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Interrogating the Lewis Acidity of Metal Sites in Beta Zeolites with ^{15}N Pyridine Adsorption Coupled with MAS NMR Spectroscopy

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45
46 **ABSTRACT:** The Lewis acidity of isolated framework metal sites in Beta zeolites was
47
48 characterized with ^{15}N isotopically-labeled pyridine adsorption coupled with magic-angle
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50 spinning nuclear magnetic resonance (MAS NMR) spectroscopy. The ^{15}N chemical shift of
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52 adsorbed pyridine was found to scale with the acid character of both Lewis (Ti, Hf, Zr, Nb, Ta
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54 and Sn) and Brønsted (B, Ga, and Al) acidic heteroatoms. The ^{15}N chemical shift showed a linear
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3 correlation with Mulliken electronegativity of the metal center in the order Ti < Hf < Zr < Nb <
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5 Ta < Sn < H⁺. Theoretical calculations using density functional theory (DFT) showed a strong
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7 correlation between experimental ¹⁵N chemical shift and the calculated metal-nitrogen bond
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9 dissociation energy, revealing the importance of active site reorganization when determining
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11 adsorption strength. The relationships found between ¹⁵N pyridine chemical shift and intrinsic
12
13 chemical descriptors of metal framework sites complement adsorption equilibrium data and
14
15 provide a robust method to characterize, and ultimately optimize, metal-reactant binding and
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17 activation for Lewis acid zeolites. Direct ¹⁵N MAS NMR detection protocols applied to the
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19 Lewis acid-base adducts allowed the differentiation and quantification of framework metal sites
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21 in the presence of extraframework oxides, including highly quadrupolar nuclei that are not
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23 amenable for quantification with conventional NMR methods.
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30 31 INTRODUCTION

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33 Pure-silica zeolites containing framework metal centers with open coordination sites have
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35 emerged as highly active, water tolerant solid Lewis acids.¹⁻⁴ For example, framework metal
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37 centers, such as Ti, Hf, Zr, Nb, Ta and Sn, have shown remarkable activity for the inter- and
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39 intra-molecular Meerwein–Ponndorf–Verley (MPV) reduction of aldehydes and ketones,⁵⁻⁷ the
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41 etherification of alcohols,^{6, 8-9} and the Baeyer–Villiger oxidation of ketones to lactones,¹⁰⁻¹² the
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43 isomerization/epimerization of carbohydrates,¹³⁻¹⁷ C-C coupling,¹⁸⁻²⁴ and hydrogen transfer
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45 reactions of high relevance to biomass conversion.²⁵⁻²⁸ The nature of the metal center and the
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47 degree of framework incorporation drastically influence reactivity.²⁹ For example, Davis and co-
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49 workers showed that octahedral extraframework SnO₂ and pseudo-tetrahedral framework Sn
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51 sites can catalyze the same reaction through completely different reaction pathways.³⁰
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3 Distinguishing framework and extraframework sites within the confines of a zeolite pore is
4 critical for assessing catalyst performance. Though reactivity studies provide the most direct
5 measure of framework incorporation, catalysts often have a complex mixture of sites leading to
6 an apparent overall activity. For example, in the isomerization of glucose to fructose with Sn-
7 Beta, various authors have attributed the observed decrease in turnover frequency with
8 increasing metal loading to the presence of framework Sn sites with different activities or the
9 formation of condensed SnO_x species.³¹⁻³²

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11 Spectroscopic methods provide additional insight into the nature of active sites and have been
12 used to obtain the site densities needed to calculate turnover frequencies. However, many of
13 these methods are difficult to implement reliably or routinely.⁶ For instance, diffuse reflectance
14 ultraviolet spectroscopy (DRUV)^{30-31, 33}, x-ray diffraction^{30, 34}, ¹¹⁹Sn Mossbauer spectroscopy³¹,
15 x-ray photoelectron spectroscopy (XPS)³³, and Raman spectroscopy^{31, 33} provide only qualitative
16 or semi-quantitative measurements. Synchrotron-based techniques are powerful, but difficult to
17 implement on a routine basis.³⁴ Magic-angle spinning nuclear magnetic resonance (MAS NMR)
18 spectroscopy can quantify the ratio of extraframework to framework metal sites, but is limited to
19 NMR-active nuclei. For instance, analysis of tin in Sn-Beta is accessible with NMR but requires
20 expensive ¹¹⁹Sn isotopic labeling.^{6, 16} Roman-Leshkov *et al.* and Hermans *et al.* have recently
21 shown that hyperpolarization techniques based on dynamic nuclear polarization (DNP) MAS
22 NMR can be implemented to characterize non-enriched Sn-Beta samples, but specialized NMR
23 equipment is required.^{31, 35} Recently, Ivanova *et al.* showed that other methods could be used to
24 obtain enhanced signals with unlabeled samples.³⁶ Other metals of interest, including Ti, Zr and
25 Hf, suffer from extreme challenges in NMR sensitivity that stem from low natural abundance,
26 large quadrupolar moment and/or low gyromagnetic ratios (as shown in Table S1).³⁷

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3 The adsorption of probe molecules has been an effective technique to interrogate acid sites in
4 zeolites. Infrared (IR) spectroscopy using pyridine to titrate solid acid sites has been utilized to
5 distinguish Lewis and Brønsted acid sites and provide quantitation with molar extinction
6 coefficients.³⁸ IR spectra of pyridine adsorption on zeolites has been used to determine acid
7 strength of several heteroatoms based on differences in vibrational frequencies.³³ The
8 frequencies for pyridine adsorbed on different Lewis acid sites (*i.e.*, Ti, Zr, Nb, Ta, Sn, Ga and
9 Al-Beta) appears in a very narrow range from 1445-1454 cm^{-1} as shown in Table S2.^{33, 39-42}
10 Gorte *et al.* showed that careful dosing of acetonitrile onto a dehydrated Sn-Beta sample gives
11 rise to vibrational signatures of the resulting adducts that differentiate framework from
12 extraframework sites with adequate resolution.⁴³ Recently, Gounder *et al.* determined molar
13 extinction coefficients for IR bands of pyridine adsorbed to Lewis acidic Sn sites and of
14 acetonitrile adsorbed to open and closed Sn sites.⁴⁴ Ivanova *et al.* used CO to characterize both
15 types of sites. As shown in Table S3, limited data exists on the full range of Lewis acidic metals.
16 Corma *et al.* performed a number of cyclohexanone adsorption experiments that cover a wider
17 range (shown in Table S4), but the resonance widths at half maximum of $\sim 25 \text{ cm}^{-1}$ do not
18 provide a high degree of resolution. We note that IR has limitations when analyzing samples in
19 the presence of water or other solvents due to unwanted adsorption frequencies that can interfere
20 with quantitative analysis.
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45 The magnetic shielding observed via NMR spectroscopy is highly sensitive to the local
46 electronic environment about the observed nucleus. As such, changes in the chemical shift for a
47 particular acid-base pair can be used to assess the Lewis acid character, to understand bond
48 activation at a specific site without bulk effects due to non-specific adsorption, and to infer
49 binding strengths both under hydrated and dehydrated environments.⁴⁵⁻⁴⁸ NMR has been used to
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3 characterize acidity of Lewis acid catalysts, for instance, by studying the interaction of
4 trimethylphosphine (TMP), trimethylphosphine oxide (TMPO), and acetone with the active
5 sites.⁴⁹ Similarly, ¹⁵N MAS NMR of adsorbed pyridine has been used to distinguish multiple acid
6 sites on γ -alumina with high resolution. Although pyridine ¹⁵N MAS NMR has been used to
7 probe the acidity of certain zeolites, the full range of Lewis acid metal-substituted Lewis acid
8 zeolites has not been investigated with this method.⁵⁰⁻⁵³

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10 Here, we assess the acid character of Beta zeolites with Lewis (Ti, Hf, Zr, Nb, Ta and Sn) and
11 Brønsted (B, Ga, and Al) acid centers by investigating the adsorption of pyridine with ¹⁵N MAS
12 NMR spectroscopy. We rationalize that the interaction of pyridine with the metal site leads to a
13 change in chemical shift of the ¹⁵N nucleus that can be correlated to fundamental measures of
14 Lewis acidity, such as bond dissociation energies and Mulliken electronegativities. We show that
15 the method is broadly applicable to investigate metal centers in zeolites under hydrated and
16 dehydrated conditions. Using direct detection MAS NMR, we show that quantitative
17 measurements can be performed on the pyridine-metal adducts, thereby yielding the ability to
18 differentiate and quantify the number of framework metal centers, including NMR-inactive
19 nuclei such as Zr and Hf.

