Distinguishing Active Site Identity in Sn-Beta Zeolites Using $^{31}$P MAS NMR of Adsorbed Trimethylphosphine Oxide

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ABSTRACT: The identity of the active sites of hydrophobic Lewis acid zeolites was elucidated by solid-state $^{31}$P nuclear magnetic resonance (NMR) spectroscopy following adsorption of trimethylphosphine oxide (TMPO) probe molecules. The adsorption of TMPO on these materials resulted in distinct $^{31}$P NMR resonances between $\delta_{\text{iso}} = 59.9$ and 54.9 ppm that correspond to unique chemical environments of the Lewis acidic heteroatoms in the Beta zeolite framework. The $^{31}$P NMR resonances were assigned to sites in Sn-Beta zeolites by correlating the variation of $^{31}$P NMR spectra during TMPO titration experiments with the corresponding changes in the $^{119}$Sn NMR spectra. This method allowed us to establish quantitative relationships between the assignments for each site and the catalytic activity for the glucose isomerization and aldol condensation reactions. The rate of glucose isomerization directly correlated with the combined integrated intensities of $^{31}$P MAS NMR resonances at $\delta_{\text{iso}} = 55.8$ and 54.9 ppm, which amounted to 12−33% of total Sn sites. In contrast, the integrated peak area of a different site at $\delta_{\text{iso}} = 58.6$ ppm was shown to correlate with aldol condensation activity. The probing method used to identify and quantify distinct active sites within the framework of low-defect Lewis acid zeolites developed in this work is applicable to a wide range of microporous materials, regardless of heteroatom identity.

KEYWORDS: zeolites, Lewis acid, phosphine oxides, probe molecule adsorption, Sn-Beta, titration, glucose isomerization, aldol condensation

INTRODUCTION

Lewis acid zeolites, such as Sn- and Ti-Beta, have emerged as exceptional catalysts for the activation of oxygenated molecules and are of special interest for biomass conversion schemes. The synthesis of these materials in fluoride media produces low-defect zeolites with increased hydrothermal stability, crystallinity, and hydrophobicity.1,2 These zeolites are capable of catalyzing a wide range of transformations, including oxidation, transfer hydrogenation, sugar isomerization, (retro)aldol, and Diels−Alder reactions.3−11 Interest in Lewis acid zeolites has led to numerous studies investigating their catalytic properties and attempting to decipher the true origin of their unique catalytic activity. However, as evidenced by many conflicting reports in the open literature, the nature of the active sites in these materials continues to be poorly understood.12,13

Experimental evidence for the active site speciation in Sn-Beta and other M-Beta zeolites is difficult to obtain given the limited spectroscopic techniques available that can resolve the identity of these sites. Tin-119 magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy has been used to show the presence of multiple tetrahedral sites in Sn-Beta catalysts, although the assignment of these sites continues to be debated.15 This technique is limited by the need for enriched $^{119}$Sn samples due to the low natural abundance (8.6%) of the $^{119}$Sn isotope and the limited metal content (up to 2 wt %) of hydrothermally synthesized Sn-Beta. Dynamic nuclear polarization (DNP) NMR15−17 and Carr−Purcell−Meiboom−Gill (CPMG) echo train acquisition14,18 are two methods that have allowed for analysis of Sn-containing zeolites at natural abundance. However, the former is not quantitative, and the latter is highly dependent on spin−spin nuclear relaxation ($T_2$) behaviors, hindering robust quantification. While powerful, MAS NMR is difficult to implement for quadrupolar nuclei with moderate to large nuclear electric quadrupole moments, such as $^{47/49}$Ti, $^{177/179}$Hf, and $^{91}$Zr.
Recently, progress has been made in developing Fourier transform infrared spectroscopy (FTIR) techniques that can analyze Lewis acid zeolite active sites with the assistance of probe molecules. Boronat et al. showed that two sites in Sn-Beta can be distinguished with FTIR by absorbing deuterated acetonitrile (CD$_3$CN), and Harris et al. quantified the concentration of each of these titrated sites in various Sn-Beta samples by accurately measuring molar extinction coefficients. However, this method cannot be employed for other M-Beta zeolites, including Zr- and Hf-Beta, as only one band between 2300 and 2310 cm$^{-1}$ is distinguishable post CD$_3$CN adsorption. Sushkevich et al. showed that CO adsorption at cryogenic temperatures provides more resolution for Zr-containing zeolites and used this method to assign an active site for the synthesis of butadiene from ethanol. The calculation of unique molar extinction coefficients for each zeolite active site is complicated by the heavily convoluted FTIR bands, making comparisons between samples, especially those with different heteroatoms, very difficult.

