Dynamic nuclear polarization NMR enables the analysis of Sn-Beta zeolite prepared with natural abundance $^{119}\text{Sn}$ precursors

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Supplementary Figure S1. Scanning Electron Microscopy image of enriched Sn-Beta illustrating crystal dimensions over which polarization must diffuse. Note the crystal size may be much smaller than the aggregates.

Supplementary Figure S2. Scanning Electron Microscopy (SEM) images of natural abundance Sn-Beta showing zeolite crystal dimensions.
Supplementary Figure S3. Powder X-ray diffraction patterns of Sn-Beta zeolites.

Supplementary Table S1. Metal content calculated from ICP measurements and pore volumes of Sn-Beta samples.

| Material                        | Si/Sn | Total pore volume [cm$^3$/g] | Micropore volume [cm$^3$/g] |
|---------------------------------|-------|------------------------------|------------------------------|
| Enriched Sn-Beta                | 102   | 0.663                        | 0.208                        |
| Natural abundance Sn-Beta       | 89    | 0.393                        | 0.212                        |
Supplementary Figure S4. $^{119}$Sn MAS NMR spectra (8.4 T) of $^{119}$Sn-enriched Sn-Beta obtained without DNP (i.e., no microwaves and a sample temperature of 300 K) showing the zeolite remains dehydrated and the solvent/radical combination does not interfere with the Sn site (green) or it does interfere with the Sn site (red). All spectra shown were acquired using a 4 mm ZrO2 rotor (80 ul fill volume); experimental times varied between 48 and 96 hours.
Supplementary Figure S5. $^{13}$C DNP NMR data acquired at 212 MHz / 140 GHz on a glucose Sn-Beta zeolite with borate using 8 W of microwave power at 85 K. (a) $^{13}$C [$^1$H] microwave on and off spectrum using 10 mM TOTAPOL and DMSO/D$_2$O/H$_2$O glassing/cryoprotecting agent, (b) $^{13}$C-$^{13}$C Proton-Driven Spin Diffusion (PDSD) correlation experiment acquired using 5 (rust) and 40 (green) ms of mixing and (c) enhancement results using 10 mM of bTbk or TOTAPOL in various glassing agents.
**Supplementary Figure S6.** 3-D structural representations and dimensions of the biradicals used in this study. The atoms are colored in the following manner: blue for nitrogen, red for oxygen, yellow for sulfur, grey for carbon, and white for hydrogen.
Catalyst Synthesis

Sn-Beta was synthesized as follows: 26.735 g of aqueous tetraethylammonium hydroxide (Sigma–Aldrich, 35% (w/w)) and 24.069 g of tetraethylorthosilicate (Sigma–Aldrich, 99% (w/w)) were added to a Teflon® (Polytetrafluoroethylene, [PTFE]) dish, which was magnetically stirred at room temperature for 90 min and then cooled in an ice bath. Then, 0.261 g of tin (II) chloride dihydrate (Sigma–Aldrich, 98% (w/w)) dissolved in 15 g of cold deionized water (DI H2O) was added dropwise. Sn(II) which oxidizes to Sn(IV) in water was used in place of SnCl2·5H2O and has resulted in Sn-Beta consistently free of extraneous framework SnO2. The solution was left uncovered on a stir plate for 10 h to reach a total mass of 35 g. Next, 2.600 g of aqueous hydrofluoric acid (Sigma–Aldrich, 48% (w/w)) was added dropwise and the mixture was homogenized using a PTFE spatula, resulting in a thick gel. Then, 0.358 g of previously-made Sn-Beta was seeded into the mixture, which was allowed to evaporate to 33.776 g, which corresponds to a final molar composition of SiO2/0.01 SnCl2/0.55 TEAOH/0.54 HF/7.52 H2O. The thick paste was transferred to a 45 ml PTFE-lined stainless steel autoclave and heated to 413 K for 40 days under static conditions. The solids were recovered by filtration, washed with DI H2O, dried at 373 K and calcined at 853 K for 10 h with a 1 K min−1 ramp and 1 h stops at 423 and 623 K, leading to an overall inorganic oxide yield of 80–90%. Enriched samples were prepared with 82%119SnCl2. We note that the resulting samples have been used in isomerization/epimerization reactivity studies and show identical results to those obtained with a zeolite prepared under identical conditions but using a Sn(IV) salt. This confirms that the Sn(II) atoms oxidize to Sn(IV) during synthesis and are tetrahedrally incorporated into the zeolite framework.

Zeolite Characterization

Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 diffractometer with Cu Kα radiation. Ultraviolet-visible (UV–vis) measurements were recorded using a Varian Cary 5000 UV–vis-NIR spectrometer with a diffuse reflectance cell after calcination without subsequent drying. The ultraviolet-visible diffuse reflectance spectrum of the calcined sample shows the presence of a unique band at 200 nm, which has been associated with Sn tetrahedrally coordinated into the zeolite framework. Sn content was measured using a Horiba Jobin Yvon ACTIVA-S ICP-AES. Catalyst samples were dissolved in a few drops of 48% HF and diluted in 2% nitric acid after evaporation of the HF. SEM spectra were recorded on a JEOL 6700F at an electron high tension of 1 kV. Nitrogen adsorption/desorption experiments were performed on a Quantachrome Autosorb iQ apparatus. Micropore volume was measured using a P/P0 of 0.01. X-band EPR was performed at 90 K on SPIROPOL and bCTbk over 24 hours; no evidence of Sn-radical reactivity was observed.

