Supporting Information

Tetraethylammonium fluoride (TEAF), cetyl trimethylammonium bromide (CTAB), 30 wt% hydrogen peroxide in water, and MCM-41 were purchased from Aldrich. The organic silanes, phenethyltrimethoxy silane (PETMS), mercaptopropyltrimethoxy silane (MPTMS), diethylphosphatoethyltriethoxy silane (DEPTES), and 2-(carbomethoxy)ethyltrichloro silane (CMETCS), were purchased from Gelest. Potassium hydroxide was purchased from Fischer Scientific.

Pure-silica beta was synthesized by dissolving the required amount of tetraethylammonium fluoride in water (6.25g TEAF/7.75 g water). Tetraethylorthosilicate and the organic silane were then added and the initially 2-phase mixture was aggressively stirred for 12-24 hours. The resulting creamy white slurry was rotovaped to remove excess water, and the appropriate amount of water was added back to the solution so that the final gel had a molar ratio of 0.55 TEAF: x Organic Silane:(1-x) SiO₂: 7.25 H₂O. x = 0.028 was used in the preparation of all zeolite beta samples for this work, even though it appears from TGA and titration that some samples have higher or lower loading in the crystalline products. Previous experience in the group has shown that attempts to incorporate higher organic loadings lead to less than 100% crystalline products. The thick gel was loaded into Teflon-lined stainless steel autoclaves and heated, with rotation, in a convection oven to 140 °C. Crystallization times for non-functionalized material was 5 days while phenethyl functionalized samples required 27 days. Crystallization times for Mercaptopropyl, diethylphosphatoethyl, and 2-(carbomethoxy)ethyl required approximately 50 days. Crystallization products were collected by filtration, washed with water and acetone, and dried at 100 °C. Non-functionalized materials were calcined in flowing air at 550 °C for six hours to remove the tetraethylammonium structure directing agent (SDA). Organically functionalized materials were contacted with 1:1 (by volume) glacial acetic acid:water mixtures for 24 hours at 80 °C to remove occluded SDA molecules. The extraction procedure was repeated 2-3 times to ensure maximum removal of the SDA. To sulfonate PE functionalized samples, ~1 g of PE-BEA was dried at 110 °C under rough vacuum and contacted with ~25 g of oleum (fuming sulfuric acid) for 12 hours at room temperature. The mixture was quenched by addition to 500 mL of cold water and samples were further washed with at least 2 L of water (4 x 500 mL). Mercaptopropyl functionalized samples were oxidized to propylsulfonic acids by contacting ~1 g of MP-BEA with ~25 g of 30 wt.% for 12 hours at room temperature. The mixtures were then filtered and dried at 100 °C and the resulting powders were acidified with 1 M H₂SO₄ for 2 hours at room temperature. Diethylphosphatoethyl groups were cleaved and converted to phosphonic acid groups by refluxing ~1 g of diethylphosphatoethyl functionalized beta in ~25 g of concentrated hydrochloric acid for 24 hours. Samples were quenched in 500 mL of cold water and washed with at least 2 L of additional water (4 x 500 mL). Finally, 2-(carbomethoxy)ethyl groups were converted to carboxylic acids by stirring ~1 g of 2-(carbomethoxy)ethyl functionalized material in 1 N hydrochloric acid for 24 hours. The powder was then filtered and rinsed with at least 2 L of water (4 x 500 mL).

MCM-48 was synthesized according to a published procedure. Tetraethylorthosilicate, potassium hydroxide, and water were combined in a Teflon jar and stirred for 10 minutes. Cetyl trimethylammonium bromide (CTAB) was then added and the mixture was stirred for an additional 10 minutes before loading into a Teflon lined stainless steel autoclave. The final molar gel composition was
1 SiO₂:1 KOH:62 H₂O:0.65 CTAB. After statically heating at 115 °C for 48 hours, the crystallization products were collected by filtration, washed with 500 mL of water and 500 mL of acetone, and dried at 100 °C. CTAB was removed from the pores of MCM-48 by calcination at 550 °C in flowing air.