Unlike vibrational spectroscopy, NMR spectroscopy is a direct nucleus-specific analytical method that provides both quantitative and qualitative information without the need for molar extinction coefficients. Indeed, coupling probe molecule adsorption with NMR spectroscopy is a powerful, yet relatively unexplored technique for investigating Lewis acid zeolites. Gunther et al. recently used pyridine adsorption with $^{13}$N MAS NMR to determine an acidity scale for various Lewis acid zeolites. This technique was used by Gounder and co-workers to distinguish two types of sites in Sn-CHA zeolites. We propose that pairing phosphorus probe molecules with $^{31}$P MAS NMR spectroscopy offers a powerful method to resolve and quantify active sites in these materials. Phosphorus-31 is an ideal probe nucleus as it is 100% naturally abundant, has a nuclear spin number $I = 1/2$, and has a high gyromagnetic ratio. These nuclear properties make $^{31}$P NMR spectroscopy a relatively sensitive technique despite the low concentrations of catalytic sites present in these zeolites, while the shortened acquisition times and high signal-to-noise (S/N) ratios compared to those for $^{119}$Sn make this quantitative NMR technique more practical. A recent review by Zheng and co-workers provides an extensive summary of how trimethylphosphine (TMP) and various trialkylphosphine oxides have been used to study acid catalysts and highlights how NMR methods including $^1$H-$^{31}$P heteronuclear correlation and $^{31}$P-$^{31}$P double-quantum correlation spectroscopy have provided additional proximity information for these probe molecules adsorbed on Bronsted acid sites. Trimethylphosphine oxide (TMPO) has been shown to effectively titrate and distinguish Bronsted acid sites with different acid strengths in aluminosilicates, and theoretical studies have predicted the ability for TMP to characterize the strength of homogeneous Lewis acids. Zhuang et al. used TMP to identify Bronsted and Lewis acidic sites in titanium-containing zeolite TS-1 and later used the conversion of adsorbed TMP to TMPO as a probe reaction for further characterization. Here, we demonstrate a robust method that allows for the identification of distinct sites in Lewis acid zeolites.

### RESULTS AND DISCUSSION

**Identification and Quantification of Tetrahedral Sn Sites in Sn-Beta.** Phosphorus-31 MAS NMR spectra were acquired after dosing a representative Sn-Beta sample (Si/Sn molar ratio of 300, Sn-Beta-300a) with different loadings of TMPO using a dichloromethane (DCM) solvent-assisted technique (Figure 1). The TMPO occupancy at each site demonstrates a robust method that allows for the identification of different Sn sites within Lewis acid zeolites.

**Figure 1.** $^{31}$P MAS NMR spectra ($\omega_{0}/2\pi$($^{31}$P) = 161.9 MHz ($B_0 = 9.38$ T), $\omega_{0}/2\pi$ = 10 kHz) of TMPO dosed on Sn-Beta-300a at different loading levels. Experimental NMR spectra are shown in black (lower traces), while the simulated spectra are shown in gray (upper traces). The gray dashed lines indicate the main resonance positions with corresponding Gaussian peak curves shown in light pink ($\delta_{wm} = 54.9$ ppm), pink ($\delta_{wm} = 55.8$ ppm), and blue ($\delta_{wm} = 54.9$ ppm). Deconvolutions for minor peaks ($\leq 1.5$ ppm, full width at half-maximum, fwhm) observed when TMPO is bound to Lewis acidic sites in Sn-Beta is a result of the low-defect zeolite pore structure that confines the TMPO molecules to specific geometries, providing a highly ordered chemical environment with a narrow range of chemical shifts associated with each type of Sn site. These confinement effects and the high sensitivity of $^{31}$P NMR allow excellent distinction between TMPO molecules in different chemical environments.
The relative quantity of TMPO occupying different sites in the Sn-Beta zeolite is reflected by the integrated areas of the $^{31}$P NMR peaks. At low TMPO loadings (e.g., TMPO/Sn molar ratio = 0.12), two resonances appear at $\delta_{iso} = 58.6$ and 54.9 ppm at a ratio of ca. 3:1. When the TMPO dosing is increased to TMPO/Sn = 0.48, the areas of these two resonances increase while maintaining an approximate 3:1 ratio. New resonances with relatively low area ($\leq 5\%$) are observed at $\delta_{iso} = 63.1, 61.3, 59.9,$ and 57.2 ppm. At TMPO loadings above unity (i.e., TMPO/Sn = 1.09 and 1.14), the $^{31}$P NMR resonances at $\delta_{iso} = 59.9$ and 57.2 ppm increase in intensity along with a new, relatively high intensity signal (20–25%) at $\delta_{iso} = 55.8$ ppm. At these higher TMPO concentrations, additional low intensity resonances ($\leq 5\%$) appear at $\delta_{iso} = 66.0, 53.6, 51.5,$ and $\leq 50.5$ ppm.

Importantly, samples with TMPO/Sn > 1 contain an excess of TMPO relative to the quantity of Sn sites, so at least one of the observed signals in the $^{31}$P NMR spectra must be generated by TMPO molecules that are not associated with Sn and/or by a second TMPO molecule bound to a Sn site that is already titrated.

The $^{31}$P isotropic chemical shifts observed for TMPO adsorbed on Sn-Beta ($\delta_{iso} = 66.0$ to 50.5 ppm) lie within the range expected for adducts formed between TMPO and either Brønsted or Lewis acids. TMPO adsorption studies on various amorphous and microporous crystalline aluminiumosilicates with Brønsted acidity featured $^{31}$P NMR signals in the range from $\delta_{iso} = 75$ to 50 ppm, and TMPO bound to Lewis acid sites in TS-1 have been assigned a chemical shift of 53.7 ppm. Density functional theory (DFT) calculations predicted that resonance frequencies of $^{31}$P nuclei in Lewis acid-TMPO adducts of B, Al, and Ti chloro and fluoro compounds lie between $\delta_{iso} = 55$ and 38 ppm. The $^{31}$P magnetic shielding for TMPO adsorbed in a zeolite is sensitive to its local chemical environment as dictated by the nature of the active site and the topology of the pore. In the context of molecular orbital theory, a stronger binding Lewis acid will pull more electron density from the highest occupied molecular orbital (HOMO) of the TMPO oxygen molecule to the lowest unoccupied molecular orbital (LUMO) of the Lewis acid, affecting the magnetic field experienced at the phosphorus nucleus. However, the interaction of the TMPO with different Sn environments such as T-site locations, coordination number, and orientation within unique pore geometries can influence the $^{31}$P chemical shift when the TMPO is bound to a Lewis acid, making it difficult to make definitive assignments of acid strength exclusively from changes in chemical shift.

