Effect of Water Treatment on Sn-BEA Zeolite: Origin of 960 cm⁻¹ FTIR Peak

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Abstract

The correlation of the ~960 cm⁻¹ IR absorption band, frequently observed in Sn-BEA zeolite, to the incorporation of Sn in the zeolite framework has been investigated. IR and NMR spectra of freshly calcined and water treated zeolites combined with first principle calculations indicate that the 960 cm⁻¹ band is not a vibration involving Sn but rather a result of isolated internal silanol groups.

Thermogravimetric analysis and temperature-programmed desorption showed the silanol groups condense to form water at temperatures between 400 and 700 °C. These silanol groups form slowly at mild relative humidity (~30-40%) and 25 °C, but in less than an hour at 98 °C in liquid water: they are expected to form in the course of an aqueous phase reaction. The water uptake observed following an one-hour liquid water treatment is 1.2 wt% in Sn-BEA with Si/Sn = 125, equal to 4-5 water molecules per Sn or 1 water molecule per 40 Si, too high for all of it to be directly linked to interaction with Sn atoms. Instead this water uptake can be explained by a site that can be hydroxylated at relatively low temperatures and dehydrated at temperatures typically used for zeolite calcination.

Keywords: Sn-BEA, Lewis-acid, FTIR, TGA, silanol

Introduction

Stannosilicates, and Sn-BEA zeolite in particular, have shown remarkable catalytic activity for a range of promising Lewis-acid-catalyzed chemistries including the Baeyer-Villiger oxidation,[1] the Meerwein-Ponndorf-Verley reaction,[2] isomerization of glucose[3] and xylose,[4] and conversion of sugars to furfural,[4] 5-hydroxymethylfurfural,[5] and lactic acid.[6] The catalyst is active in both polar and nonpolar solvents at temperatures as low as 80 °C.

Current research in synthesis methods aims to increase the prospect of Sn-BEA as an industrially catalyst through reduction in cost and environmental impact (e.g. eliminating dependence on expensive organic templates and HF)[7] and/or reduction in synthesis time,[8] but the effects of changes in the synthesis protocol are challenging to predict or explain. The specific manner in which the Sn atoms are bonded to the zeolite framework is important and affects its catalytic properties. Adding to this challenge is the importance of the post-synthesis treatment of the zeolite. Bermejo-Deval *et al.* showed that binding of sodium cations within the zeolite can alter the dominant reaction pathway, favoring isomerization to fructose in the absence of Na⁺ and epimerization to mannose in its presence.[9] Boronat *et al.* found that calcining under different conditions (e.g. humidity, gas flow, etc.) led to varying concentrations of the so-called “open” Sn sites in which a Sn-O-Si bond is hydrolyzed to form a pair of adjacent Sn-OH and Si-OH groups.[10]

Nuclear magnetic resonance (NMR) has proven valuable in studying the structure of the Sn site,[11] but is not without limitations. The most abundant NMR-active Sn isotope (¹¹⁹Sn) is only 8.5% of unenriched Sn, so measuring a single sample typically requires several days using solid state NMR. It has recently been shown that the use of dynamic nuclear polarization (DNP) NMR could alleviate this issue and can be used for characterizing Sn containing zeolites in less than a day without the need of ¹¹⁹Sn enriched samples.[12] Instead, FTIR and UV/Vis spectroscopy are frequently used to assess successful Sn incorporation into the zeolite framework due to their ease of use. [9][13-18] Analysis of FTIR spectra

have followed previous reports assigning an IR peak at 960 cm^{-1} to the Ti incorporation in zeolites, a combination of both the Si-O-Ti asymmetric stretching mode and Si-OH modes.[19, 20] For carefully-prepared, defect-free Ti zeolites, the peak intensity correlates with Ti concentration.[21]

The literature contains multiple examples of identical FTIR analysis applied to Sn zeolites,[13-18] including anecdotal observation of a correlation between peak intensity at 960 cm^{-1} and Sn concentration,[14] on the assumption that Sn should produce an absorption peak just like Ti. However, unlike Ti, there are no studies rigorously demonstrating that the absorption at 960 cm^{-1} is a reliable indicator of Sn incorporation in the zeolite framework. Indeed, other reports have expressed skepticism that the 960 cm^{-1} band exists for metals other than Ti.[22] The present work aims to resolve the assignment and origin of this peak to determine and recommend best practices for characterization of Sn zeolites going forward.

