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Zeolite Catalysis: Water Can Dramatically Increase or Suppress Alkane C−H Bond Activation

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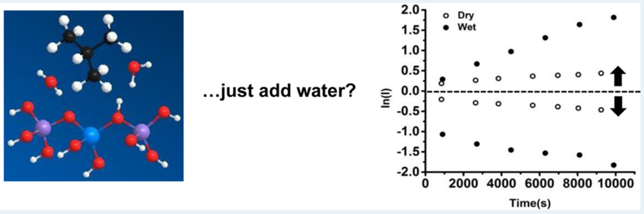
Supporting Information

ABSTRACT: Zeolite-catalyzed alkane C−H bond activation reactions carried out at room temperature, low pressure, and low reagent loadings demonstrate that water can act either to increase or to suppress the observed reaction rates. Isobutane-d_{10} undergoes hydrogen/deuterium exchange with the acidic zeolite HZSM-5 at subambient temperatures, as first reported by us (Truitt et al. *J. Am. Chem. Soc.* **2004**, *126*, 11144 and Truitt et al. *J. Am. Chem. Soc.* **2006**, *128*, 1847). New experiments demonstrate that the C−H bond activation chemistry is very sensitive to the presence of water. Isobutane reaction rate constants increase by an order of magnitude at water loadings in the range of ≤1 water molecule per catalyst active site relative to the dry catalyst. Conversely, water loadings greater than about 1−3 water molecules per active site retard isobutane reaction. In situ solid-state NMR data show that water molecules and isobutane molecules are simultaneously proximate to the catalyst active site. These results indicate that water can be an active participant in reactions involving hydrophobic molecules in solid acid catalysts, possibly via transition state stabilization, as long as the water concentration is essentially stoichiometric. Such conditions exist in well-known catalytic reactions, e.g., methanol-to-hydrocarbon chemistries, since stoichiometric water is a first-formed byproduct.



KEYWORDS: *zeolite, catalysis, water, alkane, bond activation, reactivity*

INTRODUCTION

Heterogeneous catalysis based on acidic zeolites is well-established, with successful implementation of the fundamental science prevalent in commercial industries around the world.[1,2] Industrial zeolite-based catalysis include catalytic cracking, reformulation, isomerization, and alkylation, all of which are usually executed at temperatures exceeding 250 °C.[3,4] Elucidating the steps in reaction mechanisms for many chemistries occurring inside acidic zeolites has been complicated by the historical belief that reactions require high temperatures, where secondary and tertiary reactions can take place on time scales comparable to primary reaction steps. Previously, our group was the first to demonstrate that alkane C−H bond activation can occur at or below room temperature in the acidic zeolite HZSM-5.[5,6] Using low temperature, low pressure, and low reagent loadings coupled with an in situ NMR experimental approach, primary reaction steps in the chemistry may be followed via simultaneous observation of reagent molecules and the acid site in the catalyst. In this contribution, an in situ experimental NMR approach involving the C−H bond activation of a completely nonpolar alkane reveals new information about the role of water in zeolite-based catalysis. Methanol-to-hydrocarbon (MTH) chemistry and the related ethanol-to-hydrocarbon process as well as biomass conversion are two current examples of zeolite-based catalysis where understanding the role of water is critical. The full mechanism of MTH chemistry has been one of the most hotly debated issues in the catalysis literature for the last 40 years, but what cannot be debated is that stoichiometric amounts of water are produced when methanol or ethanol reacts through a primary condensation and dehydration step.[7−12] For example, two methanol molecules condense to form dimethyl ether, releasing a water molecule in close proximity to the zeolite acid site. In essentially all mechanistic proposals, water has simply been ignored as a molecular participant. Some reports describe increased selectivity to some product molecules in MTH chemistries when water is coadded as a feed molecule.[13,14] The beneficial effects are usually attributed to the stronger adsorption of water at the active site, which reduces secondary reactions of the desired hydrocarbon products from taking place. While improved selectivity has been attributed to water in some cases, there have been no publications that indicate that water improves zeolite catalyst activity. To our knowledge, no specific studies have investigated the role that water can play in facilitating this chemistry, and the results described below for the nonpolar alkane isobutane could reveal a more general active role for water and one that could potentially answer some of the questions in MTH's controversial mechanism.