A series of control samples (Figure S1) was used to assist in the assignment of $^{31}$P MAS NMR resonances. In agreement with previous studies of TMPO adsorbed on HZSM-5 and MCM-41, the $^{31}$P MAS NMR spectrum of TMPO dosed on Sn-Beta consisted of a single resonance at $\delta_{iso} = 41$ ppm corresponding to physisorbed TMPO. The broad signal observed for this species, with a fwhm of 9 ppm, reveals that physisorbed TMPO is more disordered within the zeolite pore structure than TMPO coordinated to Lewis acid sites. No additional resonances appear for Si-Beta containing extra-framework SnO$_2$ clusters, indicating that these species do not bind TMPO to a significant degree. The $^{31}$P MAS NMR spectrum of TMPO dosed on a highly defective Si-Beta obtained by dealumination of Al-Beta (Si/Al molar ratio of 12.5) consisted of a broad resonance (fwhm = 11.3 ppm) at $\delta_{iso} = 43.5$ ppm. Importantly, NMR spectra of these controls do not show resonances centered at frequencies higher than $\delta_{iso} = 50$ ppm, such as those present in the NMR spectra of Sn-Beta samples, which we have assigned to TMPO interacting with Sn sites in framework positions.

The interaction of water molecules with TMPO and/or the Sn site(s) was ruled out using $^1$H MAS NMR spectroscopy. Clean dosed samples showed a single resonance at $\delta_{iso} = 1.5$ ppm corresponding to the methyl protons in TMPO (Figure S2a). Remnant fluoride ions from synthesis that may remain within the zeolite even after washing and calcination could also affect TMPO/Sn interactions. Fluorine-19 MAS NMR spectra (Figure S2b) showed only a minute quantity of SiF$_6^{−}$ species present in the zeolite. As such, we concluded that TMPO/F$^{−}$ or TMPO/Sn/F$^{−}$ complexes are not associated with the major resonances observed by $^{31}$P MAS NMR spectroscopy. It cannot be excluded, however, that these species correspond to the resonances featuring low TMPO occupancy, such as at $\delta_{iso} = 66.0, 63.1,$ or $\leq 50.5$ ppm.
The combined results from the incremental dosing of Sn-Beta and control experiments, along with reported assignments from the literature, were used to make preliminary assignments for the $^{31}$P MAS NMR resonances. Given that the resonances at $\delta_{\text{iso}} = 58.6$ and 54.9 ppm appear at low TMPO loadings and are selectively titrated with increased dosing, we believe that they correspond to adducts composed of one TMPO molecule bound to one framework Sn site. Based on assignments reported in the literature, $^{31}$P NMR peaks between $\delta_{\text{iso}} = 66.0$ and 61.3 ppm most likely correspond to TMPO interacting with Brønsted acidic sites. These assignments are in agreement with our results showing low occupancy for these sites, which could arise from a small number of silanol groups or other defect sites that possess weak Brønsted acidity.

The $^{31}$P resonances at $\delta_{\text{iso}} = 53.6, 51.5, \leq 50.5$ ppm account for a relatively small portion of TMPO molecules and appear only at higher concentrations, which could be due to either TMPO interacting with a weaker or minor site in the zeolite framework or TMPO binding at an existing Sn-TMPO adduct. The resonances at $\delta_{\text{iso}} = 59.9, 57.2$, and 55.8 ppm accounted for a significant fraction of TMPO; however, definitive assignment could not be made from the incremental dosing experiments alone and required correlations with other NMR measurements (vide infra).

Peak assignments were further refined by using data from $^{119}$Sn MAS NMR spectra of $^{119}$Sn-enriched Sn-Beta samples with a Si/Sn ratio of ~300 ($^{119}$Sn-Beta-300m, synthesized with $^{119}$Sn-enhanced metal precursor) dosed with TMPO (Figure 2, Table S1). As expected, pristine, dehydrated $^{119}$Sn-Beta-300m exhibits sharp $^{119}$Sn resonances at $\delta_{\text{iso}} = -434$ and $-443$ ppm corresponding to two different four-coordinate, pseudotetrahedral Sn ($^[4]$Sn) environments in the zeolite framework with approximately a 30:70 ratio (Figure 2a). In addition to these two sharp resonances, a broad component spanning the $^[4]$Sn region was observed, which could be potentially attributed to disordered Sn distributed randomly throughout the framework. When TMPO was adsorbed onto $^{119}$Sn-Beta-300m at a ratio of TMPO/Sn = 0.52 (Figure 2b), the $^{119}$Sn MAS NMR spectrum showed a single peak at $\delta_{\text{iso}} = -450$ ppm corresponding to pseudotetrahedral Sn and two new signals at $\delta_{\text{iso}} = -600$ and $-582$ ppm assigned to penta-coordinated Sn ($^[5]$Sn).

