

Supplementary information for:

Are the Brønsted Acid Sites in Amorphous Silica-Alumina Bridging?

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1. Experimental

1.1. Synthesis

1.1.1. ZSM-5

ZSM-5 (Si:Al = 25) was obtained from Zeolist in the form of an ammonium salt. The catalyst was activated at 450 °C *in vacuo* (~10 mTorr) for 16 hours and stored in an Ar glovebox.

1.1.2. ASA

Materials: Ammonium nitrate, concentrated hydrochloric acid, and sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, 98 %) were purchased from Fisher Scientific. Aluminum nitrate nonahydrate (98 %) was purchased from Sigma-Aldrich. All chemicals were used without further purification.

Nitrogen physisorption isotherms were measured in a Micromeritics Tristar surface area and porosity analyzer. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method.

The amorphous silica-alumina (ASA) was synthesized by modification of a literature procedure.¹ Briefly, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (22.26 g, 76.8 mmol) was dissolved in 200 mL of H_2O . A separate 0.95 M solution of $\text{Al}(\text{NO}_3)_3$ was prepared by dissolving 9.80 g (25.6 mmol) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 27 mL H_2O . This $\text{Al}(\text{NO}_3)_3$ solution was then added dropwise to the Na_2SiO_3 solution. After addition, the mixture was stirred at 500 rpm for 5 min at 25 °C. The pH of the solution was then adjusted to ca. 8 with the addition of HCl. The mixture was then stirred at 500 rpm for an additional 20 min followed by centrifugation to obtain a white precipitate. The solid was sequentially washed with H_2O (2×35 mL), 1.0 M NH_4NO_3 (2×40 mL), and H_2O (2×35 mL). The material was then dried in an oven at 75 °C for 16 h and calcined at 550 °C for 10 h to obtain ca. 12.5 g of white ASA powder. The BET surface area measured by N_2 physisorption isotherms was ca. 182 m^2/g (**Figure S1**).

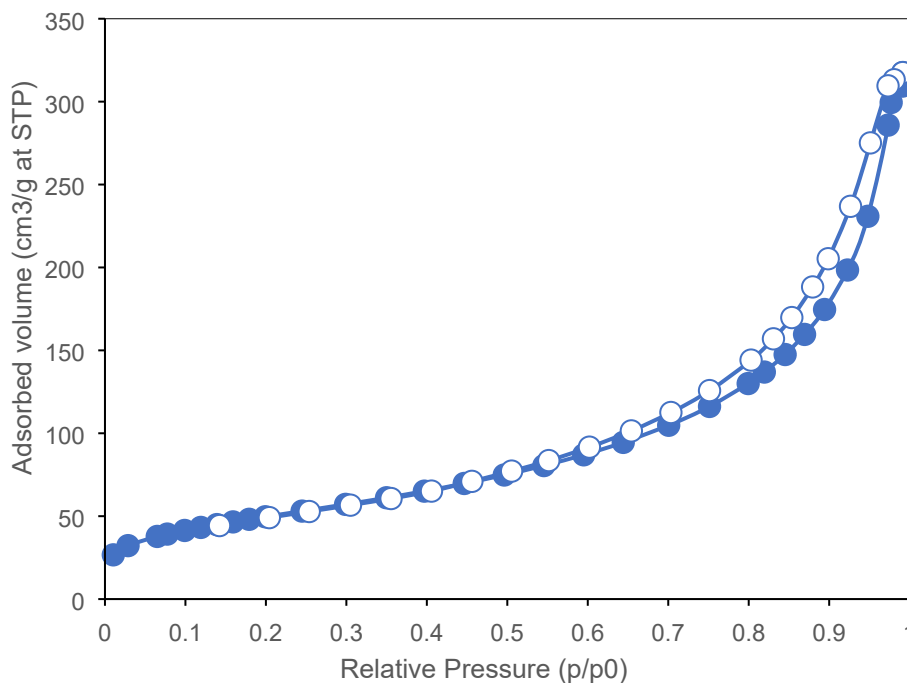


Figure S1. Nitrogen physisorption isotherm of ASA.