While seemingly unrelated, growing interest in acidic zeolite-based routes to upgrading molecular products from biomass conversion also requires clarification of water's role in the chemistry.[15−18] Biomass conversion generates molecules that

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are highly oxygenated and which may either contain or evolve significant amounts of water. Zeolites are attractive routes for their catalytic upgrading, but traditional vapor phase chemistries pose problems for cellulosic and saccharide-based feedstocks. Recently, Resasco and co-workers have shown that zeolite catalyzed reactions in water is a viable route for conversion of some biomass molecules, based on hydrophobic modifications of zeolite crystallites that prevent their degradation in an aqueous solvent environment.[19,20] They have demonstrated that silylating the external surface of HY zeolites significantly extends their catalytic lifetime for dehydration and alkylation reactions in a hot aqueous solvent environment.

There exists a general perception in the catalysis community that water effectively acts as a poison in zeolite catalysis. That conditions of gas-phase heterogeneous catalysis in the absence of water represent the conventional approach, and that water is considered a potential poison, is discussed in a recent review.[21] A direct quote from this review article reads, "*A difficulty in the use of solid acids is the severe poisoning of the acid sites by water, and in fact, most solid acids lose their catalytic activities in aqueous solutions*". In this contribution, we show that water can *both* enhance and suppress alkane reactivity in zeolites. Specifically, the rate of isobutane C−H bond activation at room temperature can be increased by an order of magnitude in the presence of ca. 1 water molecule per acid site in the catalyst. Increasing the water content to greater than 1−3 water molecules per acid reduces alkane reactivity, with complete suppression occurring at even larger water loadings.

■ EXPERIMENTAL SECTION

Zeolite ZSM-5 (Si:Al = 15) samples were obtained from Zeolyst in the ammonium-exchanged form. Isobutane-d_{10} (99.1% D) was obtained from CDN Isotopes. Calcined and dehydrated zeolite samples were prepared from the ammonium form in a glass reactor body using a gradual, stepwise vacuum calcination up to a final temperature of 550 °C. Relatively dry samples of the type shown below in Figure 1a are reproducibly prepared using pressures of $<10^{-4}$ Torr during the vacuum activation, which was achieved using an Edwards EO4K diffusion pump. Using only a mechanical rotary vane pump during activation, pressures during activation were $9{-}10 \times 10^{-3}$ Torr and resulted in a catalyst which still had noticeable residual moisture, as shown in Figure 1b, and as will be discussed in more detail below. Reference 30 also describes helium flow activation methods for reproducibly preparing dry catalysts. Samples were sealed under positive pressure and immediately placed in a dry argon glovebox. Complete calcination and dehydration of samples was verified by ^{1}H MAS NMR prior to any alkane adsorption (Figure 1). Isobutane 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.[22] The assembled apparatus was placed on a vacuum line and evacuated to a pressure of 5e $^{-4}$ Torr. Stoichiometric samples were prepared by adsorbing a specific number of isobutane molecule per Bronsted acid site (e.g., 1 equiv = 1 eqv refers to one molecule per acid site). Adsorption amounts were calculated based on a quantitative catalyst acid site density method previously described by us,[23] which yielded 0.6 mmol/g of acid site density for our dry catalysts, and which was supported by equilibrium exchange peak intensity ratios based on loadings corresponding to that acid site density (see Figure S1 in the Supporting Information). A representative spin-counting result is shown in Figure S2 of the Supporting Information. However, with increasing amounts of water present, the ability to accurately determine the acid site density via the spin-counting method is compromised due to proton exchange with the water (see below). Thus, for convenience, we report loadings relative to the theoretical maximum acid density assuming one acid site per Al, which for the Si/Al = 15 catalyst used here equates to 1.0 mmol/g. 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 experiments. The pressure in the sealed rotor, which would contain the dry catalyst and the isobutane reagent for the isotopic exchange experiments, was typically 0.1 atm or less. In specific cases, as described in the text, the rotor was deliberately opened for controlled periods of time to expose the catalyst to water in the air.