Importantly, the resonances at $\delta_{\text{iso}} = -600$ and $-582$ ppm appeared at a 3:1 ratio and could be clearly assigned to the two sites with $^{31}$P MAS NMR resonances at $\delta_{\text{iso}} = 58.6$ and 54.9 ppm, which appeared in approximately the same ratio (4:1, Figure 2e). The spinning sideband manifolds were accounted for in these area ratios due to a considerable chemical shift anisotropy (CSA) contribution observed experimentally and our inability to attenuate the spinning sidebands at moderate spinning frequencies. A minor contribution of six-coordinate Sn ($^[6]$Sn, ~5%, estimated from experiments acquired using multiple spinning frequencies at both 7.1 and 11.7 T) was observed for this sample. Unfortunately, the low S/N and appreciable spinning side bands from the $^[5]$Sn signals did not allow us to determine the exact chemical shift or concentration of this $^[6]$Sn site.

Phosphine oxides are known to form 2:1 Sn-TMPO adducts with organotin chlorides in the presence of excess phosphine.
oxide. At higher TMPO loadings, it is likely that two TMPO molecules will coordinate to a single Sn center, resulting in $[^6]Sn$ that will appear at low frequency in the $^{119}Sn$ NMR spectrum. Accordingly, the TMPO loading to TMPO/Sn = 1.17 resulted in the appearance of a high intensity resonance at $\delta_{iso}(^{119}Sn) = -735$ ppm corresponding to hexa-coordinated, pseudo-octahedral Sn (Figure 2c). The $^{31}P$ (Figure 2f) and $^{119}Sn$ MAS NMR spectra provide TMPO occupancies and relative $[^5]Sn$ speciation that are consistent with our preliminary peak assignments: the ratio of peak areas at $\delta_{iso}(^{119}Sn) = -600/-582$ ppm and $\delta_{iso}(^{31}P) = 58.6/54.9$ ppm are generally consistent at ca. 3:1 to 2:1. As expected, no four-coordinate Sn remains at this excess titration level.

Introduction of a second TMPO molecule to an existing Sn-TMPO adduct (corresponding to either $\delta_{iso}(^{31}P) = 58.6$ or 54.9 ppm) should theoretically result in two new $^{31}P$ signals: the first signal being the new $\delta_{iso}(^{31}P)$ of the original TMPO molecule now featuring a new chemical environment arising from the presence of a second TMPO molecule in close proximity and the second signal being for the second TMPO molecule. It is important to note that it is impossible to know directly from our NMR results whether TMPO at the $[^3]Sn$ site that becomes doubly titrated originally had a chemical shift at $\delta_{iso}(^{31}P) = 58.6$ or at 54.9 ppm. To further probe which $^{31}P$ resonances correspond to the TMPO molecules contributing to the $[^6]Sn$ signal, we conducted a $^{31}P$ double quantum-single quantum (DQ-SQ) NMR experiment on the TMPO/Sn = 1.17 sample (Figure S3). Despite the low S/N observed even after 670 h of continuous acquisition, the $^{31}P$ DQ-SQ NMR spectrum clearly shows that the $^{31}P$ chemical shifts at $\delta_{iso} = 59.9$ and 57.2 ppm are correlated and confirm that these two species are bound to the same $[^5]Sn$ Lewis acid site. These signals are present approximately in a 1:1 ratio in the $^{31}P$ NMR spectra of the TMPO/Sn = 1.17 sample, as well as in the $^{31}P$ NMR spectra of other samples dosed with TMPO/Sn ratios of $\sim$1 (vide infra). With this information in hand, we note that the $^{31}P$ NMR spectrum of the TMPO/Sn = 0.52 sample also featured these two signals (albeit with low intensities), which is consistent with the small amount of $[^4]Sn$ present in the corresponding $^{119}Sn$ MAS NMR spectrum. The $^{31}P$ DQ-SQ NMR spectrum also confirmed our assignments of $\delta_{iso}(^{31}P) = 58.6$ and 54.9 ppm to $[^5]Sn$ environments, as these chemical shifts were only observed in low intensity along the DQ-SQ diagonal (i.e., they are not correlated to one another or to other $^{31}P$ resonances). Unfortunately, the $^{31}P$ DQ-SQ NMR results could not discriminate between single or double TMPO binding environments for the remaining $^{31}P$ signals, including the relatively intense signal at $\delta_{iso}(^{31}P) = 55.8$ ppm, due to the low sensitivity for this experiment.

In theory, the total amount of TMPO obtained from adding the $^{31}P$ MAS NMR peak areas from the assigned $[^5]Sn$ and $[^4]Sn$ sites (i.e., $\delta_{iso} = 58.6, 54.9, 57.2$ (or 59.9), and 55.8 ppm) for a fully titrated Sn-Beta sample should equal the total amount of framework Sn sites present in the sample. When this calculation was performed using the TMPO/Sn = 1.17 sample, the sum accounted only for $69-76\%$ of the total Sn content as compared to the value obtained with elemental analysis. We also found that the fraction of $[^4]Sn$ in the TMPO/Sn = 0.52 sample (Figure 2b) calculated from the $^{119}Sn$ MAS NMR spectrum was less than the expected value. This disparity indicated that the $^{119}Sn$-Beta-300m sample had at least 20% of disordered $[^4]Sn$ (possibly appearing as a broad resonance
Catalytic activity was tested using a packed bed liquid flow reactor as described in the Experimental Procedures section of the Supporting Information, and site-time-yields (STY) for each reaction were normalized by the total Sn content measured by elemental analysis (Table 1 and Figure S9).