In the course of this investigation, the 960 cm^{-1} peak was observed with various intensities in otherwise identical Sn-BEA samples measured at different times. It is suggested then that the 960 cm^{-1} peak is not an intrinsic feature of Sn incorporation in the zeolite, but rather that it is related to the interaction of water with the zeolite. The effects of this interaction were observed to be slower or absent in Si-BEA and Ti-BEA, indicating a relationship to either the Sn site or a related defect. Aqueous-phase reactions are an integral part of biomass processing, so it is critical to understand the interaction between catalysts and water. The behavior of hydrophobic catalysts like Sn-BEA in water is also of special interest due to research suggesting the hydrophobicity of the catalyst plays a role in its exceptional catalytic properties.[23-25]

Previous reports have shown that calcination in a humid environment increases the concentration of open sites in Sn-BEA[10] (see Figure 1). It was found that open sites bind Lewis bases more strongly[18] and that catalytic activity for Baeyer-Villiger oxidation,[10] Meerwein-Ponndorf-Verly oxidation,[26] and aldehyde cyclization[18] was correlated to the concentration of open sites and not

to the concentration of closed sites, leading to the conclusion that it is specifically these open sites responsible for the catalytic activity.[10] Unfortunately, modeling the open site within the zeolite is difficult, and computational results are difficult to compare due to the different ways they construct the open site. Allowing the model to deform freely yields the silanol and tin hydroxide moieties studied by Rai *et al.*, [27] who found enhanced activity for the open site in agreement with Boronat, and further showed that the silanol group opposite the hydrolyzed Sn is catalytically active for some reactions. If the model is restricted to an unperturbed crystalline zeolite framework, the bonds will not dissociate completely, resulting in significant interaction between O_A and Si_B and between O_B and Sn (see Figure 1). This structure has been identified in the current study and independently used by Li *et al.* [28] who argued that the enhanced activity of the open site is due only to its enhanced geometric flexibility. Other authors have removed Si_B entirely, either through terminating the model at the Sn-OH bond [10, 18] or through creation of an explicit, T-atom vacancy, [29] and these reach still different conclusions. A better understanding of the structure of the open site would both improve computational models of the site as well as assist in developing novel ways to control the synthesis of crystals featuring desirable sites. In addition to the open and closed site dichotomy, tin can be present in extra-framework sites, which have still different properties from those Sn atoms incorporated in the framework and reduced catalytic activity. [11, 30] [9]

Changes to the catalyst structure as a result of hydration could be responsible for a number of observations relating to catalytic activity, whether through hydrolysis to form the highly-active open sites or through an as yet unexplained process leading to catalyst deactivation. [31] To better understand the Sn site structure and its interaction with water, hydrated zeolites displaying the 960 cm^{-1} peak were characterized and compared to untreated samples. FTIR spectra were collected of freshly calcined and water-treated zeolites and of zeolites on which deuterated acetonitrile ($d_3\text{Acn}$) was adsorbed. Density functional theory (DFT) models of the zeolite were used to predict IR spectra and assign observed

differences spectra to particular vibrations within the zeolites. Thermogravimetric analysis (TGA) and temperature-programmed desorption (TPD) were employed to quantify the condensation and removal of the water. Analysis of our data highlighted that the 960cm^{-1} absorption band can be assigned to an Si-O stretching vibration of silanol groups and as a result should not be used for evaluating the Sn insertion in the zeolite framework.

Materials and Methods

Si-BEA was synthesized according to the method of Cambor *et al.*[32] Hydrophobic Ti-BEA and Sn-BEA were synthesized according to the method of Bermejo-Deval *et al.*,[33] using mother liquors with Si/Ti ratio of 48 and Si/Sn ratio of 100. Sn-BEA was initially calcined in a flow of humidified air. In particular, the sample was calcined under flow of ~ 250 cc/min of humid air (24 Torr water vapor pressure). It was heated with a ramp rate of $1^\circ\text{C}/\text{min}$ to 550°C and it was kept at that temperature for 12 hr. Highly-defective dealuminated BEA was produced by mixing one gram of Al-BEA (Si/Al = 12.5) with 20 mL of 15.3 M nitric acid for 20 hours at 100°C . [7] The zeolite was washed and centrifuged until pH 5, then dried and calcined at 550°C . Energy-dispersive X-ray spectroscopy was used to confirm that no aluminum remained in the final material. This material (deAl) contains tetrahedral vacancies from removed Al atoms resulting in nests of interacting silanol groups.