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EXPERIMENTAL SECTION

Catalyst synthesis

Beta zeolites were synthesized based on the procedure reported by Corma *et al.*⁵⁴ using the following precursors: hafnium(IV) chloride, zirconium(IV) oxychloride octahydrate, tin(II) chloride dihydrate, titanium(IV) isopropoxide, tantalum(V) ethoxide, and niobium(V) ethoxide. Tin(II), which oxidizes to tin(IV) in water, was used in place of SnCl₄·5H₂O and resulted in Sn-Beta consistently free of extraframework SnO₂.⁵⁵ Briefly, Hf-Beta was synthesized as follows:

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3 aqueous tetraethylammonium hydroxide [27.16 g; Sigma–Aldrich, 35 wt% (TEAOH)] and
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5 tetraethylorthosilicate (23.97 g; Sigma–Aldrich, 99 wt%) were added to a Teflon
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7 [polytetrafluoroethylene (PTFE)] dish, which was magnetically stirred at 250 rpm and room
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9 temperature for 90 min. Additional deionized water (15 mL) was added, and the dish was cooled
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11 in an ice bath. Then, hafnium(IV) chloride (0.38 g; Sigma–Aldrich, 98 wt%) dissolved in ethanol
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13 (2 mL) was added drop wise while stirring. The solution was left uncovered on the stir plate for
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15 10 h to reach a total mass of 33.15 g after evaporation of ethanol and some of the water. Next,
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17 aqueous hydrofluoric acid (HF, 2.62 g; Sigma–Aldrich, 48 wt%) was added drop wise using a
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19 plastic syringe, and the mixture was homogenized using a PTFE spatula, resulting in a thick gel.
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21 Si-Beta (0.36 g) was seeded into the mixture. The preparation of Si-Beta is analogous to Sn-Beta
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23 but without seeding or metal addition. The weight of the resulting sol–gel was evaporated under
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25 light heating to 33.96 g over ca. 2 h, resulting in a final molar composition of 1 SiO₂/0.01
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27 HfCl₄/0.56 TEAOH/0.56 HF/7.5 H₂O. The thick paste was transferred to a PTFE-lined stainless
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29 steel autoclave (45 mL) and heated to 413 K for 20 days under static conditions. Mixing the
30
31 contents weekly can accelerate crystallization. The solids were recovered by filtration, washed
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33 with ultrapure deionized H₂O, and dried at 373 K. The zeolites were calcined under flowing dry
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35 air by heating to 853 K with a 1 K min⁻¹ ramp (with 1 h isothermal steps at 423 and 623 K) and
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37 kept at that temperature for 10 h. After calcination, the overall inorganic oxide yield was 80–
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39 90%.
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48 Sn-MCM-41 and Sn-MFI were synthesized according to previously published protocols using
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50 alkaline media.⁵⁶⁻⁵⁷ SnO₂/Si-Beta was prepared by incipient wetness impregnation of Si-Beta
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52 with an aqueous tin(IV) chloride solution, followed by drying at 383 K and calcination in air
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54 flow at 533 K. Mixed framework/extraframework ¹¹⁹Sn-Beta was made by calcination of the as-
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3 prepared material in a box furnace at 1173 K for 10 h with a 1 K min⁻¹ ramp and 1-hour stops at
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5 423 and 623 K flowing 100 mL/min of dry air. We note that analogous experiments showed
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7 negligible extraframework SnO₂ formation up to a temperature 1073 K, while temperatures
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9 above 1273 K led to pore collapse.
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12 **Catalyst characterization**

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14 Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was recorded on an
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16 Optima 2000 DV spectrometer (PerkinElmer Inc.). Samples were dissolved in a few drops of
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18 35% HF before dilution into 2.5% HNO₃. Powder x-ray diffraction (PXRD) patterns were
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20 collected using a Bruker D8 diffractometer using a CuK α radiation source between 5 and 45° 2 θ ,
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22 in 0.02° steps with a step time of 30 s. Ultra-violet/visible (UV/Vis) analysis was performed
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24 using a Varian Cary 5000 UV/Vis near-infrared spectrometer equipped with a Praying Mantis
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26 diffuse reflectance accessory. The spectra were collected at 190–450 nm and referenced to
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28 BaSO₄. N₂ adsorption–desorption isotherms were measured on a Quantachrome Autosorb iQ
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30 apparatus at liquid-nitrogen temperature (77 K). All samples were degassed under vacuum prior
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32 to use (623 K, 12 h). Micropore volumes were analyzed using the t-plot method.
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39 **Pyridine adsorption**

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41 Sample preparation consisted of weighing 100 mg of the catalyst, sealing in a 5 mL microwave
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43 vial and connecting to a Schlenk line. The air within the sample was purged out by alternating
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45 three times between vacuum and Ar, followed by heating the sample to 423 K for 2 h under
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47 dynamic vacuum. We note that these conditions have been shown to be sufficient to dehydrate
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49 defect-free Lewis acid zeolites synthesized in fluoride media. Samples were pre-dried before
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51 pyridine adsorption to promote uniformity among the sites and prevent competitive adsorption.
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53 The sample vial was refilled with Ar and removed from the Schlenk line. Next, ¹⁵N-labeled
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3 pyridine adsorption was performed by flowing pyridine saturated Ar over the sample at 423 K .
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5 Specifically, the vial containing the dried zeolite sample was connected with a cannula to another
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7 purged and septum-sealed vial containing ^{15}N pyridine under Ar flow (~ 30 mL/min). An open
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9 needle was then inserted into the vial containing the zeolite to avoid pressure build-up. For
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11 weakly binding oxide samples, such as SnO_2 -Beta, ZrO_2 -Beta, and Si-Beta, the adsorption
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13 temperature was reduced from 423 to 373 K. After 30 min, the sample vial was isolated,
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15 reconnected to the Schlenk line and placed under vacuum for 1 h at the corresponding adsorption
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17 temperature to remove physisorbed pyridine. Afterwards, the sample was transferred into a
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19 glovebox where it was opened and packed into an O-ring sealed ZrO_2 NMR rotor. For
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21 experiments probing hydrated sites, the zeolite sample was exposed to ambient moisture after
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23 dosing with pyridine.
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29 For quantitative runs, 10 mg of dry 98% ^{15}N -labeled glycine (Cambridge Isotope
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31 Laboratories, Andover, MA) was used as an internal standard by mixing together with the
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33 pyridine-dosed catalyst using a glass stir rod before packing into a rotor. For all pyridine
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35 quantitation experiments, zeolites were calcined under dry air immediately before pyridine
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37 dosing.
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41 **Nuclear magnetic resonance**

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43 MAS NMR experiments were performed on home-built spectrometers (courtesy of D. J.
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45 Ruben, Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology) operating at
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47 360 and 500 MHz (^1H Larmor frequency). The 360 MHz NMR spectrometer was equipped with
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49 either a double resonance home-built (FBML-MIT) or a triple resonance Varian-Chemagnetics
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51 probe (Palo Alto, CA), which were doubly tuned to $^{119}\text{Sn}/^1\text{H}$. The 500 MHz NMR spectrometer
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53 was equipped with a triple resonance Varian-Chemagnetics probe (Palo Alto, CA) doubly tuned
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3 to $^{15}\text{N}/^1\text{H}$. Powdered samples were packed into either 3.2 mm (26 μl fill volume) or 4 mm (80 μl
4 fill volume) outer diameter ZrO_2 rotors equipped with Vespel drive- and top-caps. Top-caps were
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6 fill volume) outer diameter ZrO_2 rotors equipped with Vespel drive- and top-caps. Top-caps were
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8 equipped with rubber O-ring seals to inhibit water contamination of the sample (Revolution
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10 NMR, Fort Collins, CO). Dry samples were prepared by heating to 423 K under a 10 Pa vacuum
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12 and packing the NMR rotor in an Ar-filled glovebox.