**Glucose Isomerization.** The rate of glucose isomerization for Sn-Beta ranged from 9.5 to 29.3 (mol fructose) (mol total Sn)\(^{-1}\)h\(^{-1}\), with catalysts synthesized using SnCl\(_2\)-2H\(_2\)O as the Sn precursor typically showing higher activity than those synthesized using Sn metal dissolved in HCl. Additionally, catalysts with higher Sn loadings (Sn-Beta-100 and Sn-Beta-150m) appeared to be less active when normalized by total Sn content, suggesting that less of the metal was incorporated into the zeolite in configurations active for glucose isomerization. This effect is not surprising considering the thermodynamic limitations of incorporating a high Sn content (100:1 Si/Sn molar ratio) via hydrothermal synthesis.\(^{42}\) Indeed, the crystallization time required for Sn-Beta-100 was 32 days compared to 7 days for Sn-Beta-300b.

To establish a relationship between Sn speciation in Sn-Beta and the glucose isomerization activity, STYs were plotted against the % integrated peak area normalized by total Sn content (Figure S10). Resonances used for these comparisons were chosen according to our assignments for \(^{[5]}\)Sn and \(^{[6]}\)Sn (vide supra). Note that if a particular Sn configuration is responsible for catalytic turnover, then the addition of the integrated peak area from the \(^{31}\)P spectra corresponding to 100% of the \(^{[5]}\)Sn area and 50% of the \(^{[6]}\)Sn area (i.e., the area of only one of the two TMPO resonances from the pair) should correlate with the reaction rate. Since the NMR analysis alone could not conclusively inform which \(^{[5]}\)Sn site gained a second TMPO molecule to produce the \(\delta_{iso}^{(\text{P})}\) of 59.9/57.2 ppm pair, we considered both options: (a) \(\delta_{iso}^{(\text{P})} = 54.9 + 59.9/57.2\) ppm and (b) \(\delta_{iso}^{(\text{P})} = 58.6 + 59.9/57.2\) ppm. The resonance at 55.8 ppm was included in the analysis for other combinations because it contributed a significant fraction of the \(^{31}\)P peak area for several samples. Other resonances with relatively low occupancy were not considered in site combinations due to their small contribution to the total area relative to the increase in error from adding more sites. Nonetheless, all the trends from individual resonances are plotted for completeness in the Supporting Information (Figures S11 and S12). One would expect that if a unique site titrated by TMPO were responsible for catalytic activity, then a plot of the STY versus the \(^{31}\)P peak areas associated with that site would exhibit a positive linear trend that intersects the origin. Such a trend was only observed for glucose isomerization when combining the contributions from the \(^{31}\)P NMR resonances at \(\delta_{iso} = 55.6\) and 54.9 ppm (Figure 3a). This combination yielded a relatively good linear fit with an R\(^2\) value of 0.69 and intersected the origin within error. Including either doubly titrated site, \(\delta_{iso} = 59.9\) or 57.2 ppm (Figure S10e and h), with this set also resulted in linear fits, but the x-intercepts were significantly offset, suggesting these combinations overcounted sites (i.e., it included sites that were not active). Similar trends were obtained when combining all possible sites (both \(^{[5]}\)Sn sites and one \(^{[6]}\)Sn, Figure S10b and c). The analysis for a single \(^{[5]}\)Sn site at \(\delta_{iso} = 54.9\) ppm (not including 55.8 ppm), a single \(^{[6]}\)Sn site at \(\delta_{iso} = 58.6\) ppm, or the combination of the \(^{[5]}\)Sn site at \(\delta_{iso} = 58.6\) ppm plus either of the \(^{[6]}\)Sn sites at \(\delta_{iso} = 59.9\) or 57.2 ppm did not produce linear fits.

From these data, we concluded that the active site for glucose isomerization corresponds to the site(s) titrated by TMPO having a \(^{31}\)P resonance located at \(\delta_{iso}^{(\text{P})} = 55.6\) and 54.9 ppm. The concentration of this active site ranged from 12 to 33% of the total Sn content for our samples, which is in remarkable agreement with the concentrations of glucose isomerization active sites (13–33%) calculated by Harris et al. using acetonitrile adsorption and FTIR spectroscopy for a variety of fluoride-synthesized Sn-Beta samples.\(^{20}\) These data also suggest that the \(^{[6]}\)Sn with \(\delta_{iso}^{(\text{P})} = 59.9/57.2\) ppm are not associated with the \(^{[5]}\)Sn peak at \(\delta_{iso}^{(\text{P})} = 54.9\) ppm. While it is clear that the TMPO resonance that appears at \(\delta_{iso}^{(\text{P})} = 55.8\) ppm is important for reactivity, we cannot conclusively assign its identity due to the low S/N and high error in our \(^{119}\)Sn NMR measurements. However, we hypothesize that it likely arises either from a \(^{[6]}\)Sn environment resulting from the double titration of the site with \(\delta_{iso}^{(\text{P})} = 55.8\) ppm.

![Figure 3. Site time yield (STY) for (a) glucose isomerization in water and (b) aldol condensation of benzaldehyde and acetone in toluene catalyzed by different Sn-Beta catalysts plotted against the percent integrated \(^{31}\)P peak area normalized by P and Sn content at (a) \(\delta_{iso} = 55.8\) and 54.9 ppm and (b) \(\delta_{iso} = 58.6\) and 57.2 ppm. The integrated \(^{31}\)P peak area is related to the concentration of TMPO bound to Sn sites with a particular geometry: % Integrated \(^{31}\)P peak area at X ppm = (mol TMPO/g-cat) (mol Sn/g-cat)\(^{-1}\) (area % at \(\delta_{iso} = X\) ppm). The red lines are linear fits of the data.](image-url)
exhibited by Sn-Beta samples for the two reactions (Figure S9).