Organic silanes were grafted onto the surfaces of MCM-41 and MCM-48 using the following procedure. Approximately 1 g of powder was dispersed into 100 mL toluene for 10 minutes with stirring. 0.30 mmol organic silane/g MCM-41(8) was added by syringe to the dispersion, and the mixture was allowed to stir for 1 hour before the temperature of the oil bath was increased to 120 °C, causing the toluene to reflux. Higher loadings were also prepared during this investigation by using up to 4 mmol organic silane/g MCM-41(8). The grafting procedure was allowed to proceed for 24 hours. Grafted samples were collected by filtration and subsequently washed with 1 L of toluene (2 x 500 mL), 1 L of ethanol (2 x 500 mL), and 2 L of acetone (4 x 500 mL). The aforementioned post treatments were used to functionalize or modify the attached organic moieties.

Attempts to synthesize hydrophyllic, nanocrystalline zeolite beta (possibly a better comparison to MCM-41 and MCM-48 as they are also hydrophyllic, containg many hydroxyls) containing mercaptopropytrimethoxy silane, diethylphosphatoethyltriethoxy silane, or 2-(carbomethoxy)ethyltrichloro silane, led to crystallization without any incorporated organic. This difficulty may arise from the crystallization kinetics associated with the use of TEAF versus TEAOH. Synthesis of BEA containing phenethyltrimethoxy silane requires approximately 27 days, while mercapto propyltrimethoxy silane, diethylphosphatoethyltriethoxy silane, or 2-(carbomethoxy)ethyltrichloro silane require nearly twice that time.

Prior to proton conductivity measurements samples were ground with a mortar and pestle and further washed with water by repeated sonication/centrifugation while monitoring the effluent pH. Samples were washed until the effluent pH was the same as the washing water (and until measured conductivity values did not change with subsequent washing).

²⁹Si CPMAS and ¹³C CPMAS NMR spectra were recorded using a Bruker Avance 200 MHz (¹H) spectrometer and 7mm zirconia rotors, unless otherwise noted. TGA data were collected using a Netzsch STA 449 C and Pt/Rh samples dishes. Powder X-ray diffraction patterns were collected using a Scintag XDS 2000 with Cu k-α radiation.