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15 ^{15}N cross polarization (CP)⁵⁸ MAS NMR spectra were acquired with a spinning frequency set
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17 to 9 kHz ($\omega_r/2\pi$) and regulated with a Bruker (Billerica, MA) MAS controller. The recycle delay
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19 was set to 1.5 seconds, 64k co-added transients were acquired and the temperature was
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21 maintained at 290 K. The spin-lock on ^{15}N during CP was optimized to match the Hartmann-
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23 Hahn condition⁵⁹ under MAS with $\gamma B_1/2\pi = 50$ kHz on protons during a contact time of 2.0 ms,
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25 which was maintained constant for all samples. Proton pulses and two pulse phase modulation
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27 (TPPM) decoupling⁶⁰ were optimized for $\gamma B_1/2\pi = 83$ kHz. All spectra were referenced
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29 externally to liquid ammonia (0 ppm NH_3). CP MAS NMR revealed the bound Brønsted sites
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31 and selectively probed bound pyridine molecules. ^{15}N chemical shielding anisotropy
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33 experiments⁶¹ were acquired using CP MAS NMR and a spinning frequency of 5 kHz
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35 (supporting information).

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37 For quantitative purposes, ^{15}N MAS NMR analyses used direct detection (Bloch) and spin-
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39 lattice relaxation times (T_1) were measured using either an inversion recovery or saturation
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41 recovery experiment. Typical T_1 's were on the order of 200 to 800 ms for ^{15}N and recycle delays
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43 were chosen to be 5 times T_1 (or greater) for all NMR experiments. All spectra were acquired
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45 using a 9 kHz spinning frequency and between 16384 and 32764 co-added transients. Spectra
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47 were processed using 125 Hz of an exponential apodization function. Spectra fitting of the
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49 pyridine and glycine resonances were performed using a single Lorentzian and the baseline with
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one sine function using least squares. All quantitative data were carefully fitted to account for the spinning side band intensity of the larger CSA of bound pyridine (span, $\Omega = 370$ ppm, skew, $\kappa = 0.8$) relative to the internal ^{15}N glycine ($\Omega < 15$ ppm, $\kappa = 0.05$) standard.

^{119}Sn MAS NMR spectra were acquired by performing a Hahn-echo (^{119}Sn , $\gamma B_1/2\pi = 50$ kHz) with recycle delays between 10 and 40 s, between 8192 and 35850 co-added transients, and a spinning frequency of 8 kHz. Typical T_1 's were on the order of 2 to 8 s for ^{119}Sn and recycle delays were chosen to be 5 times T_1 of the slowest relaxing site. ^{119}Sn spectra were referenced externally using a secondary reference solid, SnO_2 (-604.3 ppm, relative to tetramethyltin, 0 ppm).

Quantum chemical calculations

Detailed methods can be found in the supporting information. Simulations were run on a Unix cluster implementing Gaussian G09 revision B.01.⁶² A 17 tetrahedral model (17 T) of the Beta zeolite T2 site was created from the International Zeolite Association (IZA) crystallographic structure and the outer atoms were frozen with hydrogen atoms pointing in the direction of missing oxygen atoms for cluster termination. Hybrid density functional theory (DFT) geometry optimizations and energies were run at B3LYP/Def2-TZVPD level of theory⁶³⁻⁶⁵ and counterpoise corrections were applied to remove basis set superposition error. All of the metal atoms except Ti used an effective core potential (ECP). The reported energy values represent the electronic contribution to enthalpy and were not adjusted for the thermal correction since the vibrational frequencies of the zeolite cluster may be non-physical. Additional data were gathered at B3LYP/Def2-TZVP and Def2-TZVPPD to demonstrate convergence. Detailed descriptions of the methods used appear in the Supporting Information.

RESULTS AND DISCUSSION

The adsorption of ^{15}N -pyridine onto metal-substituted zeolites will form adducts that feature specific ^{15}N isotropic chemical shifts (δ_{iso}). The ^{15}N δ_{iso} of pyridine and pyridinium (protonated pyridine) are 317 and 211 ppm, respectively, yielding a 106 ppm chemical shift range that can be used to assess the acid character of specific pyridine-acid adducts⁶⁶⁻⁶⁷ Note that pyridine adsorption on an acid site causes a reduction in the span (Ω) of the ^{15}N CSA and the δ_t component, which lies in the plane of and tangential to the pyridine ring. This change appears as δ_{11} and δ_{22} in the chemical shift tensor for pyridine and pyridinium, respectively.⁶⁷ Consequently, after binding to an acid, the pyridine resonances will appear at lower frequency, which is opposite to the expected trend for the interaction between electron density-withdrawing sites and electron density-shielding nuclei (see Figure 1).

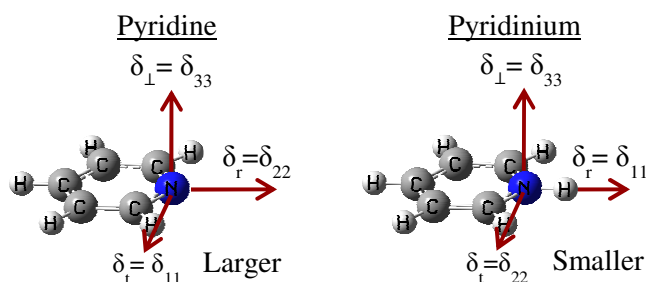


Figure 1. Rotation of CSA components into the pyridine radial δ_r , tangential δ_t , and perpendicular δ_{\perp} reference frame. The pyridine δ_t decreases upon binding to a proton or Lewis acid site, causing it to change from δ_{11} to δ_{22} in NMR nomenclature ($\delta_{33} \leq \delta_{22} \leq \delta_{11}$).

Figure 2 shows the ^{15}N δ_{iso} of pyridine adsorbed on a series of porous materials, including pure silica zeolites, metal-substituted and metal-impregnated zeolites, as well as mesoporous Sn-MCM-41. In the absence of framework metals, the defect-free Si-Beta showed no resonances associated with pyridine, while Si-Beta containing extraframework Sn and Zr oxides showed very weak Lewis acidity, with the appearance of a ^{15}N resonance near 318 ppm. Taken together,

these control experiments show that in the absence of framework metal sites, pyridine does not interact with a defect-free zeolite framework and that extra-framework heteroatoms feature ^{15}N chemical shifts to higher frequency (increase in ppm) of the chemical shift scale that correspond to weakly (or physisorbed) bound pyridine molecules. Our findings also agree with other surface and mesoporous silica studies as summarized in Table 1.