For glucose isomerization due to the di‐aldol condensation proceed via di‐aldol condensation. Glucose isomerization and aldol condensation are competitive reactions. For example, while Sn-Beta-150m featured the lowest activity for glucose isomerization, it showed the highest activity for aldol condensation. This can be attributed to the different activation barriers for each reaction. Catalytic activity results were only found for the combination of the [5]Sn site at δ_{iso} = 58.6 ppm and either δ_{iso} = 59.9 or 57.2 ppm of the [6]Sn site pair. As shown in Figure 3b, the trend for combining δ_{iso} = 58.6 and 57.2 ppm fits especially well with an R² value of 0.79 and a y‐intercept at the origin. Importantly, these results support our hypothesis that [6]Sn TMPO sites at δ_{iso} (31P) = 59.9 and 57.2 ppm correspond to the double titration of the δ_{iso} (31P) = 58.6 ppm site. The goodness of fit worsens (R² = 0.49) and the y‐intercept increases when using the peak area for δ_{iso} = 59.9 ppm instead of 57.2 ppm for the [6]Sn position in combination with the [5]Sn at δ_{iso} = 58.6 ppm, likely because of the poor fitting of the peak at 59.9 ppm for one of the samples (Sn-Beta-300a, TMPO/Sn = 1.14). This sample had a much higher value (24%) for the δ_{iso} = 59.9 ppm peak area than that for the slightly lower loading on the same zeolite (Sn-Beta-300a, TMPO/Sn = 1.09, 13%). When this potential outlier was removed, the fit improved to R² = 0.81, and the slope and y‐intercept more closely matched those seen for the fit using the δ_{iso} = 57.2 ppm values. Indeed, a careful balance of TMPO loading must be kept in order to fully titrate the tetrahedral sites without introducing new environments that convolute the spectra and prevent proper analysis.

We reasoned that if the [5]Sn site at δ_{iso} (31P) = 58.6 ppm is active for the aldol condensation, then direct titration of these sites with TMPO should result in a proportional decrease in catalytic activity. Titration experiments were conducted by dosing Sn-Beta-300b at two TMPO loadings, 16 and 57%, before testing the catalytic activity for aldol condensation in a packed bed reactor. ICP-MS experiments performed post‐reaction showed that over 97% of the dosed TMPO molecules remained bound to the catalyst after reaction. However, 31P MAS NMR spectra of the samples acquired after reaction (Figures 4b and d) showed changes in the environment of the bound TMPO compared to the prereaction spectra (Figures 4a and c), with a large fraction of the total integrated signals appearing at frequencies greater than 59 ppm. These changes can be attributed to deviations from the ideal geometry for TMPO-Sn complexes that could be caused either by alterations to the zeolite structure during reaction or by the presence of adsorbed compounds that remained in the pores after reaction.

Figure 4. (a–d) 31P MAS NMR spectra (ω_{r} = 161.9 MHz (B_{0} = 9.38 T), ω_{r}/2π = 10 kHz) of TMPO dosed on Sn-Beta-300m before (a and c) and after (b and d) it was used as the catalyst for aldol condensation of benzaldehyde and acetone in a packed bed reactor, as shown in Figure S17. TMPO/Sn = 0.16 for a and b and TMPO/Sn = 0.57 for c and d. Spinning sidebands appear outside the field of view. Dashed lines at δ_{iso} = 58.6 ppm (blue) and δ_{iso} = 54.9 ppm (violet) are used as a guide to show shifts after reaction. (e) STY for aldol condensation of benzaldehyde and acetone plotted against the % titration on a total Sn basis. The dashed grey line in d is the theoretical linear titration curve where 0% titration results in full activity and 100% titration results in no activity.

54.9 ppm or from a separate [5]Sn site that has similar reactivity to the site at δ_{iso} (31P) = 54.9 ppm. Importantly, these assignments are consistent with the ratio of the two [4]Sn sites (δ_{iso} = −443 and −434 ppm, 70:30) seen in the 119Sn MAS NMR spectra of pristine 119Sn-Beta-300m. For the TMPO analysis of this sample, the ratio of integrated peak area for sites associated with δ_{iso} (31P) = 58.6 and 59.9/57.2 ppm versus sites associated with δ_{iso} (31P) = 55.8 and 54.9 ppm is ca. 2:1. Taken together, these data suggest that the 31P resonances at δ_{iso} (31P) = 58.6 and 59.9/57.2 ppm, which are assigned to [4]Sn and [6]Sn, respectively, originate from the [4]Sn site at δ_{iso} (119Sn) = −443 ppm. Analogously, the 31P resonances at δ_{iso} (31P) = 55.8 and 54.9 ppm can be attributed to TMPO binding the [4]Sn site at δ_{iso} (119Sn) = −433 ppm.