1.1.3. Isotope Labeling

To selectively probe the most acidic sites, ASA and ZSM-5 were uniformly deuterated with an excess of D₂O for at least 30 min. The catalyst was then activated *in vacuo* at 450 °C for ~16 h. The catalysts were then labeled at the most acidic sites with ¹H through a benzene H/D exchange reaction. Briefly, an excess of benzene was added to the activated sample under an argon atmosphere and the sample was allowed to react for 15 and 60 min for the ZSM-5 and ASA catalysts respectively. Benzene was then removed under dynamic vacuum with a pressure of at most ~10 mTorr.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on the uniformly protonated and deuterated ASA and ZSM-5 catalysts. The catalysts were activated at 450 °C under dynamic vacuum, as described above and packed into the DRIFTS cell using an Ar glovebox. The DRIFT spectra were measured using a Bruker Vertex 80 FT-IR spectrometer equipped with HeNe laser and a photovoltaic MCT detector. The data were processed using the OPUS software. All spectra were collected by averaging 64 scans at 4 cm⁻¹ resolution using the diffusion reflectance mode. The spectra are depicted in **Figure S2** below.

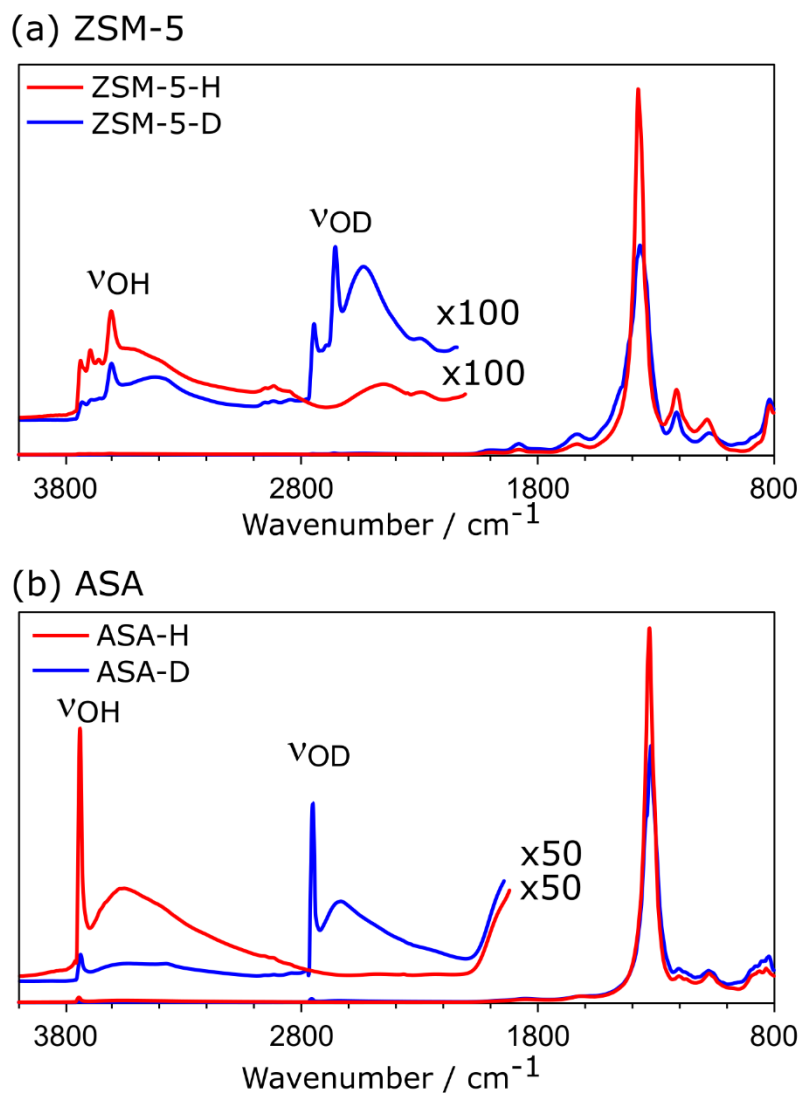


Figure S2. DRIFTS spectra acquired on the fully protonated (red) and deuterated (blue) ZSM-5 (a) and ASA (b) catalysts. The hydroxyl regions in (a) and (b) are magnified by factors of 100 and 50, respectively. Deuteration leads to an important increase in OD stretches for both materials and a reduction in OH stretches.

ASA was also enriched to c.a. 20% ^{17}O to perform an $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR experiment.^{2,3,4} First, the material was activated as described above. A small excess of H_2^{17}O was then added to the material inside an Ar wetbox. The activated ASA's strained siloxane linkages were broken by the isotopically labeled water, leading to the incorporation of ^{17}O at the surface. ASA was reacted with H_2^{17}O for 6 h, after which the sample was dried and reactivated *in vacuo*. This process was repeated a second time to increase the enrichment level.

1.2. NMR Spectroscopy

1.2.1. *in situ* NMR

In an Ar glovebox, ~40 mg of unlabeled catalyst was added to an *in situ* 5 mm MAS rotor. 40 μL of deuterated benzene (C_6D_6) was then added to the rotor, which was subsequently sealed and quickly transported to a 400 MHz Agilent DD2 NMR spectrometer equipped with a Chemagnetics MAS probe. The rotor was spun to a frequency of 5 kHz and ^1H NMR spectra were acquired every minute using a Bloch decay sequence.