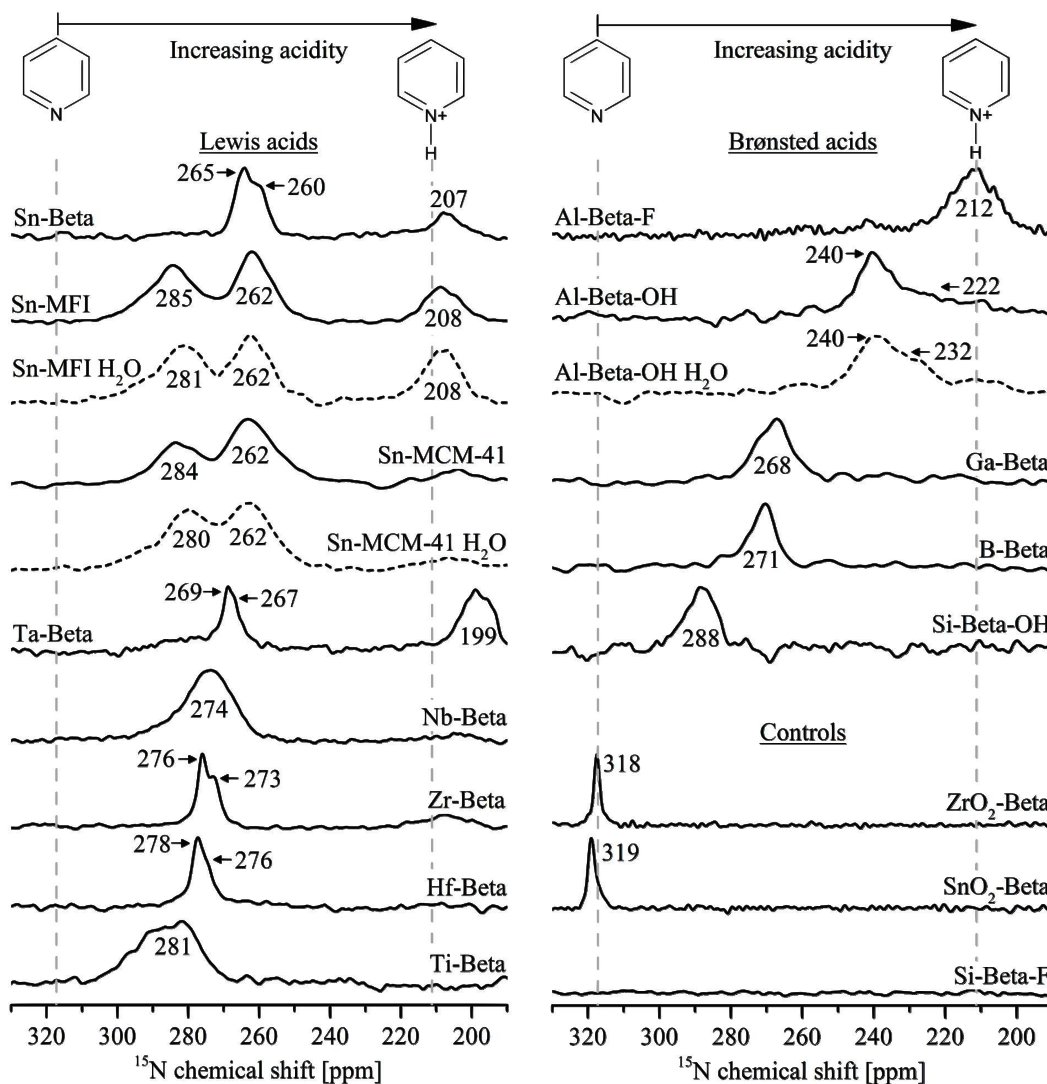


Figure 2. ^{15}N CP MAS NMR of pyridine adsorbed on metal-substituted zeolites. Spinning sidebands appear outside the field of view. Colored dashed data correspond to spectra of hydrated samples. While vertical gray lines correspond to non-bound pyridine (left) and pyridinium (right). H-Al-Beta-F had a Si/Al=50, H-Al-Beta-OH had a Si/Al=19 and all other materials had Si/Metal \approx 100.

Table 1: Summary of ^{15}N solid-state NMR chemical shift of nitrogen heterocycles in various environments

Sample	δ_{iso} (ppm, ± 1)	Ω (ppm)	κ	δ_{t} (ppm)	δ_{r} (ppm)	δ_{\perp} (ppm)	Ref.
Pyridine	317	622	0.46	580	413	-42	⁶⁶⁻⁶⁷
Physisorbed Pyridine (Mg-F-OH)	330	n.d.	n.d.	n.d.	n.d.	n.d.	⁶⁸
Physisorbed Pyridine Beta zeolite	319	n.d.	n.d.	n.d.	n.d.	n.d.	This Study
Collidine	307	539	0.4	530	375	9	⁶⁹
H ₂ O- Pyridine	300	n.d.	n.d.	n.d.	n.d.	n.d.	⁷⁰
Si-O-H- Pyridine	290	n.d.	n.d.	n.d.	n.d.	n.d.	⁷⁰
Mg-O-H- Pyridine	292	n.d.	n.d.	n.d.	n.d.	n.d.	⁶⁸
SnBeta- Pyridine	264	390 \pm 20	0.9 \pm 0.1	380	401	11	This Study
ZrBeta- Pyridine	278	365 \pm 20	0.8 \pm 0.1	375	411	47	This Study
MBeta- Pyridine (range)	270 \pm 10	370 \pm 20	0.80 \pm 0.1	-	-	-	This study
Co-Pyridine	265	488	0.96	423	430	-58	⁷¹
Mg-Pyridine	280	n.d.	n.d.	n.d.	n.d.	n.d.	⁶⁸
Al-Pyridine	233	n.d.	n.d.	n.d.	n.d.	n.d.	⁷²
Pyridinium	211	352	0.62	284	351	-1	⁶⁷
Mg- Pyridinium	205	n.d.	n.d.	n.d.	n.d.	n.d.	⁶⁸
Collidine- HB(Ph) ₄	187	250	0.05	189	309	59	⁶⁹

NB: All ^{15}N data is referenced relative to liquid ammonia (0 ppm). Solid $^{15}\text{NH}_4\text{Cl}$ is 39.3 ppm (relative to liquid ammonia), solid $^{15}\text{NH}_4\text{NO}_3$ is 22 ppm (relative to liquid ammonia) and $\text{CH}_3^{15}\text{NO}_2$ (neat) is 380.55 ppm (relative to liquid ammonia).⁵

The ^{15}N δ_{iso} of pyridine resolve the Brønsted acids in the expected order of acid strength as follows: silanols < B-Beta < Ga-Beta < Al-Beta. The resonance at 288 ppm for weakly acidic