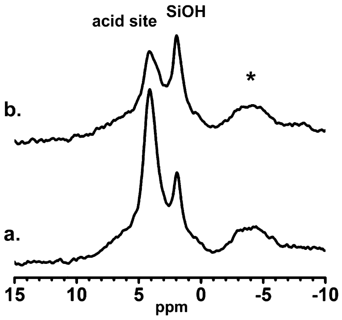

Figure 1. ^{1}H MAS NMR spectra of identically prepared Si/Al = 15 HZSM-5 catalysts, in which an apparent loss of Bronsted acid site intensity at 4.2 ppm is observed in (b) versus (a). The broad signal denoted by * is a constant-area background signal from the probe. The spectra were obtained at 5 kHz MAS speeds.

^{1}H MAS (magic-angle spinning) NMR data were collected on a Bruker DSX 300 MHz spectrometer, with spinning rates varying from ca. 5−6 kHz. ^{1}H spectra were obtained using a Carr-Purcell spin-synchronized echo pulse sequence using an echo time (τ) equal to one period of the rotor. Recycle delays were 15 s for all experiments. While faster MAS speeds are accessible in our laboratory, it is well-known that for zeolites in which protons are dilute spins that increased MAS rates do not provide decreased line widths over that obtained at 5−6 kHz (see Maciel et al. *J. Magn. Reson.* **1989**, *82*, 454 and refs 25 and 30). ^{1}H spin−lattice relaxation times were measured using saturation-recovery experiments. All spectra were acquired at room temperature. Spectra were deconvoluted and integrated using the commercial software package Origin. Deconvolution results to determine spectral areas for the water, acid site, isobutane, and silanol peaks were obtained using least-squares fitting via minimization of residuals. Mixed Gaussian−Lorentzian line shapes were used in the analysis. In every case, only one line was used in the fit for each physically relevant species in the sample, and sideband intensities, when observed, were included in the calculations. This procedure has been shown to be highly reproducible for determination of zeolite acid site concentrations, with a standard deviation for multiple experiments of ca. 3%, as described previously in refs 6 and 23.

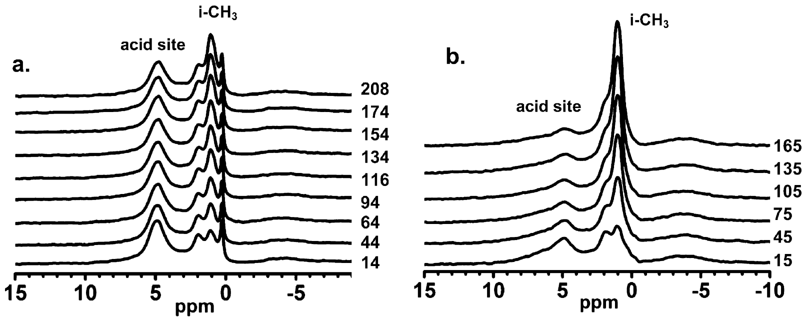

Figure 2. ^{1}H MAS NMR exchange stack plots at 296 K of (a) a catalyst corresponding to that shown in Figure 1a and (b) a catalyst corresponding to that in spectrum of Figure 1b, in which 0.94 and 1.0 equiv of isobutane-d$_{10}$ are adsorbed, respectively. The total elapsed time following isobutane adsorption, in minutes, is indicated. The very sharp peak at 0.2 ppm in (a) is from an inert polydimethylsiloxane (solid) chemical shift and intensity standard, which verifies the ca. 1-ppm change in chemical shift for the acid site following adsorption, and the constant silanol signal intensity.

RESULTS AND DISCUSSION

^{1}H solid-state NMR has been used extensively during the last three decades to probe acid sites in acidic zeolites.[24−28] In HZSM-5, two types of acid sites have been suggested to explain the 4.2 ppm and the broad 5−9 peaks, but with the low-field type representing only a small fraction of the total number of possible Bronsted acid sites.[29] Based on multiple experiments, Beck and co-workers assigned this 5−9 ppm peak to Bronsted sites that were in structurally unique locations relative to the 4.2 ppm Bronsted sites, i.e., interacting with multiple framework oxygens.[29] Subsequently, this same feature in HZSM-5 was assigned to strongly bound residual water which was not removed by the vacuum dehydration method.[30] The ensuing discussion will illustrate how small deviations in the initial catalyst conditions can have significant implications. Figure 1 shows two representative spectra for calcined and dehydrated HZSM-5, in which each catalyst was prepared using the vacuum-dehydration regimen (as described in the Experimental Section). Specific steps were taken to ensure that each catalyst was not exposed to air or moisture after dehydration in vacuum. Clearly, the relative peak shapes and heights for the Bronsted acid site resonance at 4.2 ppm are different for the two catalysts. In each case, a downfield shoulder extending from 5 to 9 ppm is observed. Significant differences in the 4.2-ppm Bronsted acid site peak intensity and shape are noticeable in Figure 1, and the ensuing data and discussions will indicate that the origin of these differences is that the amount of residual water in the catalysts is not the same and, most importantly, that this difference translates into important but unexpected reactivity differences.