Aldol Condensation. TMPO analysis was also conducted to determine the active site speciation for aldol condensation of benzaldehyde (BA) and acetone in toluene. The STYs for this reaction ranged from 5.1 to 7.8 (mol BA) (mol Sn)^−1 (Figures 4c and 4d). As shown in Figure 4c, the trend for combining δ_{iso} = 58.6 and 57.2 ppm fits especially well with an R² value of 0.79 and a y‐intercept at the origin. Importantly, these results support our hypothesis that [6]Sn TMPO sites at δ_{iso} (31P) = 59.9 and 57.2 ppm correspond to the double titration of the δ_{iso} (31P) = 58.6 ppm site. The goodness of fit worsens (R² = 0.49) and the y‐intercept increases when using the peak area for δ_{iso} = 59.9 ppm instead of 57.2 ppm for the [6]Sn position in combination with the [5]Sn at δ_{iso} = 58.6 ppm, likely because of the poor fitting of the peak at 59.9 ppm for one of the samples (Sn-Beta-300a, TMPO/Sn = 1.14). This sample had a much higher value (24%) for the δ_{iso} = 59.9 ppm peak area than that for the slightly lower loading on the same zeolite (Sn-Beta-300a, TMPO/Sn = 1.09, 13%). When this potential outlier was removed, the fit improved to R² = 0.81, and the slope and y‐intercept more closely matched those seen for the fit using the δ_{iso} = 57.2 ppm values. Indeed, a careful balance of TMPO loading must be kept in order to fully titrate the tetrahedral sites without introducing new environments that convolute the spectra and prevent proper analysis.

We reasoned that if the [5]Sn site at δ_{iso} (31P) = 58.6 ppm is active for the aldol condensation, then direct titration of these sites with TMPO should result in a proportional decrease in catalytic activity. Titration experiments were conducted by dosing Sn-Beta-300b at two TMPO loadings, 16 and 57%, before testing the catalytic activity for aldol condensation in a packed bed reactor. ICP-MS experiments performed post‐reaction showed that over 97% of the dosed TMPO molecules remained bound to the catalyst after reaction. However, 31P MAS NMR spectra of the samples acquired after reaction (Figures 4b and d) showed changes in the environment of the bound TMPO compared to the prereaction spectra (Figures 4a and c), with a large fraction of the total integrated signals appearing at frequencies greater than 59 ppm. These changes can be attributed to deviations from the ideal geometry for TMPO-Sn complexes that could be caused either by alterations to the zeolite structure during reaction or by the presence of adsorbed compounds that remained in the pores after reaction.
Thermogravimetric analysis (TGA) of the 16% TMPO titration catalyst postreaction showed a 2.3 wt % loss between 423 and 913 K (Figure S16), confirming that organic deposits remained occluded in the pores after drying. Additionally, we were unable to rule out the possibility that a TMPO molecule originally adsorbed at a specific site (e.g., the $\delta_{\text{iso}} = 54.9$ ppm site in the 16% titration sample) could desorb and then readorb at a different location in the material during reaction, since the experiments were conducted at elevated temperatures (383 K) in organic solvent (toluene). The steady state STYs for Sn-Beta samples titrated with TMPO at 16 and 57% decreased by 7.5 and 52%, respectively, compared to the nontitrated control sample (Figures 4e and S17). This decrease in activity can be attributed to TMPO molecules binding to active sites and preventing their participation in catalysis. Since the postreaction characterization showed that TMPO remained in the zeolite throughout the reaction but could not cocrorate which sites remained titrated (and we do not know if a site can remain active while singly titrated as opposed to doubly titrated), we could not explicitly correlate the drop in activity to the titration of a specific site. However, these results confirm that TMPO must bind to active sites, thus validating our TMPO-based method to investigate active site speciation.