Water-treated zeolites were produced by exposing the zeolites to water with chemical potential greater than that resulting from ambient humidity ($\sim 30\text{-}40\%$ in our lab). In most cases, the zeolite was immersed in Type 1 ultrapure liquid water (EMD Millipore) in a sealed vial and heated under static conditions at 98°C for a predetermined length of time. The contents were then vacuum filtered for 30 minutes, and the filter paper and powder were dried for 30 minutes in a drying oven at 105°C . These zeolites are hereafter labeled “WT-X” where X is the time spent at 98°C in hours. Zeolites treated at room temperature displayed the same effects, but more slowly, requiring days of treatment rather than

hours. To demonstrate that the treatment is due to water and not an aqueous contaminant, the treatment was carried out with water vapor also. 40 mg of fresh Sn-BEA was placed in a glass test tube. The tube was placed inside a Parr reactor containing 100 μ L of water which was then sealed and evacuated. The interior of the reactor contained 24 Torr of water vapor in vapor-liquid equilibrium with the liquid, ensuring the chemical potential of water in the adsorbed phase was equivalent to zeolites immersed in liquid water. The zeolite was removed from the reactor after 10 days and analyzed to compare to zeolites processed in liquid water. “Fresh” zeolites are those which have not been water-treated since calcination at 600 °C.

FTIR spectra were measured using a Nicolet 8700 FTIR (Thermo Scientific). Framework bands were collected at 25 °C using a “Golden Gate” ATR cell (Specac). Spectra were baseline-corrected and corrected for ATR with refractive index of 1.40. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected using pure zeolite in a “Praying Mantis” cell (Harrick Scientific). Samples were degassed for one hour in a 30 sccm flow of helium at 400 °C to remove physisorbed water. After degassing, all DRIFT spectra were collected at 120 °C in order to prohibit water re-adsorption from trace humidity within the gas lines. Spectra were converted to Kubelka-Munk units and intensities were scaled by the area of the overtone bands at 2000 and 1880 cm^{-1} . Deuterium exchange was conducted by using D_2O for the water treatment, and loading the sample cup before the sample had fully dried.

IR spectra of adsorbed d_3Acn were collected in transmission mode using a Galaxy FTIR (Mattson Instruments). The sample was piled in the path of the beam and degassed at 200 °C for one hour then cooled to room temperature. The background was collected, and then d_3Acn was adsorbed by 50 ml/ms of He passing through a bubbler. After confirming adsorption, the bubbler was closed off from the He, and the sample was heated at 10 °C/min punctuated by 10 minute holds at 60, 80, 100, and 120 °C during which multiple spectra were collected.

TGA data were collected with a TGA/DSC 1 STARe system (Mettler Toledo) in a flow of 80 sccm of dry nitrogen. Samples were heated to 700 °C at 20 °C/min then held for 1 hour. Sample weight was normalized by final dry mass and extrapolated onset temperature (T_{onset}) was calculated as the intersection of tangents drawn from the baseline and through the point of inflection.[34] The first derivative (dTGA) was calculated numerically in Origin and smoothed using an FFT filter with a 30 second window to identify the peak desorption temperature (dT_{max}). Weight loading was calculated by drawing tangents to the baseline before and after desorption steps and subtracting the difference of the tangents at the inflection point.

Temperature programmed desorption mass spectrometry (TPD-MS) data were collected in a glass reactor under 50 mL/min flow of helium fed to an in-line mass spectrometer (Pfeiffer Vacuum) scanning from 5-100 amu. The sample was held at 20 °C for two hours, then ramped at 10 °C/min to 700 °C and held for one hour. Mass spectra were compared to dTGA curves to identify adsorbates.

Liquid nitrogen physisorption and water adsorption experiments were carried out in a 3flex adsorption system (Micromeritics Instrument Corporation). Samples were degassed under vacuum overnight at 200 °C and backfilled under nitrogen prior to adsorption.

^{29}Si NMR spectra of fresh and WT Sn-BEA were collected at room temperature with an AVIII 500 solid state NMR spectrometer (Bruker Corporation) with Larmor frequencies of 500.13 MHz for ^1H and 99.36 MHz for ^{29}Si . A 4 mm HX double resonance probe was used, and the spinning speed was 10 kHz. ^{29}Si single pulse and ^1H - ^{29}Si cross polarization MAS spectra were collected for each sample. Each spectrum consists of 2400 scans with pulse delays of 30 seconds for single pulse spectra and 5 seconds for cross polarization spectra.