The subtle differences in Bronsted acid site peaks in Figure 1a and Figure 1b are much more significant than simple spectroscopic anomalies, as revealed by rate measurements for the isobutane-d$_{10}$/HZSM-5 isotopic exchange reaction. Figure 2 shows the time series of spectra obtained following adsorption of isobutane-d$_{10}$ on these acidic HZSM-5 catalysts. The starting catalyst, i.e. prior to isobutane exposure, for the data in Figure 2a corresponds to that shown in Figure 1a, and similarly Figure 2b corresponds to that shown in Figure 1b. In each case, essentially one equivalent of isobutane-d$_{10}$ is adsorbed on the catalyst using previously described methods, in the absence of air or moisture, and spectra are obtained as a function of time. As previously described in detail,[5,6] two key features are noted from these data: (1) The Bronsted acid site peak originally at 4.2 ppm shifts to 4.9−5.1 ppm with subsequent decrease in intensity as H/D exchange occurs with isobutane-d$_{10}$, and (2) a protonated signal arises from the methyl group of isobutane (1.1 ppm). The silanol peak at 1.9 ppm is unaffected by adsorption, as previously reported.[5,6,24,25]

The isobutane/HZSM-5 exchange reaction is not new, but surprising new observations are apparent from Figure 2. Comparison of individual time points in Figure 2b to comparable points in Figure 2a, e.g. 165 min versus 174 or 45 versus 44 min, clearly indicates that the H/D exchange reaction proceeds at a higher rate on the catalyst in Figure 2b. The two key peaks involved in the exchange are labeled for clarity in Figure 2. The result is unexpected, since the first time point in each of the Figure 2 plots as well as the data in Figure 1 indicate that the catalyst in Figure 2b has a broad, less well-defined acid site signal and an apparent reduction in the number of acid sites relative to that in Figure 1a/Figure 2a. While not shown here, the exchange reactions shown in Figure 2a were also measured after 12 days of reaction to ensure isotopic equilibration. The integrated area ratio of the isobutane CH$_3$ peak to the acid site signal ranged from 8.5 to 10:1, which is near the expected 9:1 ratio for the targeted 1 equiv isobutane loading. This control experiment demonstrates that our MAS rotor system is sealed and no loss of isobutane or ingress of water occurs, and that within reasonable error, we can control the intended isobutane adsorption amount. The results depicted in Figure 2 are representative of results observed in multiple experiments. To reiterate, examination of the spectral differences in Figure 1 as well as the first spectra in each of the time series shown in Figure 2 leads us to propose that the key difference between these two catalysts is the amount of residual water left following activation and dehydration, even though no pronounced water signal is observed in Figure 1b or Figure 2b. For the sake of discussion, we will call the catalyst in Figure 1a/Figure 2a the “dry” catalyst, and the one in Figure 1b/Figure 2b the “wet” catalyst. A quantitative treatment of the data shown in Figure 2 is summarized in Figure 3. Integrated peak areas for the isobutane CH$_3$ signal and the zeolite acid site are plotted versus the reaction time for the initial rate region of the exchange. The positive slope points correspond to the growth of CH$_3$ signal from H/D exchange, while the negative points are from the decreasing acid site signal. The “dry” versus “wet”, i.e., the experiments in Figure 2a versus Figure 2b, are denoted by open and closed symbols, respectively. There are two important conclusions from this data. First, the reaction with the dry catalyst exhibits equal rate constants for the loss of the acid site signal and the gain of the isobutane methyl signal, as expected for a two-site H/D exchange process between only the catalyst and the reactant. Second, the exchange rate