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3 silanols defines a lower limit of Brønsted acid strength. The fluoride synthesized Al-Beta showed
4 a chemical shift of 212 ppm that is consistent with a fully protonated pyridine molecule, thus
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8 defining the upper limit of Brønsted acid strength in this scale (see Figure 3).
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11 In contrast to Brønsted acid sites, the interaction of pyridine with a Lewis acid site leads to a
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13 more diverse chemical shift range. This phenomenon can be rationalized from the Ramsey
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15 expression for NMR chemical shift by noting that the energy of the nitrogen sp^2 lone pair
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17 electron is located just below that of an anti-bonding π orbital associated with the pyridine ring.⁷³
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19 Binding to a Lewis acid allows the nitrogen electron lone pair to enter a definite lower energy σ
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21 bond with each metal center, leading to larger transitions to the anti-bonding π orbital and,
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23 consequently, a smaller chemical shift component. The isotropic chemical shift is the average of
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25 the chemical shift components and a reduction in the δ_t chemical shift component moves the
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27 resonance to lower frequency (*i.e.*, closer to pyridinium). Interestingly, the radial (δ_{22} in pyridine
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29 and δ_{11} in pyridinium) and perpendicular (δ_{33}) components of the chemical shift tensor are
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31 related exclusively to electronic transitions internal to the pyridine molecule. Since the lone pair
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33 is not involved in pyridine ring resonance and the pyridine geometry does not change drastically
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35 upon binding to a Lewis acid site, these chemical shift components are not significantly
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37 perturbed upon adsorption. Taken together, these features provide a robust and highly sensitive
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39 probe for assessing Lewis acid character.
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47 For our samples, the ^{15}N δ_{iso} of pyridine resolves the Lewis acid centers over a 20 ppm range,
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49 with the following order: $\text{Ti} < \text{Hf} < \text{Zr} < \text{Nb} < \text{Ta} < \text{Sn}$. Among the different Sn-containing
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51 structures, Sn-Beta shows the highest frequency Lewis acid character with a ^{15}N chemical shift
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53 of 260 ppm. Two overlapping ^{15}N pyridine resonances are observed for most materials, which
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55 we hypothesize correspond to the strong and weak sites in analogy with the two ^{119}Sn resonances
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3 observed in the ^{119}Sn NMR spectrum of dehydrated samples for tetrahedrally-coordinated Sn
4 atoms.^{6, 16} Sn-MFI and the mesoporous Sn-MCM-41 have similar Sn resonances centering at 262
5 ppm as well as a resonance near 285 ppm consistent with the presence of silanol groups (i.e., Si-
6 OH---Pyridine) in the framework.⁷⁰ In an earlier work, Van der Waal *et al.* mention that, as a
7 hard Lewis acid, Ti prefers hard Lewis bases such as oxygen over pyridine (a Lewis base with
8 intermediate hardness).⁷⁴ In the presence of silanol groups, the authors suggest that pyridine
9 would preferentially deprotonate the Brønsted acidic silanol group rather than coordinating
10 directly with the Lewis acid site. However, we observe that the δ_{iso} of ^{15}N pyridine adsorbed on
11 Ti-Beta (281 ppm) is distinct from that on Si-Beta with defect sites (288 ppm) indicating that
12 pyridine likely preferentially interacts with framework Ti sites. The δ_{iso} of ^{15}N pyridine adsorbed
13 on framework Sn (*ca.* 263 ppm) is drastically different from that adsorbed on extraframework
14 SnO_2 (319 ppm) and, similarly, the δ_{iso} of ^{15}N pyridine adsorbed on framework Zr (275 ppm)
15 differs from that adsorbed on extraframework ZrO_2 (318 ppm). Hf and Zr have similar
16 resonances because Hf appears below Zr in the periodic table and the elements have similar
17 covalent atomic radii due to the Lanthanide contraction (*i.e.*, 1.50 Å vs. 1.48 Å). Nb and Ta show
18 intermediate ^{15}N δ_{iso} of 274 and 268 ppm, respectively. These metals are active in many
19 reactions catalyzed by isolated framework Hf, Zr and Sn sites and offer a higher charge to radius
20 ratio. Sn- and Ta-containing samples also exhibited small resonances associated with strong
21 Brønsted acidity near 210 ppm. For Ta, this effect may result from an inductive effect of the =O
22 group similar to that observed in sulfated zirconia. These NMR trends are in agreement with
23 prior work investigating probe molecule adsorption on zeolites with IR spectroscopy (*vide*
24 *supra*).

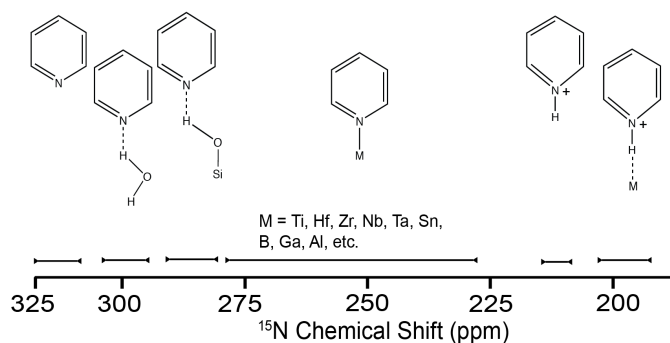


Figure 3: ^{15}N Solid-state NMR chemical shift scale of various pyridine binding environments.

In order to understand the catalytic behavior of Lewis acid sites in the presence of water, additional ^{15}N MAS NMR experiments were performed to study the substituted Beta zeolites under hydrated conditions. We anticipated that water would interact strongly with the metal site in the hydrophilic materials but more weakly in the hydrophobic materials, thereby influencing hydrogen bond networks near the active site.⁷⁵⁻⁷⁶ For the fluoride-synthesized zeolites, the results of pyridine adsorption are indistinguishable for dehydrated and hydrated samples, thus showing that the ^{15}N chemical shift data generated under dehydrated conditions may be applicable to hydrophobic materials under hydrated conditions. Extended silanol nests in hydrophilic materials can stabilize hydrogen bond networks and promote the presence of an extended water network in the pores. This effect is manifested in the slight changes in isotropic chemical shift for the hydroxide-synthesized and mesoporous materials that feature defect sites and terminal hydroxyl groups. As shown in Figure 2, a slight shift to lower frequency (decrease in ppm) in the leftmost ^{15}N resonance is observed for the Sn-MFI and Sn-MCM-41 samples, which is consistent with a displacement of pyridine from the weakest sites with water.⁷⁰

Changes in the width of the isotropic chemical shift and chemical shift anisotropy provide further information on the modes of complexation between pyridine and the metal center, while numerical analysis of the spinning sideband pattern provides additional structural information.⁷⁷

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3 The wide resonances observed for Ti-Beta correspond to a high degree of flexibility for the
4 pyridine-Ti adduct geometry. The ability for ^{15}N -pyridine molecules to bind to various T-sites is
5 thought to limit our ability to resolve $^1J(\text{M}, ^{15}\text{N})$ (where $\text{M} = ^{27}\text{Al}, ^{69/71}\text{Ga}, ^{93}\text{Nb}$ and ^{181}Ta) J-
6 couplings. J-couplings between ^{15}N -pyridine and highly abundant NMR-active nuclei may
7 contribute to the breadth of the ^{15}N isotropic chemical shift, as shown previously in pyridine
8 containing cobalt coordination complexes ($^{15}\text{N} - ^{59}\text{Co}$ (100% N.A.)).⁷¹ Slow spinning
9 experiments to study the chemical shift anisotropy (CSA) are shown in Figure S6 and
10 summarized in Table 1. Sn and Zr showed nearly identical patterns consistent with a similar
11 orientation of the chemical shift tensor. Additionally, a hydrated Sn-Beta showed the rise of a
12 disordered structure between 210 and 215 ppm, which we attribute to pyridinium interacting with
13 the metal center or simply residing as a physisorbed species within the pores.
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Assessing Lewis acidity

Using the ^{15}N isotropic chemical shift to assess Lewis acidity enables us to establish correlations with fundamental measures of Lewis acidity. There have been many attempts to find a fundamental parameter that quantifies Lewis acidity, which has proven to be particularly difficult for solids. The simplest and most widely used measure is the binding strength of a basic molecule onto an acid site. The most fundamental description for this interaction is represented by Fukui functions that describe the electron density in a frontier orbital resulting from a small change in the total number of electrons. These functions can be used to determine the degree of electrophilicity of an active site. Pearson *et al.* showed that the Mulliken electronegativity (χ) and the hardness (η), analogous to the first and second derivatives of energy with respect to number of electrons, respectively, can be used to measure Lewis acidity with more accuracy.⁷⁸ Applying a finite difference approximation for the first derivative and three-point finite difference approximation for the second derivative leads to operational definitions in terms of ionization potential (I) and electron affinity (A) as follows:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_V = \frac{1}{2}(I + A) \quad (1)$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_V = \frac{1}{2}(I - A) \quad (2)$$

Where μ is electronic chemical potential, E is the energy, N is the number of electrons, and V is the potential. As such, the Mulliken electronegativity can be interpreted as a finite difference approximation of the electronic energy with respect to the number of electrons, which provides a measure of how strongly a Lewis acid site can polarize a reactant.