DFT calculations were performed using the Gaussian quantum chemistry package.[35] Clusters of zeolite BEA were cut from the periodic slab centered on the T1, T5, and T9 sites commonly studied in the literature.[10] These sites (incorporated in two, one, and zero 4-T rings respectively) were taken to

represent the nine possible sites in BEA zeolite. The clusters extend four coordination layers from the T9 site (i.e. T9-O-Si-O-Si). Terminal Si atoms were saturated with hydrogen, which were fixed in space to retain the cluster's structure. Some oxygen atoms, which were five coordination layers away, were included also because they connected two included Si atoms. The T9 cluster is pictured in Figure 2A and consists of the T9 site, 19 additional Si atoms, 29 O atoms, and the H atoms needed to saturate the orbitals.

Figure 2B shows a cluster in which the tetrahedral atom has been removed (corresponding to deAl-BEA) leaving behind a nest of coordinated silanol groups. Due to the uncertainty regarding the structure of the open site, only the closed site was studied with DFT. Figure 2C shows an open site model generated by cleaving a Sn-O-Si bond and replacing it with hydroxyl moieties. As in all other cases, the structure was permitted to fully relax with only the terminal hydrogens frozen. The hydroxyl groups spontaneously reoriented themselves into the planar configuration shown. The Sn-O and Si-O bond lengths to each oxygen were nearly identical; however, NBO analysis showed that only one of each bond carried electron density at any given time, that is, two opposite electronic structures are possible for that geometry. This configuration is similar to the one studied by Li *et al.* under periodic boundary conditions.[28]

Geometry optimizations and frequency calculations were carried out with the b3lyp functional[36] and the pseudopotential basis set lanl2dz[37] (the most used from a limited selection of basis sets parameterized for both Sn and Ti). FTIR spectra were computed from vibrations by assigning a Gaussian distribution to each vibrational mode with a variance such that the full-width at half maximum of an individual peak was equal to 54. Spectra centered on each of the 3 classes of T site were averaged together and scaled in frequency by 0.9. These parameters reproduced the experimental spectra collected for Si-BEA and Ti-BEA.

Results and Discussion

Figure 3 shows calculated, scaled, composite IR spectra for each element (including deAl). Individual vibrations for each calculation are given in the supplemental information. The intense anti-symmetric Si-O-Si stretches corresponding to an IR peak at 1100 cm^{-1} are observed as the largest peak in the model. Both the symmetric Si-O-Si stretch centered at 800 cm^{-1} and the bending modes from 660 to 500 cm^{-1} are observed in the region from 750 to 400 cm^{-1} in the calculated spectra. The region from 950 to 750 cm^{-1} in the calculated spectra shows no absorption bands for the siliceous material.

The peak at 960 cm^{-1} for Ti-BEA corresponds to the antisymmetric Ti-O-Si stretches.[21] Sn-substituted clusters have analogous stretches but they are less intense and less red-shifted from the Si-O-Si frequency compared to those in the Ti-substituted cluster. As a result, the Sn-O-Si contribution to the calculated spectra is difficult to distinguish from the spectrum of Si-BEA. DeAl-BEA does not show a peak at 960 cm^{-1} , but does show a series of new absorption peaks in the region from 900 to 660 cm^{-1} arising from strongly coupled Si-O and O-H stretches in the silanol nest. Based on these calculations, IR absorbance in the region between 1000 and 800 cm^{-1} was expected for Ti-substituted BEA while isomorphically substituted Sn-BEA (the closed site) should be nearly indistinguishable from Si-BEA.

Spectra were calculated for the open-site structure shown in Figure 2C and for the site modeled by Rai *et al.*[27] The former has a collection of vibrations between 1000 and 900 cm^{-1} , but none are intense or consistent across multiple sites, such that the ensemble spectrum remains indistinguishable from Si-BEA. The model of Rai *et al.* displayed peaks at 1050 cm^{-1} and 870 cm^{-1} , but not at 960 cm^{-1} . These calculations therefore cannot ascribe the 960 cm^{-1} absorption to the open site, but given the uncertainty in modeling its structure, and the sensitivity of the IR spectra to interactions with neighboring atoms/ groups the actual geometry may yield different spectra.

ATR spectra of fresh zeolites (Figure 3B) show a clear contrast between Si-BEA, Ti-BEA, and deAl-BEA. Sn-BEA cannot be distinguished from Si-BEA in agreement with calculated spectra and in conflict

with work citing a peak at 960 cm^{-1} as evidence of Sn incorporation. Further, the deAl-BEA shows a shoulder feature at 980 cm^{-1} . Using the 960 cm^{-1} peak as evidence of Sn incorporation is therefore capable of leading to both, a false negative for Sn-BEA, and potentially a false positive in the case of a crystal with many internal silanol defects, rendering it inconclusive as an analytical procedure.