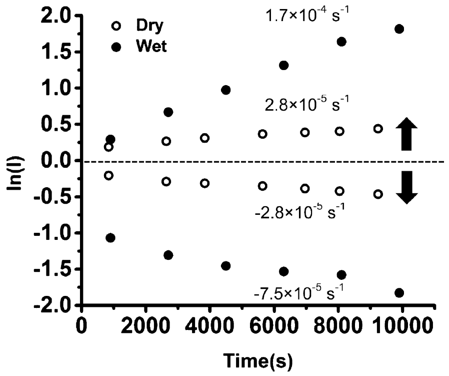

Figure 3. Semilogarithmic plot for the room-temperature exchange data shown in Figure 2, with areas taken from the 1.1 ppm isobutane CH_3 (positive points) and 5.0 ppm acid site (negative points) peaks. Note that the rate constants provided in the figure indicate identical exchange rates for the reaction in the dry catalyst but inequivalent methyl and acid proton signal intensity changes for the less dry, or "wet", catalyst.

constant for the growth of the CH_3 proton signal in the "wet" catalyst is an order of magnitude larger than in the dry system, and it is larger than its corresponding acid site signal change (solid points). That the growth of the "wet" CH_3 signal is faster than the loss of the Bronsted acid site signal is consistent with our proposal that this catalyst has some residual water that can exchange with the acid site, serving as a secondary proton source to replenish the acid signal following a deuterium exchange event with the isobutane-d_{10} through a three-site exchange process. No bulk or free water signal is observed in any of the spectra in Figure 1 or Figure 2, due to an intermediate exchange rate between the protons of the water and the acid site, and the interference of that motion with coherent MAS averaging. However, as will be described in detail more below using the control experiments of Figure 4, loss of acid site intensity prior to adsorbing a reagent like deuterated isobutane can only occur if water is present, and with increasing water amounts the acid site signal continues to decrease and ultimately disappears.

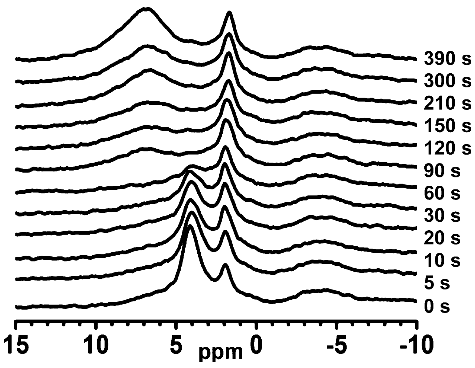

Figure 4. ^1H MAS NMR spectra of an HZSM-5 catalyst acquired at room temperature versus total time of exposure to ambient moisture (50−60% relative humidity), starting from the dry catalyst. After each exposure step, the rotor was resealed with a grooved plug and cap and the next spectrum acquired. Note that 20−30 s of ambient air exposure produces spectra equivalent to that shown in Figure 1b and in the first slice of Figure 2b.

Why does the acidic zeolite catalyst that appears to contain a higher number of Bronsted acid sites exhibit a slower reaction rate? As proposed above, the most logical assumption is that there are differing amounts of residual water on the catalysts following preparation, with the catalyst in Figure 1b/Figure 2b containing some amount of residual water while that in Figure 1a/Figure 2a is dry. While no obvious bulk/free water signal is present in any of the spectra above, which would appear as a narrow line at 4 ppm, some authors have suggested that the broad, heterogeneous downfield shoulder observed in the 6−9 ppm region comes from some type of residual water, while others have suggested that other acid site types in the lattice give rise to this feature.[29,30] In order to test this hypothesis, controlled exposure to ambient moisture was used to determine if spectra like that in Figure 1a could be changed to that in Figure 1b. Figure 4 shows the results from this experiment, in which the dry catalyst in a sealed MAS rotor was opened and deliberately exposed to 50−60% ambient humidity for the indicated periods of time. At time zero, the catalyst spectrum is identical to that previously shown in Figure 1a, and with increasing exposure times up to 30 s transforms into that previously shown in Figure 1b. The acid site signal at 4.2 ppm becomes broad and more complex in the 30-s exposure spectrum and is actually impossible to discern by the 90-s exposure. With longer exposure times, a new peak appears at 6.8−7 ppm, which is assigned to water clusters inside the zeolite channels, as previously reported.[25,26] In the 20−60 s exposure time range, the acid site peak becomes broad and heterogeneous, but no obvious water peak is observed. The key point here is that the spectra in the 20−60 s exposure range closely approximate that shown in Figure 1b, and also that for the reaction in Figure 2b for which the faster C−H exchange rate constant was measured. While not shown here, additional control experiments in which the dry catalyst was exposed to controlled amounts of water vapor (0.2−1 eqv) in the vacuum line manifold produced essentially identical spectral changes.