Hard-soft acid base theory (HSAB) uses chemical hardness to describe deviations from a pure electronegativity analysis. Indeed, such deviations exclude the possibility of establishing a

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3 universal scale for all Lewis acid–base interactions. The HSAB theory suggests that hard acids
4 prefer to bind with hard bases and soft acids prefer to bind with soft bases. When the difference
5 between the highest occupied molecular orbital (HOMO) of the donor and lowest unoccupied
6 molecular orbital (LUMO) of acceptor is large, charge control involving electrostatic interactions
7 is dominant and hard-hard interactions are favored while, for smaller differences, frontier-
8 orbitals at the outer edge of a molecule are dominant. In the numerical version of HSAB,
9 represented in Equation 3 below, the difference in electronegativity drives the electron transfer
10 and the sum of the hardness parameters acts as a resistance leading to an overall charge transfer
11 of ΔN where C refers to the Lewis acid and B to the base. HSAB however does not take into
12 account the shapes and phases of the participating orbitals, says little about hard-soft complexes,
13 and fails to explain variations in the strength of bonds.
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$$\Delta N = \frac{\chi_C - \chi_B}{2(\eta_C + \eta_B)} \quad (3)$$

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33 Several different measures of Lewis acidity have been proposed including LUMO energy,
34 electronegativity, degree of electron transfer and strength of interaction between the acid-base
35 pair. Corma *et al.* proposed using the LUMO energy of a mixed oxide as a measure of Lewis
36 acidity; however the authors noted that this comparison only holds for Lewis acid sites of the
37 same central atom, in the same valence state, and with the same coordination number.⁷⁹ LUMO
38 energies are difficult to obtain experimentally but correlate linearly with electron affinity.⁸⁰
39 Similarly, the HOMO energies correlate with ionization potential and the HOMO-LUMO gap is
40 important to determine the extent of interaction between an acid base pair.
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52 The values of the relevant parameters describing Lewis acid character for different metals are
53 summarized in Table 2.
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Table 2. Experimental values for ionization potential (I), electron affinity (A), Mulliken electronegativity and hardness taken from literature.⁷⁸

	Ionization potential, I [kJ/mol]	Electron affinity, A [kJ/mol]	Mulliken electronegativity, χ [kJ/mol]	Hardness, η [kJ/mol]
Pyridine	900	-60	420	500
Ti	658	8	333	325
Hf	650	80	370	300
Zr	660	41	351	310
Nb	670	100	400	300
Ta	761	31	397	366
Sn	708	121	410	294
B	800	27	414	387
Ga	600	30	310	280
Al	578	44	312	267
Si	786	134	460	326
H+	1310	72	693	620
Proportional to	HOMO	LUMO	HOMO+LUMO	HOMO-LUMO

As shown in Figure 4, electron affinity and Mulliken electronegativity show a linear correlation with the experimentally determined ^{15}N isotropic chemical shift values (or averaged isotropic chemical shift from the resonances of strong and weak sites). Furthermore, using the proton electronegativity for Al-Beta-F shows that the linear trend extends over the entire chemical shift range spanned by Lewis and Brønsted acid sites. The observed ^{15}N pyridine trend is noteworthy because it captures the interaction of pyridine with metal centers featuring significantly different electronic states (Figure 3). We note that different coordination environments often lead to different chemical shifts, especially for polarizable metal atoms. Also, nitrogen is directly bound to the metal and the reduction of chemical shielding anisotropy not directly related to the metal's ability to function as a Lewis acid points to a more fundamental association. We posit that the linear correlation between the ^{15}N isotropic chemical shift and Mulliken electronegativity occurs because of the correspondence between the HOMO-LUMO energy gap and the ionization

energy-electron affinity energy gap. The former appears in the Ramsey expression of chemical shift and the latter in the definition of Mulliken electronegativity. The similarity in the M-O-Si coordination environment facilitates establishing such correlation. The partial electron transfer (ΔN) calculated according to equation 3 does not alter the trend, suggesting that the hard-soft nature of the system does not significantly perturb the chemical shift.

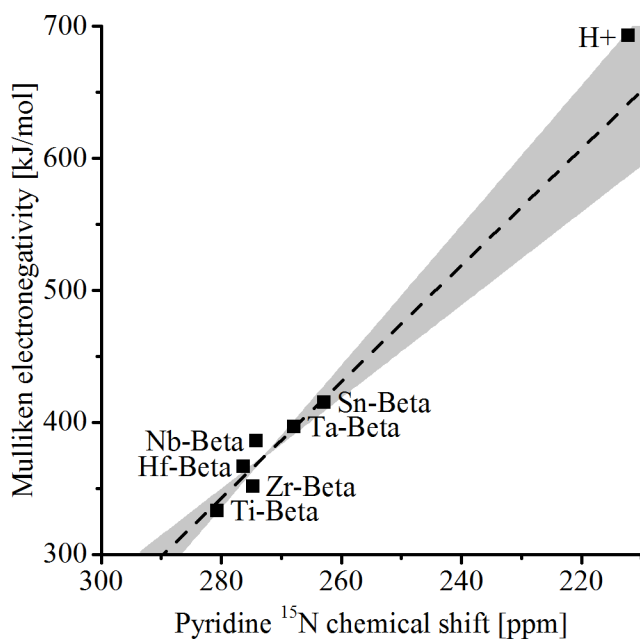


Figure 4. Experimental Mulliken electronegativity vs. pyridine ^{15}N MAS NMR chemical shift. The chemical shift shown is un-weighted average of the isotropic chemical shifts associated with strong and weak sites. The dashed line and grey envelope show a regression with standard errors.

Quantum chemical calculations

The strength of interaction between the acid-base pair is proportional to orbital overlap and inversely proportional to its HOMO-LUMO energy difference. Adsorption isotherms at multiple temperatures or calorimetry can provide experimental measures of pyridine binding strength; however, these techniques have technical challenges and competing effects are difficult to separate. Evidently, covalent bonding in an acid-base pair is a function of many parameters other

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3 than the degree of electron transfer. Quantum chemical calculations are ideal to determine the
4 metal-nitrogen bond dissociation energies and the energetics associated with active site
5 reorganization.
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10 Specifically, density functional theory (DFT) provides fundamental insight into the structure
11 and bonding of the catalyst substrate complex such as bond distances and charge distributions in
12 order to support the use of chemical shift as a proxy to evaluate Lewis acidity. DFT includes the
13 effects of orbital overlap and provides a deeper understanding of HOMO-LUMO interactions.
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15 Determining the pyridine dissociation energy and geometric distortion energy of the metal site
16 can address the possibility that reactant activation can differ from adsorption enthalpy due to
17 geometric changes induced by the flexibility of the metal in the framework. Additionally, NMR
18 calculations allow comparing calculated chemical shielding components with experimental data
19 to validate the model and verify pyridine complexation on specific metal sites. Consistency
20 between the two sets of data facilitates assignment of resonances and rule out the binding of
21 multiple pyridine molecules on a single site.
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36 To this end, we developed a 17 tetrahedral site model that incorporates both geometric
37 constraints and local distortion of the crystal lattice. Specifically, the model fixes the outer atoms
38 at specific crystallographic locations, but allows the inner five tetrahedral sites with their
39 associated oxygen atoms to relax (see Figure S7). Heteroatom substitutions were confined to the
40 T2 site of a Beta zeolite, in accordance with prior studies suggesting the preferential substitution
41 of Sn into this site.⁸¹ Nb and Ta exist in a +5 oxidation state and were modeled with a M=O
42 functional group. We note that the present study did not model the preferential substitution of
43 small B, Al and Ga atoms, which may localize to other sites. Simulations starting with two
44 pyridine molecules resulted in one of the two molecules moving away from the metal site;
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consequently, the cluster models included only a single pyridine molecule bound to a single metal center.