Figure 4 shows DRIFT spectra in the framework and hydroxyl regions of Si-BEA (Fig. 4A), Ti-BEA (Fig. 4B), Sn-BEA (Fig. 4C), and deAl-BEA (Fig. 4D). The 1100 cm^{-1} peak seen in ATR cannot be discerned in DRIFT because the absorbance is too high. A small shoulder is visible at 975 cm^{-1} for Si-BEA but not for Sn-BEA. Ti-BEA shows clear peaks at 968 cm^{-1} , 960 cm^{-1} , and 943 cm^{-1} as previously described.[20] Following one hour of water treatment, Si and Ti-BEA remain unchanged while WT-1 Sn-BEA shows a clear new peak at 960 cm^{-1} . It is likely that previous studies reporting a 960 cm^{-1} peak for Sn-BEA were in fact observing this new peak, formed by hydration from the air or leftover from insufficient calcination. Spectra of deAl-BEA must be examined cautiously as the dealumination treatment does damage the zeolite framework, disturbing some peaks and making the spectra difficult to scale. However, it is observed that the 960 cm^{-1} peak is present for WT-1 deAl BEA and not for fresh deAl-BEA.

In the hydroxyl region, an additional peak at 3695 cm^{-1} was observed in Si-BEA but not in other zeolites matching an unidentified Si-OH stretch previously observed at 3680 cm^{-1} in MFI-type zeolites.[38] As in this case, that band was observed only when the isolated silanol peak at 3735 cm^{-1} and the broader peaks at 3500 cm^{-1} were both low. Examining the intensity of the isolated silanol peak at 3735 cm^{-1} , fresh Si-BEA and Ti-BEA samples displayed equivalent peak areas (less than 5% difference) while the corresponding peak was twice as large for fresh Sn-BEA. Far more significant, however, was the change in absorbance upon water treatment. Absorbance increased only slightly for Si-BEA and Ti-BEA but increased by 500% in Sn-BEA. We note the tremendous change in a qualitative sense, but have not attempted to calibrate this increase with the concentration of silanol groups. Quantitative analysis was instead conducted using TGA (see below).

Based on these spectra, Sn-BEA appears to dissociatively adsorb water molecules in the form of silanol groups, causing the large increase in peak intensity at 3735 cm^{-1} . The peak is too sharp to include hydrogen-bonding silanol groups, but may include geminal and triple hydroxylated sites, which are difficult to distinguish from single, isolated silanol sites.[39] The framework spectra also explain previous observations of the 960 cm^{-1} peak in association with Sn-BEA. The 960 cm^{-1} peak is not specific to a Sn-O vibration in the fresh Sn-BEA zeolite but instead increases as the concentration of silanol groups increases. In both hydroxyl and framework regions, longer water treatments (e.g. 48 hours) were found to reproduce this effect in other BEA zeolites suggesting that the effect is not unique to Sn but that it occurs more rapidly and with greater impact in Sn-BEA than in others (spectra of WT-48 zeolites are shown in Figure S2A).

To test the relationship between the formation of silanol groups and the presence of Sn, Sn-BEA was synthesized with lower nominal Sn loadings (Si/Sn ratios of 300 and 500). These samples were examined also and the IR spectra (Figure S2B): Sn-BEA-300 shows silanol intensity intermediate between Si-BEA and the Sn-BEA-100 discussed thus far, both when fresh and when water-treated. Sn-BEA-500 is indistinct from Si-BEA. These data show that rapid silanol formation is indeed dependent upon the concentration of Sn in the zeolite.

All changes discussed above relate to silanol groups and do not necessarily prove any change in the actual Sn site in particular. However, it is plausible that the increase in silanol groups also corresponded to an increase in the population of open sites or in the displacement of Sn centers to extraframework Sn. IR spectra of adsorbed d_3Acn is commonly used for analysis of the Sn site itself, though the interpretation of the spectra is disputed. Boronat *et al.* have assigned four peaks to d_3Acn on the basis of DFT calculations.[10] From weakest to strongest adsorption, they are 2266 cm^{-1} (physisorbed on SiO_2), 2275 cm^{-1} (adsorbed on Si-OH), 2308 cm^{-1} (adsorbed on closed Sn site), and 2316 cm^{-1} (adsorbed on open Sn site). Others have argued that the change from 2266 to 2275 cm^{-1} results

from loading or solvent effects rather than from a different adsorption site, and also did not observe a separate band at 2316 cm^{-1} . [30] The 2316 cm^{-1} peak was not observed in this study either, but the presence of the 2308 cm^{-1} peak did confirm framework Sn with Lewis acidity in both samples.