Our proton conductivity apparatus consisted of a Delrin® sample holder with 4 mm diameter sample wells. Samples were compressed, after equilibration with bulk water for 1-2 hours, between two 4 mm diameter Pt cylinders using a torque screwdriver. Other reports⁴-⁷, and our own experiments suggest equilibration with bulk water (added, by pipette, on top of the uncompressed powder in the sample holder) occurs in less than an hour. A digital micrometer was connected to, but electrically isolated from, the Pt cylinders for in-situ sample thickness measurement. Samples were compressed for the duration of the measurement by applying a torque of 80 in-oz to the micrometer screw. A schematic of the sample holder is shown in Figure S1. A Solartron 1260 analyzer was used to scan a 100 mV ac voltage⁶-⁷ over the frequency range 1 Hz-5 MHz. Reported values are averages from 2-3 measurements.
Figure S1. Sample holder used for proton conductivity measurements. Powder samples were loaded on top of the bottom Pt contact and allowed to equilibrate with water. The top contact was then inserted and the sample was compressed by applying torque to the micrometer with a torque screwdriver. An aluminum frame (not shown) held the structure in place, and the micrometer was zeroed before loading each sample.
**Figure S2.** X-ray data of i) pure-silica zeolite beta (BEA) containing a. no organic silane (but uncalcined), b. sulfonated phenethyl groups (S-PE-BEA), c. oxidized mercaptopropyl groups (S-MP-BEA), d. cleaved diethylphosphatoethyl groups (P-BEA), and e. cleaved 2-(carboxethoxy)ethyl groups. ii) a. MCM-41, b. S-PE-MCM-41, c. S-MP-MCM-41, d. P-MCM-41, e. C-MCM-41. iii) a. MCM-48, b. S-PE-MCM-48, c. S-MP-MCM-48, d. P-MCM-48, e. C-MCM-48.
Figure S3. $^{29}$Si CPMAS NMR spectra of i) acetic acid extracted pure-silica beta samples as follows: a. PE-BEA, b. MP-BEA, c. P-BEA, d. C-BEA. The T3 resonance centered at -70 ppm is indicative of a C-Si-(OSi)$_3$ bond. ii) grafted MCM-41 samples as follows: a. PE-MCM-41, b. MP-MCM-41, c. P-MCM-41, d. C-MCM-41. T1, T2, and T3 resonances are clearly seen near -50 ppm, -60 ppm, and -70 ppm, respectively, indicative of C-Si(OH$_{3-x}$)Si$_x$ where x is from Tx. Spectra of functionalized MCM-48 samples gave spectra similar to those shown in ii.
Figure S4. $^{13}$C CPMAS NMR of i) pure-silica beta samples as follows: a. PE-BEA showing two aromatic resonances and two alkyl resonances arising from the ethyl chain, b. S-PE-BEA showing the same two ethyl resonances but now three aromatic resonances arising from sulfonation, c. MP-BEA, d. S-MP-BEA, e. C-BEA showing a carbonyl resonance centered near 175 ppm and a broad resonance around 25 ppm arising from ethyl carbons. Spectra were collected on a Bruker Avance 500 MHz spectrometer with a 4mm rotor. Residual TEA$^+$ gives rise to resonances near 5 ppm and 50 ppm seen in all spectra. ii) representative MCM-41 samples as follows: a. PE-MCM-41, b. S-PE-MCM-41, c. MP-MCM-41, d. S-MP-MCM-41, e. P-MCM-41 before concentrated HCl reflux, f. P-MCM-41 after concentrated HCl reflux, g. C-MCM-41 before HCl reflux, h. C-MCM-41 after HCl reflux. Spectra of functionalized MCM-48 samples gave spectra similar to those shown in ii.
Figure S5. $^{31}$P CPMAS NMR of HCl refluxed a. P-MCM-41, b. P-MCM-48, and P-BEA. The resonance centered around 32 ppm arises from the di-acid phosphorous while the shoulder at lower chemical shift is from phosphorous with uncleaved ethoxy groups.
Figure S6. Thermogravimetric analysis data of i) acetic acid extracted, organically functionalized pure-silica beta samples as follows: a. P-BEA b. C-BEA, c. unsolfonated PE-BEA illustrating the effective removal of most of the structure directing agent, d. S-MP-BEA, e. S-PE-BEA. ii) representative functionalized MCM-41 samples as follows: a. unfunctionalized MCM-41, b. P-MCM-41, c. C-MCM-41, d. S-MP-MCM-41, e. S-PE-MCM-41. MCM-48 samples gave similar results as those shown for MCM-41 in ii.
Figure S7. FTIR spectra of a. representative MCM-41, b. P-MCM-41 prior to HCl treatment showing a band at 2990 cm\(^{-1}\) from the ethoxy groups attached to the phosphorus and a small band at 1390 cm\(^{-1}\) from the P=O., c. HCl treated P-MCM-41 where the band at 2990 cm\(^{-1}\) is now missing, indicating cleavage of the ethoxy groups, d. C-MCM-41 prior to HCl treatment showing a band at 1730 cm\(^{-1}\) from the carbonyl and a band at 1460 cm\(^{-1}\) from the methyl ester, e. HCl treated C-MCM-41 showing a carbonyl band at 1730 cm\(^{-1}\), but no band at 1460 cm\(^{-1}\) indicating cleavage of the methyl ester.\(^5\)
Figure S8. Representative impedance spectra of functionalized MCM-41 samples. i) C-MCM-41, ii) P-MCM-41, iii) S-MP-MCM-41, iv) S-PE-MCM-41. Figures in the left column show the commonly observed semicircle observed at higher frequencies and a low frequency tail generally attributed to charge accumulation at the contacts. Figures in the right column show magnitude and phase of the impedance as functions of frequency. A minimum in the phase curve corresponds to the low-frequency, real-axis intercept of the semicircular arcs depicted in the first column.
<table>
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<th>Sample Identity</th>
<th>$\sigma$ (S/cm)</th>
<th>TGA Loading (mmol/g)</th>
<th>Acid Loading (meq/g)</th>
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**Table S1.** MCM-41 samples with higher loading (4 mmol/g added to refluxing toluene). The same trend of increasing conductivity with increasing organic acid strength is observed. Note $a$. Ran out of material prior to base reaction/acid back titration.