The model for Sn-Beta was extended by one shell of oxygen atoms (see Figure S7) in order to allow relaxation of both shells of Si atoms near the Sn center. For group IV and V transition metals, the LUMO is the unfilled dz^2 orbital, which is less sensitive to the coordination geometry. In contrast, the LUMO of Sn is a linear combination of the 4 Sn-O σ^* orbitals, making bonding very sensitive to coordination geometry. Sn delocalizes electron density from an incoming base to its four adjacent framework oxygen atoms, lengthening and polarizing its bonds in the process and resulting in a distortion of the crystal lattice. Even without substrate binding, X-ray adsorption spectroscopy (XAS) data on Sn-Beta had previously shown distortion of the Beta lattice to at least two Si atoms away from the Sn site.³⁴

Table 3. Calculated pyridine-metal (M-N) bond distances, metal-oxygen (M-O, M=O) bond distances, bond dissociation (D_0) and relaxation ($\Delta E_{M \text{ relax}}$) energies for several Lewis acid zeolites.

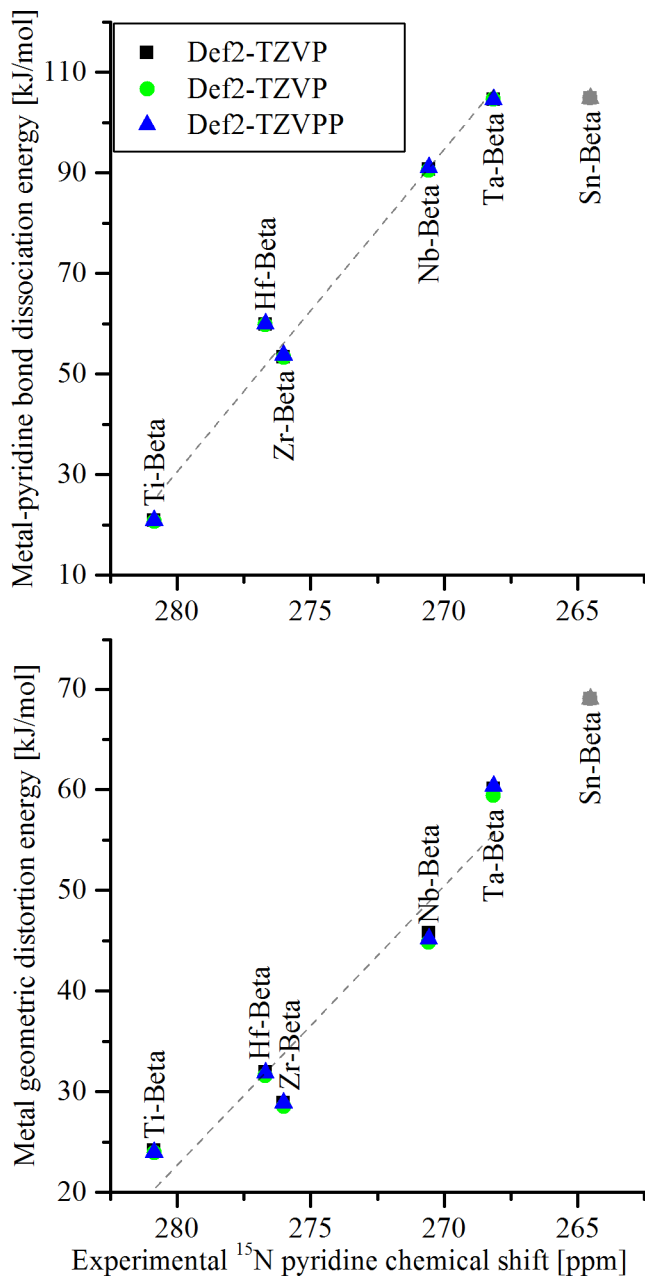
Material	M-N [Å]	M-O [Å]	M=O [Å]	D_0 [kJ/mol]	$\Delta E_{M \text{ relax}}$ [kJ/mol]
Ti-Beta	2.67	1.79	n.a.	21	24
Hf-Beta	2.58	1.94	n.a.	60	32
Zr-Beta	2.61	1.94	n.a.	53	29
Nb-Beta	2.44	1.91	1.73	91	45
Ta-Beta	2.41	1.92	1.76	105	59
Sn-Beta*	2.39	1.93	n.a.	105	69

*denotes an extended model

+ DFT methods used: B3LYP/Def2-TZVPD

Table 3 shows the results of the geometry optimization for several Lewis acid zeolites. There is a strong correlation between the dative covalent bond length and bond dissociation energy for all six substituted zeolites, which suggests that a 30 kJ/mol increase in adsorption energy brings the nitrogen 0.1 Å closer to the metal site. As shown in Figure 5, the metal-N bond dissociation energies show a strong correlation with experimental ^{15}N chemical shift values, indicating

consistency between the two Lewis acidity scales. The good fit presumably results from error cancellation associated with adsorption energy as an energy difference. In Figure 5, Sn appears ca. 23% off the trend line, likely because of limited flexibility of the cluster model combined with not accounting for expansion of the zeolite unit cell. Hf also showed a ca. 16% offset from the trend line likely due to the presence of f-electrons with stronger σ bonding.⁸²



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3 **Figure 5.** Distortion and dissociation energetics associated with pyridine adsorption calculated
4 with DFT. The chemical shift shown is un-weighted average of the isotropic chemical shifts
5 associated with strong and weak sites.
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8 Allowing the metal site to return to its most stable state without pyridine resulted in geometric
9 distortion energies analogous to those reported by Bell *et al.*⁷⁵ The calculated geometric
10 distortion energies also correlate with chemical shift. Relaxation of the metal site can recover a
11 portion of the metal pyridine dissociation energy and the sum of the dissociation and the
12 geometric distortion energy provides an estimate of the adsorption energy. The trend resembles a
13 plot for catalyst active site distortion energy vs heteroatom radii,⁷⁵ potentially due to the near
14 linear trend of chemical shift with metal-N bond length. This trend may correlate to the atomic
15 radii and polarizability discussed by Bell *et al.*⁷⁵ As an additional correlation illustrating Lewis
16 acidity changes in metal-substituted zeolites, pyridine Mulliken charges are plotted in Figure S8
17 and show increasing charge transfer to the metal cluster with increasing Lewis acidity. Def2-
18 TZVP and Def2-TZVPP calculations trend better than Def2-TZVPD likely resulting from the
19 greater basis set balance without diffuse functions.
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36 As shown in Figure S8, NMR calculations on the structures showed the expected correlation
37 between calculated ¹⁵N isotropic chemical shielding and experimental isotropic chemical shift,
38 suggesting the model involving a single pyridine bound directly to the metal center adequately
39 represents the system. The simulations also showed that stronger Lewis acids had smaller
40 chemical shift anisotropies resulting from movements of the δ_{33} chemical shift component,
41 which is consistent with the description of the pyridine system put forth at the beginning of the
42 discussion section. Chemical shift anisotropy contains directionally dependent information and
43 the similar pattern suggests a similar complex structure, a requirement to function as an effective
44 probe of Lewis acidity. The reduction of the ¹⁵N CSA observed here when compared to pyridine
45 can be explained by the pyridine binding to a metal site within the beta-zeolite^{67, 69, 71} and a fast
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3 axially symmetric C_2 rotation of the pyridine ring as described by Shenderovich et al., further
4 supported by our fast ^{15}N T_1 values⁶⁸ and poorer efficiency in the CP based NMR experiments.
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6 We note that it is important to perform both direct and CP based experiments in order to identify
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8 free pyridine when performing these studies.
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12 The systems of interest have a number of computational challenges, including the presence of
13 inorganic and organic groups, high valence heavy metal atoms with relativistic corrections,
14 aromatic bonds within the pyridine and diffuse lone pairs. These challenges are addressed in
15 more detail in the Supporting Information section. We note that the largest source of error is the
16 finite cluster size. Owing to the computational complexity of modeling an entire zeolite pore, the
17 model neglected the effects of non-specific physisorption. Typically, physisorption resulting
18 from van der Waals forces involves an enthalpy change as high as 40 kJ/mol. Corma *et al.*
19 showed a 60 kJ/mol adsorption energy for toluene adsorption on fluoride synthesized Si-Beta.⁸³
20 Application of the dispersion-corrected $\omega\text{B97X-D}$ functional on the Sn 17T cluster model
21 increased the binding energy by approximately 30 kJ/mol. These differences should not affect
22 the trends between the different substituted Beta zeolites but would result in an offset when using
23 small molecules such as pyridine and glycine to relate calculated and experimental values. A
24 larger periodic model might better address expansion of the Beta unit cell and the potential for
25 double Sn substitutions.
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45 **Quantifying framework sites**