Figure 5 shows difference spectra of adsorbed d_3Acn . Both fresh and WT Sn-BEA had similar intensity at 2266 cm^{-1} , which in both cases rapidly shrank upon reaching 60°C . In fresh Sn-BEA, the 2275 cm^{-1} peak was initially only visible as a shoulder, half as intense as 2266 cm^{-1} . Once the 2266 cm^{-1} peak vanished, the 2275 cm^{-1} peak became visible, but it too had largely disappeared after 10 minutes at 60°C and was completely absent at 80°C . In WT Sn-BEA, the 2275 cm^{-1} peak was more intense than the 2266 cm^{-1} band and persisted longer, disappearing only following 10 minutes at 100°C . So as long as Boronat's assignment holds, [10] these spectra provide further evidence of silanol formation as a result of water treatment, as evidenced by the increased absorbance at 2275 cm^{-1} for WT-1 Sn-BEA. As mentioned above, the 2316 cm^{-1} corresponding to the stronger-binding open sites was not observed in either sample.

To understand the nature of these vibrations, the H atoms of WT Sn-BEA were partially exchanged with D_2O , producing the spectra in Figure S3. The sample was loaded into the sample cup while still damp with D_2O , then dried at 50°C for 30 minutes in a flow of nitrogen before following the procedure used for all other DRIFT samples. The 3735 cm^{-1} band was still present but was lower in intensity compared to WT-1 in Figure 4D. The loss in intensity resulted from exchange for SiO-D groups appearing in a new band at 2753 cm^{-1} . By contrast, the 960 cm^{-1} peak was red-shifted only slightly to 940 cm^{-1} , consistent with previously observed "next-nearest neighbor" isotopic shift [40] suggesting that accessible H only neighbors the bond responsible for the 960 cm^{-1} peak, which is most likely the Si-O stretch of the isolated silanol in agreement with previous assignment. [19]

Under this interpretation, the absence of the 960 cm^{-1} peak from fresh Sn-BEA indicates one or both of two possibilities. First, since fresh Sn-BEA has a much lower population of silanol groups, the

peak may be concealed by the neighboring 1100 cm^{-1} peak. Second, the silanols formed by water treatment may be structurally different to those innately present in fresh Sn-BEA (and visible at 3735 cm^{-1} even in the fresh sample) and it is only these WT silanol groups that absorb at 960 cm^{-1} . This latter hypothesis is supported by the different decomposition temperatures of the water-treated silanol groups and those which are always present.

TGA was used to examine the regeneration of the zeolite (Figure 6). As expected, Ti and Sn-BEA contained more physisorbed water than Si-BEA. Sn-BEA also had a slightly higher desorption temperature than Ti-BEA. WT-1 Sn-BEA showed a greater difference compared to the other WT-1 zeolites (TGA in Fig. 6C and dTGA in Fig 6D). Upon heating the WT Sn-BEA, weakly bound water is lost immediately, while some more strongly bound water is lost gradually in the temperature range from 170 to $400\text{ }^{\circ}\text{C}$. These desorption processes are typical of all zeolites, though the quantity of water lost in the second period suggests some hydrophilic character. These periods of desorption were followed a rapid desorption between 400 and $700\text{ }^{\circ}\text{C}$ accounting for 1-1.5 wt% of the zeolite. This sudden increase in desorption rate is best explained by an activated process which becomes kinetically relevant only above $400\text{ }^{\circ}\text{C}$. This adsorbate (hereafter: Ads_{400}) was hypothesized to be responsible for the increase in absorbance at 3735 cm^{-1} and its subsequent decrease back to the initial state upon calcination at $600\text{ }^{\circ}\text{C}$.

Table 1 lists temperatures and weight loadings for multiple samples in order to display the variation in these parameters. Samples 1-1 through 1-3 correspond to three samples drawn from the same treatment and measured on separate days. Both loading and desorption temperatures of Ads_{400} showed only minor variation for these samples, indicating that the variation is intrinsic to the sample and not to the TGA or analysis technique. Other entries in Table 1 show the greater variation that was observed between samples treated independently. The water loading in WT-1 Sn-BEA-300, WT-1 Sn-BEA-500, and WT-48 Si-BEA was too low to detect in TGA; it was only observed through an increase in silanol intensity in FTIR.

