechanisms where H/D exchange proceeds via carbenium ion chemistry pathways involving trace contaminants. Our findings suggest a direct protonation pathway via the primary Bronsted acid site. The initiation step occurs at the primary Bronsted site ([H<sup>+</sup>Z<sup>-</sup>]<sub>1</sub>), as supported by (1) the formation of a stoichiometric adsorption complex with this primary site, (2) equal H/D exchange rates from the isobutane and primary acid site, (3) the less reactive nature of the second acidic site ([H<sup>+</sup>Z<sup>-</sup>]<sub>2</sub>) with respect to isobutane, and (4) the lack of any skeletal rearrangement in reactor/GC and in-situ <sup>13</sup>C NMR data. Future work will involve computational chemistry to support a reasonable step-by-step mechanism, particularly with respect to the implications for alkylate synthesis in solid acids.<sup>22,23</sup>

**Acknowledgment.** We thank the American Chemical Society for support of this work through PRF #38293-G5, and North Carolina State University for support through the Faculty Research Professional Development program.

JA0558802