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47 Direct detection methodologies using ^{15}N glycine as an internal standard were used to indirectly
48 quantify the framework metal sites in ^{119}Sn -Beta and Zr-Beta zeolites. A linear correlation was
49 observed between the amount of adsorbed pyridine and framework tin content (calculated from
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51 ^{119}Sn MAS NMR data and ICP analyses) for samples with Si/Sn molar ratios ranging from ca.
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3 100 to 350 (see Figure 5). This correlation can be used as a calibration curve to determine
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5 framework content for any metal in a Beta zeolite. To demonstrate the applicability of the
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7 method to quantify framework atoms even in the presence of extraframework species, a pristine
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9 ^{119}Sn -Beta sample (Si/Sn = 115) was subjected to a heat treatment with the purpose of converting
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11 framework tin species into extraframework SnO_2 clusters. Heating the sample at 1173 K for 10 h
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13 in dry air converted 14% of the framework atoms into extraframework species (as determined by
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15 ^{119}Sn MAS NMR). Nitrogen adsorption data confirmed that the structure (i.e., crystallinity and
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17 micropore volume) of the zeolite structure remained intact after heat treatment (see
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19 Table S6). The ^{15}N pyridine MAS NMR quantification method effectively captured the change in
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21 framework content. Importantly, this method can be applied to quantify metal centers that cannot
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23 be easily analyzed directly with NMR. For example, as shown in Figure 6, the Zr content of
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25 various Zr-Beta samples was successfully quantified with this approach. We note that a recent
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27 infrared spectroscopy study suggested that pyridine can only access 62% of Sn sites in Sn-Beta,
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29 which contrasts the near quantitative adsorption values observed for our samples.⁸⁴ We
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31 hypothesize that the difference in dosing temperatures between both studies (423 vs 323 K)
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33 impacts the diffusion and adsorption events within the entirety of the zeolite crystal.⁸⁴
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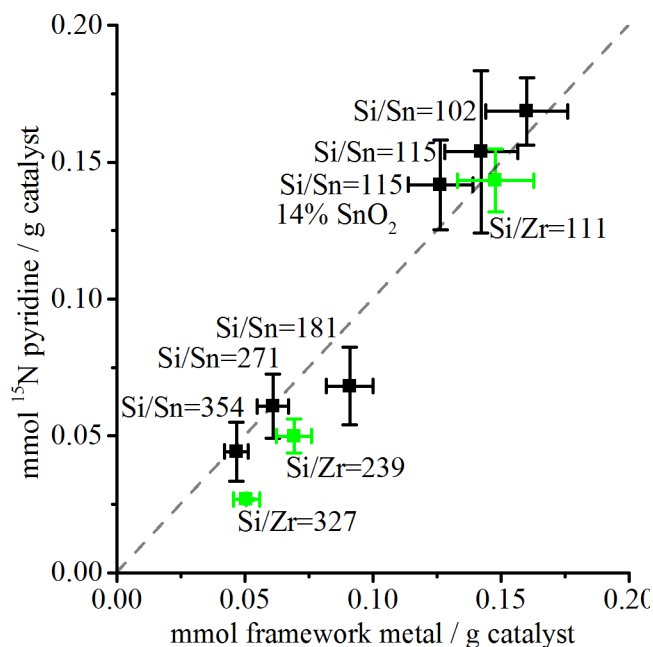


Figure 6. Quantification of adsorbed pyridine using ^{15}N MAS NMR. The dotted line represents a parity line. The Y-error bars are based on the signal-to-noise of each spectra; each experimental data point was analyzed in triplicate and the error bars represent two times the sample standard deviation. X-error bars represent the range of errors (ca. 10%) typically obtained during elemental analysis, including zeolite dissolution and ICP characterization.

CONCLUSION

A ^{15}N MAS NMR-based method is presented for assessing the strength and number of framework metal sites using pyridine as a probe molecule. MAS NMR analysis of the ^{15}N chemical shift of adsorbed pyridine on metal-substituted zeolites (e.g., Sn, Ti, Zr, Hf, Nb, Ta, B, Ga, and Al) shows linear correlations with several fundamental descriptors and is applicable to heteroatoms that are difficult to analyze with traditional methods. ^{15}N MAS NMR spectra of pyridine displayed good resolution for both Lewis and Brønsted acids and control experiments showed complete resolution of framework sites from inactive SnO_2 . Spectra of these water tolerant solid acids were obtained under dehydrated and hydrated conditions, showing the role of

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3 water in hydrophilic materials. The ^{15}N chemical shift of pyridine resolved the identity of
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5 different heteroatoms in Beta zeolite, including framework sites in the presence of
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7 extraframework oxides. A linear correlation of ^{15}N chemical shift with Mulliken
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9 electronegativity was found which is consistent with HSAB theory of Lewis acidity. DFT studies
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11 demonstrated the utility of adsorption energy as a measure of Lewis acidity and illustrated the
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13 importance of considering active site reorganization when computing adsorption equilibrium.
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15 The selective insight generated by this technique into activation of framework sites complements
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17 adsorption equilibrium data and facilitates rational catalyst selection to optimize reactant
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19 binding. Lewis acids are more diverse than Brønsted acids and this diversity offers the ability to
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21 develop highly selective processes. This method is general and can be easily implemented to
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23 compare the Lewis acid strength of samples with the same heteroatom but synthesized with
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25 different methodologies.^{32, 85-88} Recent kinetic results on the substituted Beta materials⁸⁹ suggest
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27 that higher solvent polarity results in tighter binding to the Lewis acid center and decreased
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29 flexibility in the transition state. Current efforts are focused on investigating the impact of
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31 condensed phases and solvents with different dielectric constants on binding properties.
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38 **Supporting Information**

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41 Methods for quantum chemical calculations, data in infrared spectroscopy frequency for probe
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43 molecules, powder XRD patterns, elemental analysis data, ^{15}N NMR chemical shift data and
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45 calculated parameters are available free of charge via the Internet at <http://pubs.acs.org>.
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54
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