A number of possible explanations for this phenomenon have been dismissed. WT Sn-BEA was analyzed via TPD-MS to confirm that Ads_{400} was water rather than an unknown contaminant introducing during water treatment. Mass spectra of detected masses are shown in Figure S4 with comparison to the matching dTGA curves. Spectra for 17 and 18 amu (corresponding to water) show two desorption peaks physisorbed water at roughly 120 °C, and a second desorption peak matching the dTGA curve of Ads_{400} . Background spectra for 28, 32, and 40 amu were observed as well. The 44 amu spectrum showed an increase in current beginning at 270 °C and reaching a broad, flat peak at 450 °C potentially indicating adsorption of carbonate, however, the signal was 20 times weaker in magnitude than the 18 amu spectrum and did not qualitatively match the desorption peak behavior shown in the dTGA curves. The water is not molecularly adsorbed either, as this would be clearly visible in IR and would not display the activated desorption behavior in TGA. These data confirm that Ads_{400} corresponds to a population of silanol groups that condense desorbing water.

^{29}Si NMR was employed to confirm that the adsorbate complex was silanol. ^{29}Si NMR spectra and cross-polarization ^1H NMR spectra for fresh and WT-1 Sn-BEA are shown in Figure S5. The fresh sample shows the crest at -102 ppm typical of zeolite BEA.[41] The WT-1 sample instead shows a clear peak associated with Q^3 isolated silanol groups.[38, 42-45] Absent from the WT-1 spectra is a peak at -92 ppm, corresponding to Q^2 geminal silanols. From this it is concluded that the water treatment produces only one silanol per Si atom. Lastly, the WT-1 spectrum shows a shift at -106 ppm. This peak is most often association with Si-O-Al bonds which are absent in this sample, but the position of the Q^3 peak has been observed to vary within this range.[43] It is plausible that -106 is a different geometry of Q^3 peak just as -112, -113, and -116 ppm represent different Q^4 sites.

The N_2 physisorption data demonstrated only slight differences in micropore pore volume and surface area between fresh and WT-1 Sn-BEA (see Supporting Information Table S1). These changes were too small in magnitude to serve as a cause for the other observed phenomena.

This secondary, rapid desorption of water has not been previously discussed in the literature, even in work explicitly examining water desorption via TGA. Anderson and Klinowski[46] investigated dealuminated, high-silica MOR zeolite using TGA and defined the hydrophobicity index h as the ratio of water desorbed by 150 °C to the total quantity of water desorbed; however, their TGA experiment showed no sign of the secondary desorption at high temperatures. Rather, the hydrophilic zeolites in that study and others[47] show the early, rapid desorption of weakly bound water followed by the more gradual release of more strongly bound water, and it was only this gradual desorption which previously defined hydrophilic zeolites. Hydrophobic zeolites, as Sn-BEA is generally understood to be, contained virtually no water above 150 °C. The sudden increase in desorption rate indicates the water is not merely strongly bound, but is desorbing through an activated process which becomes kinetically relevant only at temperatures of 400 °C and higher.

The quantity of water desorbed in the condensation corresponds to roughly 0.6 mmol per gram of zeolite. If the silanol groups were specific to only the external surface of the crystals, ($23.4 \text{ m}^2/\text{g}$ as measured via N_2 physisorption), there would be 14 molecules of water (and therefore 28 silanol groups) per square nanometer, an unreasonably high figure. As such, the external surface alone cannot account for the water loading, and a significant fraction of the isolated silanol groups must exist within the zeolite pores. Conversion of tetrahedral, closed-site Sn (at most 0.13 mmol/g of zeolite) to octahedral, open-site Sn would account for only 3 out of the 4-5 water molecules per Sn site. Further, previous work has also shown that 150 °C is adequate to desorb the octahedrally-coordinated water from both closed and open sites,[11] such that the condensation of open sites would desorb water at a 1:1 ratio with Sn, accounting for at most 20% of Ads_{400} . As such, an additional hydroxylation site is necessary to explain the water uptake.