1.2.2. ^1H fast-MAS

Dry, activated ASA and ZSM-5 catalysts were packed into either 1.3 or 1.8 mm rotors in a glovebox and spun to a frequency of 25 kHz using either a Bruker AVANCE III 600 (ASA) or a Agilent DD2 400 (ZSM-5) MHz spectrometer. 1D ^1H spectra were acquired using a Hahn-echo sequence with the echo delays set to 40 μs and using 100 kHz rf pulses in 128-256 scans. Chemical shifts were referenced externally using to the DSS (3-(trimethylsilyl)-1-propanesulfonic acid sodium salt) methyl resonance at 0 ppm.

In the case of the $^1\text{H}\{^{27}\text{Al}\}$ S-RESPDOR experiments, dipolar recoupling was achieved using the SR4_1^2 recoupling sequence ($\nu_{\text{1H}} = 50$ kHz),⁵ which was applied to ^1H 's. The recoupling time was incremented in steps of 2 rotor periods to a total recoupling time of 6 ms. Each sub-spectrum was acquired in 64 scans with the recycle delay set to 2 s. All hard ^1H pulses had a rf power of 100 kHz while the rf power for the 60 μs ^{27}Al saturation pulse was optimized to 60 kHz to maximize the dephasing. Spectra were deconvoluted using DMFIT.⁶

1.2.3. $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR

$^{17}\text{O}\{^1\text{H}, ^{27}\text{Al}\}$ NMR experiments were conducted using DNP enhancement with a Bruker AVANCE III 400 MHz MAS-DNP spectrometer equipped with a 3.2 mm low-temperature MAS probe and a 264 GHz gyrotron microwave source. In an Ar glovebox, isotopically labeled ASA was packed into 3.2-mm sapphire rotors and impregnated with a 16 mM solution of the TEKPol polarizing agent⁷ dissolved in dry, perdeuterated, 1,1,2,2-tetrachloroethane. The samples were transported in sealed vials to the spectrometer, where they were then inserted into a pre-cooled probe at a temperature of 100 K. Samples were spun to a frequency of 11.111 kHz. ^1H hyperpolarization was transferred to hydroxyl ^{17}O sites using a 180 μs PRESTO-II polarization transfer⁸ using a R18_1^7 recoupling sequence ($\nu_{\text{1H}} = 100$ kHz). The PRESTO-II echo delay was extended to enable a $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR experiment (see Figure S5b).³ The ^{17}O and ^{27}Al radiofrequency powers equaled 16.7 and 100 kHz, respectively. The TRAPDOR dephasing time was incremented in steps of 720 μs up to a total of 10 ms. 1024 scans were accumulated for each sub-spectrum, with a 2 s recycle delay.