DNP Sample Preparation

In a typical preparation, 100 mg of zeolite was dried under vacuum at 473K and transferred into a glovebox. The zeolite powder was prepacked into 3.2 mm sapphire rotors. Small aliquots of 10 mM biradical (i.e. bTbk, TOTAPOL, SPIROPOL and bCTbk) in 1,1,2,2-tetrachloroethane (TCE) were added to the rotor of either dry (packed under N2 atmosphere) or wet (in-air) Sn-Beta zeolites using a glass Hamilton syringe. The TCE solution was prepared outside the glovebox and without special anhydrous conditions. In the presence of a unique band at 200 nm, which has been associated with Sn tetrahedrally coordinated into the zeolite framework, Sn content was measured using a Horiba Jobin Yvon ACTIVA-S ICP-AES. Catalyst samples were dissolved in a few drops of 48% HF and diluted in 2% nitric acid after evaporation of the HF. SEM spectra were recorded on a JEOL 6700F at an electron high tension of 1 kV. Nitrogen adsorption/desorption experiments were performed on a Quantachrome Autosorb iQ apparatus. Micropore volume was measured using a P/P0 of 0.01. X-band EPR was performed at 90 K on SPIROPOL and bCTbk over 24 hours; no evidence of Sn-radical reactivity was observed.

DNP MAS NMR

119Sn{1H} DNP MAS NMR experiments were performed on a 9.4 T Bruker Avance III DNP NMR spectrometer equipped with a 263 GHz gyrotroon delivering high power microwaves to the sample. Experimental data were recorded using a 3.2 mm triple resonance (HXY) MAS probe doubly tuned to 1H (ν1 = 400 MHz) and 119Sn (ν1 = 150 MHz). The 1H field position was set to the maximum field position for bTbk, bCTbk and TOTAPOL and shifted by ~50 kHz for SPIROPOL. All DNP NMR data were acquired under MAS, ω2/2π of 10,000 (3) Hz, a sample temperature of T = 100 K, a recycle delay of 1.3 x T1 and between 512 and 20,480 co-added transients.119Sn{1H} cross-polarization MAS experiments were acquired using a mixing time of 2 or 6 ms for the hydrated and dehydrated samples, respectively. Data were acquired using high power 1H (ω2/2π = 71 kHz) decoupling using SPINAL-64, the Hartmann-Hahn match condition was optimized with ω2/2π = 70 kHz for 119Sn and placing a ramp on 1H’s. Spectra were referenced with respect to tin oxide (SnO2, -604.3 ppm) at room temperature (T = 298 K) and cross-polarization was
with contact times between 0.4 and 4 ms and high-power Varian-Chemagnetics probe (Palo Alto, CA) which were singly and doubly tuned to Vezin, H.; Lafon, O.; Amoureux, J.-P. with powdered SnO$_2$ (−604.3 ppm) as an external standard relative to trimethyltin (0 ppm). Sample temperatures were maintained between 294 and 300 K.

Magic-angle spinning nuclear magnetic resonance (MAS NMR) experiments were performed on a custom designed spectrometer (courtesy of D. J. Ruben, Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology) operating at 360 MHz (1'H, 8.4 T). The spectrometer was equipped with either a double resonance homebuilt (FBML-MIT) or a triple resonance Varian-Chemagnetics probe (Palo Alto, CA) which were singly and doubly tuned to $^{119}$Sn and $^{119}$Sn/1'H, respectively. Powdered samples were packed into 4 mm (80 µl, fill volume) outer diameter ZrO$_2$ rotors equipped with Vespel drive- and top-caps. Top-caps were equipped with rubber O-ring seals, inhibiting water contamination within the sample (Revolution NMR, Fort Collins, CO) and solvent evaporation over the experiment. Dehydrated enriched $^{133}$Sn, Sn-Beta samples were prepared by heating to 473 K under a 0.1 mbar vacuum and packing the NMR rotor in an Ar-filled glovebox. $^{133}$Sn MAS NMR spectra were acquired using either a Hahn-echo ($^{133}$Sn, $\omega_0/2\pi$=50 kHz) or CP experiments with recycle delays between 4 and 30 seconds. All spectra were acquired with a spinning frequency, $\omega_s/2\pi = 8,000$ (5) Hz and between 32,384 and 172,800 scans. CP experiments were acquired with contact times between 0.4 and 4 ms and high-power 1'H decoupling (TPPM, $\omega_C/2\pi = 83$ kHz). $^{133}$Sn spectra were referenced with powdered SnO$_2$ (−604.3 ppm) as an external standard relative to trimethyltin (0 ppm). Sample temperatures were maintained between 294 and 300 K.

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