Using the data in Figure 4, a reasonable estimate of the amount of water present in the enhanced rate experiments above can be determined. Comparing the 0 and 390 s spectra in Figure 4, and using the fixed area 2-ppm silanol signal as an internal standard, the total integrated area of the 7-ppm water signal at 390-s exposure corresponds to ca. 1 equiv of water per initial acid site. We conclude that less than 1 equiv of water exists on the 20- or 30-s exposure spectra in Figure 4 and therefore also in the catalysts in Figures 1b and 2b. Again, control experiments in which adsorptions of 0−2 equiv of water were adsorbed onto dry HZSM-5 using the vacuum line manifold produced spectra with similar features to those shown in Figure 4. A graphical summary of the relationship between the reaction rate for isobutane C−H activation reaction and catalyst water content is shown in Figure 5, with reduced exchange rates occurring once the water content increases above the ca. 1−2 eqv level.

An increased reaction rate for the C−H bond activation in the presence of ca. ≤ 1 eqv of water indicates that the water molecule(s) must be simultaneously proximate to isobutane and the Bronsted acid site. It is important to recognize that the system is not static and the dynamics of isobutane diffusion are in the fast exchange regime of the NMR time scale, as previously reported, in which population weighted average chemical shifts were observed for fractional isobutane loadings.[5,6] Average lifetimes for isobutane residence at an acid site are reported to be ca. 1 μs at 300 K.[31] Figure 4 demonstrates that water is also rapidly diffusing and/or hopping between acid sites, since the initial 30−90 s exposures

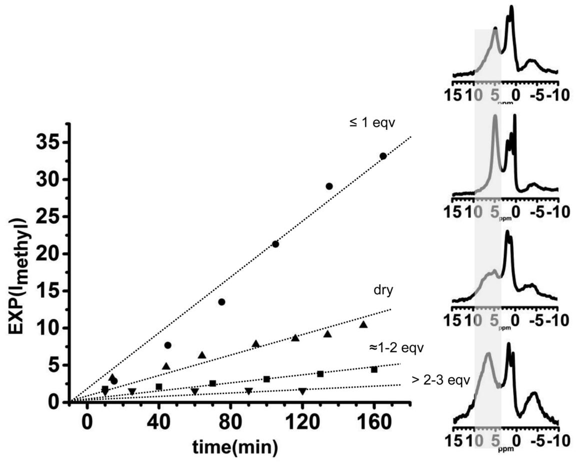

Figure 5. Linearized single-exponential growth plots of the isobutane CH_3 peak area in the ^1H MAS exchange spectra as a function of reaction time, for four different water loadings in equivalents. The dashed lines are simply drawn as guides to the eye through the raw data points. The corresponding spectra for the first time point in the exchange series are shown near their trend line, ordered from top to bottom. Note that the ca. ≤ 1 eqv loading corresponds to a spectrum with clear acid site peak but no obvious water peak (shaded box inset), the ca. 2 eqv loading corresponds to a spectrum with neither a well-defined water nor acid peak due to proton exchange in the intermediate time scale regime, and the ca. 2–3 eqv loading spectrum has a well-defined water peak but no acid site peak.