From these observations, it is concluded that the water treatment produces silanol groups within the zeolite structure. The formation is related to the existence of heteroatoms in the zeolite

framework, but is not adequately described by formation of open sites alone. The ambient humidity typical of a laboratory likely has some impact, which may explain previous observation of the 960 cm^{-1} peak, but the effect is much stronger when deliberately induced with water at high chemical potential, either through immersion in liquid water or in water vapor in VLE. These hydroxyls are stable up to at least $400\text{ }^{\circ}\text{C}$ and rapidly condense at an onset temperature between 400 and $700\text{ }^{\circ}\text{C}$, a temperature too high to be molecularly adsorbed water and too low to be the silanol groups that terminate the external surface of the zeolite.

Conclusion

IR spectra of Sn-BEA were compared to Si-BEA, dealuminated BEA and Ti-BEA. The 960 cm^{-1} peak commonly used in literature as evidence of Sn framework incorporation was found to be absent from freshly calcined Sn-BEA in agreement with computational predictions. As such, it is inadvisable to apply this analytical technique to identify Sn incorporation in the framework of zeolite BEA. We believe that other characterization techniques, (i.e. DNP-NMR) albeit more elaborate to implement, are probably more suitable for assessing the incorporation of Sn in the zeolite framework without having to use a ^{119}Sn enhanced source in the Sn-BEA synthesis.[12, 48]

In contrast to the freshly calcined samples, the 960 cm^{-1} peak was observed in Sn-BEA zeolites which had been exposed to water. It was assigned to a Si-O stretch in a silanol group formed upon water treatment of the zeolite in a process taking less than an hour at $98\text{ }^{\circ}\text{C}$. Their presence was confirmed by an increase in IR intensity at 3735 cm^{-1} , by ^{29}Si NMR, and by IR spectra of adsorbed d_3Acn . TGA showed that these silanol groups were stable at temperatures as high as $400\text{ }^{\circ}\text{C}$, but condense to produce water and desorb between 400 and $700\text{ }^{\circ}\text{C}$, temperatures insufficient to condense the silanol groups that terminate the external surface of the zeolite.

The extent of hydroxylation is proportional to the Sn concentration in the zeolite; however, it also occurs in Ti-BEA and siliceous BEA, albeit at a slower rate and lower loading of water. The water loading is also too high to be linked to direct interaction with Sn atoms. Rather, the phenomenon is best explained by a defect in the zeolite that can be hydroxylated by water at relatively low temperatures and dehydrated at temperatures typically used for zeolite calcination. This defect is most abundant in BEA zeolites with high Sn concentration, but exists in smaller quantity even in siliceous BEA synthesized using HF. It is not specific to the HF synthesis route either as it exists in dealuminated commercial H-BEA.

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Table 1: Desorption temperatures and water loadings for water-treated zeolites. VT-10d was water treated for 10 days at room temperature with the water-vapor process as described in the methods section.

Sample #	Material	T _{onset} (°C)	dT _{max} (°C)	Wt% Ads ₄₀₀
1-1	Sn WT-1	442	507	1.2
1-2		440	511	1.2
1-3		440	504	1.2
2		383	414	1.3
3		568	656	1.0
4		455	501	1.1
5	Sn VT-10d	488	548	1.7
6	Ti WT-1	596	652	0.3
7	Ti WT-48	585	651	1.3
8	deAl WT-1	535	609	0.7

Closed Site

Open Site

Figure 1: Schematic of closed and open Sn sites in Sn-BEA zeolite.

Figure 2: Zeolite clusters studied in DFT model. Clusters shown are centered on the T9 site. Background structure drawn in wireframe for B and C to enhance clarity.

Figure 3: (A) Calculated ensemble spectra for each BEA zeolite studied. Sn-BEA spectrum corresponds to the closed site. (B) ATR spectra measured immediately following calcination at 600 °C.

Figure 4: DRIFT spectra of freshly calcined (lower spectrum) and WT-1 (upper spectrum) zeolites. Y-scale in Kubelka-Munk units is arbitrary but consistent for all spectra. A: Si-BEA, B: Ti-BEA, C: Sn-BEA, D: deAl-BEA.

Figure 5: Difference spectra of adsorbed d3Acn on fresh and WT-1 Sn-BEA. Spectra were collected at the same points in the temperature desorption program for both zeolites. Heating rate: 10 °C/min punctuated by 10 minute holds at 60, 80, 100, and 120 °C. At each intermediate temperature one spectrum was recorded as soon as the temperature was reached (solid line) and one after the sample was held at that temperature for 7.5 min (dotted line).

Figure 6: TGA curves (left) and dTGA curves (right) for fresh (top) and WT-1 (bottom) zeolites. Si-BEA (black lines), Ti-BEA (blue lines) and Sn-BEA (red lines)