Discussion of Active Site Assignments for Sn-Beta. The difference in Sn-Beta active site assignment for glucose isomerization and aldol condensation is striking and significant. The current results are especially illuminating, as many theoretical and experimental researchers have previously proposed that the same site, a hydrolyzed “open” site, is the catalytic site for both of these reactions. This hypothesis cannot account for the activity for both types of reactions discussed in this research, as Sn sites corresponding to $\delta_{\text{iso}}$ (119Sn) = 58.6 and 59.9/57.2 ppm, i.e., $\delta_{\text{iso}}$ (119Sn) = −600 ppm, in our Sn-Beta zeolites are shown to catalyze aldol condensation while sites corresponding to $\delta_{\text{iso}}$ (119Sn) = 55.8 and 54.9 ppm, i.e., $\delta_{\text{iso}}$ (119Sn) = −582 ppm, are active for glucose isomerization. The molecular connectivity of tetrahedral Sn centers is important and a widely debated topic in the field of Lewis acid zeolites. The question of whether a fully connected distorted tetrahedron (closed site) or a singly hydrolyzed Si−O−M (open site) is the more active site for various reactions has been addressed several times in the open literature. Most studies have indicated that open sites are the active sites for glucose isomerization, as these configurations possess greater flexibility that reduces geometric distortion energy penalties for transition state formation and have added functionality due to the formation of metal hydroxy and silanol groups. However, a recent study by Ivanova and co-workers indicated that the experimental evidence for assigning a 119Sn MAS NMR resonance at $\delta_{\text{iso}} = −423$ ppm to an “open” configuration may be due to incomplete drying of the samples before analysis. Our TMPO dosing method is conducted under anhydrous conditions to prevent the interference of water on TMPO-Sn interactions, and the pretreatment conditions (573 K, 50 mTorr, > 12 h) would likely condense any open sites that would have formed in the materials after calcination. Therefore, we hypothesize that the 31P MAS NMR resonances at $\delta_{\text{iso}} = 58.6$ ppm and $\delta_{\text{iso}} = 54.9$ ppm correspond to TMPO bound to Sn atoms present in different crystallographic positions, or T-sites, in the framework. First-principle calculations on cluster models of Sn-Beta with dehydrated closed sites performed by Wolf and co-workers show that T-site dependence alone can explain experimentally observed 119Sn MAS NMR chemical shifts. Additionally, several studies focused on DFT calculations have shown that local geometry influences the substitution of Lewis acidic heteroatoms into siliceous zeolite frameworks and that the acidity of the site as measured by probe molecule binding will depend on the T-site location. Although we expect our materials to contain only closed sites before analysis via the TMPO method, it is entirely possible for water to hydrolyze Si−O−Sn bonds during reaction to form open sites in situ. This is especially relevant for glucose isomerization where the solvent is water but might not be a major factor for the aldol condensation reaction carried out in toluene. DFT calculations of Sn-Beta zeolites have shown that the thermodynamic favorability of forming an open site depends on the T-site position. Thus, the 31P MAS NMR resonances appearing at $\delta_{\text{iso}} = 55.8$ and 54.9 ppm, which were the only signals correlated with glucose isomerization activity, likely represent a TMPO molecule titrating a Sn site located at a T-site that is more prone to form an open site. This hypothesis resolves the contradictions on this topic found in the literature and is consistent with a recent study by Gounder and co-workers showing via coupled 119Sn DNP NMR measurements and DFT calculations that tetrahedral Sn sites in Sn-CHA are closed when dehydrated and hydrolyze upon hydration. Probing the Acid Sites of Lewis Acid Zeolites with Other Heteroatoms. We demonstrate the general applicability of our method to probe a wide range of Lewis acid heteroatoms by analyzing Ti-, Zr-, and Hf-Beta samples. The 31P MAS NMR spectra shown in Figure 5 demonstrate that
TMPO adsorption can resolve at least two distinct metal sites in the range of δiso ~60 to 50 ppm for all three framework heteroatoms. Additional resonances at frequencies higher than δiso = 60 ppm appear with relatively small integrated peak areas that, similar to the Sn-Beta samples, could be due to Brønsted acidity in these Lewis acid zeolites. The variability of the resulting 31P MAS NMR chemical shifts (up to 5.6 ppm difference between materials) suggests unique interactions between TMPO and the Lewis acid sites in these materials, which is expected since the electronic structures of the framework metal centers will vary depending on heteroatom identity. This effect is also consistent with reactivity studies showing a different order of catalytic activity for Sn, Ti, Zr, and Hf sites depending on the reaction used. For example, for the isomerization of lactose, the initial turnover rates for Sn-Beta are 60 times higher than those for Ti-Beta. In addition, the activation energy of Ti-Beta for the Meerwein–Ponndorf–Verley (MPV) reduction of methyl levulinate was 69 kJ/mol compared to 52 kJ/mol for the other M-Betas. In the case of olefin epoxidation catalyzed by M-Beta zeolites, Bregante and Flaherty demonstrated that activation enthalpies are correlated with two experimental descriptors of Lewis acid strength: heat of adsorption for acetonitrile and the ligand to metal charge transfer energy between the dioxygen reactive intermediates and the metal center. The periodic trends observed for these descriptors in the group IV M-Betas share similarities with the 31P NMR chemical shift of adsorbed TMPO: the value of the descriptors increases going down the group in the periodic table, with those for Ti-Beta differing significantly from the relatively similar values determined for Hf- and Zr-Beta.

While further studies are needed to corroborate if 31P chemical shifts of adsorbed TMPO can serve as a robust descriptor for Lewis acidity and catalytic activity, clearly TMPO adsorption can be used to verify and quantify framework concentration of these sites among the materials studied are consistent with the concentration of “open” sites that have previously been shown to be the active sites for this reaction. For aldol condensation, we have shown that the activity corresponds to a different type of Sn configuration in Sn-Beta, which manifests in the 31P NMR spectra at δiso = 58.6 ppm with double titrations at δiso = 59.9 and 57.2 ppm. Overall, this method could be used to analyze any Lewis acid zeolite for any of the reactions that they catalyze to determine which sites are responsible for catalytic activity. This research elucidates structure–function relationships in Lewis acid zeolites, enabling catalyst improvement through rational design.

**METHODS**

Zeolites were synthesized according to reported protocols and characterized by PXRD, N2 adsorption/desorption, DRUV, SEM, and ICP-MS. TMPO dosing was conducted on freshly calcined zeolite samples that were degassed overnight under dynamic vacuum at 573 K to remove any adsorbed water. Samples were thereafter handled under dry nitrogen conditions. A DCM solution containing a known amount of TMPO was added to the sample tube with the zeolite and stirred overnight at room temperature. Finally, DCM was removed via heating to 353 K under a vacuum. For 31P and 119Sn MAS NMR analysis, samples dosed with TMPO were packed under an inert atmosphere into zirconia MAS NMR rotors with gastight caps. A Gaussian deconvolution method was used to analyze the quantitative 31P MAS NMR spectra, and the % integrated peak area normalized by Sn content was calculated using the following formula: (mol site)/(mol total Sn) = (mol P/g-catalyst from ICP-MS) × (% peak area for specified site)/(mol Sn/g-catalyst from ICP-MS). Packed bed flow reactions were conducted in a tubular stainless steel reactor under differential conditions. Detailed methods and procedures can be found in the Supporting Information. No unexpected or unusually high safety hazards were encountered during this work.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b03533. Experimental procedures including synthesis protocols, catalyst characterization methods, TMPO doing procedures, NMR methods, and reaction procedures; supplemental data and figures for catalyst characterization, NMR, reactivity, and titration (PDF)

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**Notes**

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Extraframework Tin Sites in Zeolite Beta React Glucose Differently. Water.

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