show no new water signals while the acid site simultaneously broadens and becomes unobservable, which indicates an exchange coalescence broadening. It is well-known that even in the absence of excess water, protons in HZSM-5 catalysts (like that shown in Figure 1b) exhibit thermally activated exchange between the Bronsted protons at 4.2 ppm and the broad residual water feature at 6.9 ppm; indeed, variable-temperature experiments show expected narrowing and broadening of these peaks due to proton exchange between the residual water and the Bronsted sites.[30,31] At room temperature, the acid site peak widths and the residual water peak widths, like that shown in Figure 1b or the low water loadings in Figure 4, are broadened due to an intermediate exchange rate on the NMR time scale, and this broadening cannot be eliminated by magic-angle spinning. Also, the spin–lattice relaxation times (T_{1H}) for Bronsted acid site protons decrease by a factor of 5 when even less than one equivalent of small molecule adsorbates are introduced, due to the rapid reorientation and diffusion of that adsorbate relative to framework Bronsted sites. Finally, the inequivalent exchange rates for the isobutane and Bronsted sites in "wet" catalyst, previously shown in Figure 3, demonstrates that both water and isobutane simultaneously access the Bronsted sites. Therefore, water and isobutane must encounter one another within the catalyst framework. Using ^{27}Al solids NMR and computational analysis of proton affinities and framework topology, Kletnieks and co-workers have proposed that three water molecules are required to deprotonate a Bronsted acid site in HZSM-5 to form a static tetrahedral Al site which is not under lattice strain.[32] While not shown here, we previously reported H/D exchange between isobutane-d_{10} at 0.25 and 0.5 eqv loading and HZSM-5.[6] Certainly, Figure 2 shows that the H/D exchange occurs at 1 eqv isobutane, and the proton affinity of isobutane is lower than that of water (163 vs 170 kcal/mol).[33] Therefore, it is reasonable to expect that water can participate in the room-temperature proton exchange reactions described above, even at less than 3 eqv loadings, as the reaction involves dynamic proton transfer instead of proton removal from the framework.

The uncertainties in measuring adsorption of small amounts of gases as well as the differences in the theoretical acid site density based on Al content (1.0 mmol/g) and spin counting (0.6 mmol/g) necessarily mean that the quoted water amounts might be off by as much as a factor of 2. However, the reactivity trend is accurate, and whether activity begins to decrease a 2 or 3 eqv of water is less important than trying to understand how lower water loadings definitely lead to increased reactivity relative to the dry zeolite. Water could influence the isobutane/HZSM-5 reaction in several ways. First, water can possibly enhance the proton transfer rate via a bimolecular reaction pathway involving a lower energy transition state than that for pure isobutane, as has been recently discussed for a metal-catalyzed reaction in Fischer–Tropsch catalysis.[32] However, if the water loading is too high, then water molecules will cluster at the acid site and prevent isobutane access, since the proton affinity for water dimers and trimers is much higher (200–230 kcal/mol) than that of a single water molecule or for isobutane.[33] Therefore, one expects that any synergistic benefit from water in zeolite-catalyzed hydrocarbon reactions should occur at low water loadings, as we find experimentally. The possibility that acidic proton diffusion/mobility is enhanced in the presence of low water levels, e.g. a type of mobil Zundel cation or protonic conduction mechanism mediated by H_3O^+ "carriers", seems likely. As stated in the Introduction, several reactions, including the controversial methanol-to-hydrocarbon reaction, produce stoichiometric water at 1-eqv loadings at early stages in the reaction. To date, almost no attention has been devoted to the role that water plays in these mechanisms, and if it can participate in the reaction of the completely nonpolar reagent like isobutane, it is logical to expect that water can actively participate in mechanisms involving more polar substrates. Future work will include computational support to discern the relative contributions of these two possibilities.[34]

CONCLUSIONS

Zeolite-catalyzed alkane C–H bond activation reactions carried out at room temperature, low pressure, and low reagent loadings demonstrate that water can act either to increase or to suppress the observed reaction rates. Isobutane reaction rate constants *increase by a factor of 10* at water loadings in the range of ca. ≤ 1 water molecule per catalyst active site relative to the dry catalyst. Conversely, water loadings greater than about 2–3 water molecules per active site retard isobutane reaction, which can be understood based on the much higher proton affinity of water clusters compared to single water or isobutane molecules. In situ solid-state NMR data show that water molecules and isobutane molecules are simultaneously proximate to the catalyst active site. These results indicate that water can be an active participant in reactions involving hydrophobic molecules in solid acid catalysts, possibly via transition state stabilization, as long as the water concentration is essentially stoichiometric. Such conditions exist in well-known catalytic reactions, e.g., methanol-to-hydrocarbon and biomass-generated ethanol-to-hydrocarbon chemistries, since stoichiometric water is a first-formed byproduct. Future work will focus on computational support for rational mechanisms that explain how water can enhance alkane reaction coordinates in acidic zeolites.

■ ASSOCIATED CONTENT

Supporting Information

Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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