2. Supplementary Figures

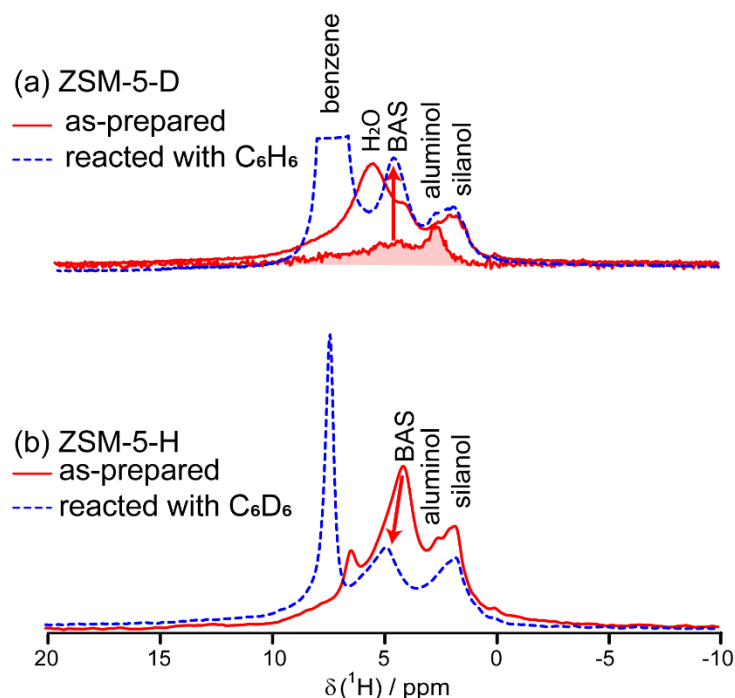


Figure S3. (a) ^1H MAS NMR spectra acquired on a ZSM-5 sample that was deuterated with D_2O (red) and then back-exchanged with benzene (dashed blue), showing a selective enrichment of the BAS sites. The shaded spectrum corresponds to a $^1\text{H}\{^{27}\text{Al}\}$ S-RESPDOR difference spectrum acquired with $960\ \mu\text{s}$ of $\text{SR}4_1^2$ dipolar recoupling. (b) ^1H MAS NMR spectrum of as-synthesized ZSM-5 (red) and the spectrum acquired following H/D exchange with C_6D_6 . In addition to lowering in intensity, we also see a slight shift in the peak position of the BAS signal, presumably due to trace moisture in the solvent.

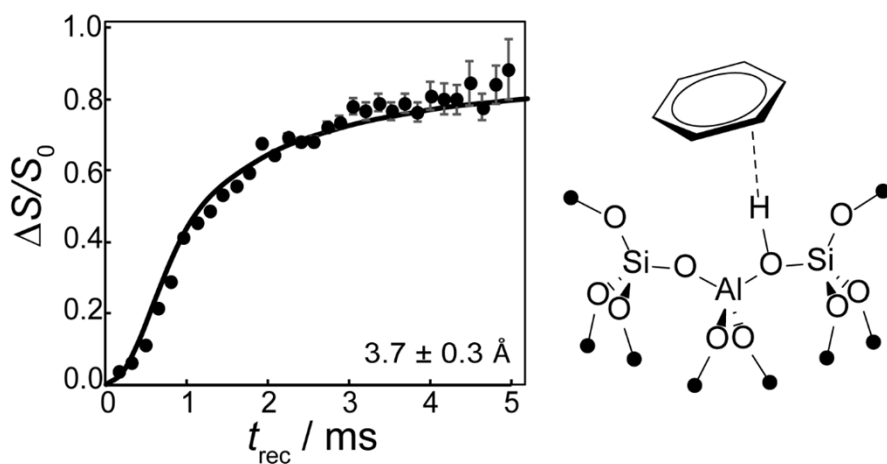


Figure S4. $^1\text{H}\{^{27}\text{Al}\}$ RESPDOR data from the benzene resonance in the ZSM-5 catalyst, displaying its strong association with a BAS (right) as described in reference 9.

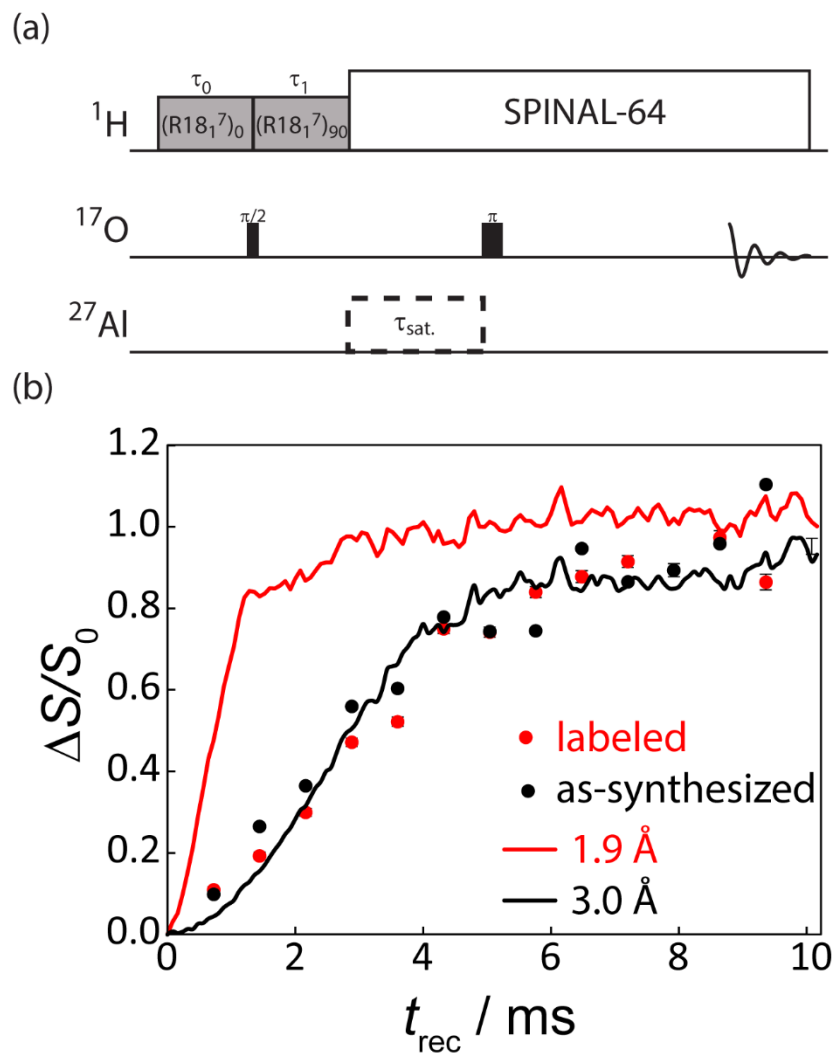


Figure S5. DNP-enhanced, $^{17}\text{O}\{^1\text{H}\}$ PRESTO-based $^{17}\text{O}\{^{27}\text{Al}\}$ TRAPDOR pulse sequence (a) and data (b) data acquired on ASA catalysts, both pre- and post-labeling at the BAS sites. No difference is observed between the material, indicating the decomposition of the acid sites under DNP conditions. The red simulation corresponds to the expected behavior from a BAS, while the black curve is the best-fit distance of $3.0 \pm 0.2 \text{ \AA}$.

3. References

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