Proton Conductivity in Sulfonic Acid-Functionalized Zeolite Beta: Effect of Hydroxyl Group

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Direct methanol fuel cells (DMFCs) and proton exchange membrane fuel cells (PEMFCs) have received considerable attention throughout the past decade because they are considered promising energy conversion devices for automobiles, homes, and portable electronics. One of the critical components of these fuel cells is the proton conducting membrane electrically separating the anode from the cathode, and Nafion is the standard for new materials comparison. Nafion, while exhibiting excellent proton conductivity at low temperatures and high levels of hydration ($\sim 10^{-1}$ S/cm under conditions comparable to those used herein), has drawbacks including measurable methanol crossover and loss of hydration and proton conductivity at temperatures above 100 °C. To address some of these issues, a number of reports suggest using various additives including metal oxides,[1–5] clays,[6] mesoporous materials,[7–11] and zeolites.[12–15]

Among the oxide additives, acid functionalized mesoporous silicas and zeolites are advantageous because of their high acid strength (e.g., $-SO_3H$), adjustable acid group density, and the possiblity to block methanol crossover and increase water retention at high temperature while allowing fast proton transport through the pore space. Acid functionalized mesoporous materials (by grafting or co-condensation) are used as solid catalysts, but only a few studies focus on their proton conducting properties.[9,10,16–22] Organically functionalized zeolite beta was first synthesized in our laboratory for catalysis applications nearly a decade ago.[23] Holmberg and co-workers investigated this solid as a potential proton conducting material.[24] In their report, they synthesized zeolite beta containing phenethyl moieties from synthesis gels containing varying amounts of aluminum and suggested, after sulfonation of the phenyl ring, possible cooperativity between the negatively charged aluminum framework sites (counterbalanced by a proton or tightly bound tetraethyl ammonium ion, TEA^+) and the strong Bronsted acidity of the sulfonic acid in generating the observed proton conductivity, as the sample with the highest measured proton conductivity was crystallized from a synthesis gel having the lowest SiO_2/Al_2O_3 ratio (SiO_2/Al_2O_3 denoted here by X).

One goal of this study is to test the hypothesis of cooperativity between the sulfonic acid sites and the framework acid sites generated by framework aluminum by synthesizing molecular sieves with the *BEA framework that contained both sulfonic acid groups and varying concentrations of framework aluminum sites by either direct synthesis, as in the case of nanocrystalline beta, or by post-synthetic insertion of aluminum in the hydroxyl nests left by the removal of framework zinc in CIT-6 (the zincosilicate analogue to zeolite beta).[25] As shown below, framework aluminum is not maintained upon generation of the sulfonic acid sites. Instead of generating a series of samples with variable aluminum contents, the solids ended up being a series of samples that possess significantly different amounts of hydroxyl groups. Thus, in this communication, attention is paid to the effects of the hydroxyl group in the materials by choice of synthesis method and post-synthesis "annealing" of the framework silanols. Namely, sulfonic acid functionalized and unfunctionalized molecular sieves with the *BEA framework topology (pure silica, ammonium, or proton exchanged) are prepared, and conductivity results are compared to sulfonic acid functionalized MCM-41. Furthermore, ammonium and proton exchanged nanocrystalline zeolite beta

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Table 1. Summary of Sample Characterization and Proton Conduction Data[a]

sample	σ (S/cm)	SiO_2/Al_2O_3 (EDS)	SiO_2/Al_2O_3 (rxn mixture)	TGA (mmol/g)	titration (mequiv/g)
PS-BEA	8.8×10^{-6}	∞	∞	[b]	−0.003
O-PS-BEA	2.3×10^{-5}	∞	∞	[b]	0.0012
S-PE-PS-BEA	5.4×10^{-4}	∞	∞	0.17	0.18
BEA-50_80SA	1.1×10^{-5}	∞	50	[b]	[b]
BEA-400_80SA	6.4×10^{-6}	∞	400	[b]	[b]
BEA-1000_80SA	1.7×10^{-5}	∞	1000	[b]	[b]
NH_4-BEA-50	2.8×10^{-3}	30	50	[b]	[b]
NH_4-BEA-100	1.2×10^{-3}	73	100	[b]	[b]
NH_4-BEA-400	2.3×10^{-3}	69	400	[b]	[b]
NH_4-BEA-1000	1.2×10^{-3}	65	1000	[b]	[b]
H-BEA-50	7.0×10^{-4}	35	50	[b]	[b]
H-BEA-100	6.1×10^{-4}	75	100	[b]	[b]
H-BEA-400	4.8×10^{-4}	60	400	[b]	[b]
H-BEA-1000	3.1×10^{-4}	86	1000	[b]	[b]
S-PE-BEA-50	4.9×10^{-3}	∞	50	0.19	0.23
S-PE-BEA-100	6.7×10^{-3}	∞	100	0.24	0.30
S-PE-BEA-400	6.8×10^{-3}	∞	400	0.51	0.78
S-PE-BEA-1000	4.5×10^{-3}	∞	1000	0.23	0.24
S-PE-CIT-6_80AA	6.8×10^{-3}	∞*	33*	0.23	0.29
S-PE-CIT-6_135AA	1.2×10^{-3}	∞*	33*	0.24	0.23
MCM-41	2.9×10^{-5}	[b]	[b]	[b]	0.0055
O-MCM-41	1.5×10^{-5}	[b]	[b]	[b]	0.0052
S-PE-MCM-41	8.3×10^{-3}	[b]	[b]	0.59	0.87

[a] ∞*, for zincosilicate; ∞, no Al detected; PS, pure-silica from fluoride synthesis; O, oleum treated; 80SA, extracted with 18 M H_2SO_4 at 80 °C; NH_4, ammonium exchanged nonfunctionalized; H, proton exchanged nonfunctionalized; PE, phenethyl functionalized; S, sulfonated with oleum; 80AA and 135AA, extracted with acetic acid at 80 and 135 °C. [b] Not measured.

are investigated in an attempt to separate factors that contribute to the observed proton conduction and to better design future materials.

Zeolite beta synthesized from gels containing tetraethylammonium hydroxide as the structure directing agent is known to have a high density of internal hydroxyl group nests,[26] and the removal of framework aluminum only increases this density. Similarly, when CIT-6 is treated with acetic acid at 80 °C, hydroxyl nests remain and the material is hydrophilic, but when treated with acetic acid at 135 °C the hydroxyl nests are annealed and the material becomes hydrophobic.[25] In contrast, pure silica zeolite beta crystallized from fluoride containing gels is known to possess many fewer hydroxyl defects[27] than the corresponding hydroxide-based synthesis product and is hydrophobic. For comparison, MCM-41 has many dangling hydroxyl groups and is hydrophilic. As shown and discussed below, the presence of hydroxyl groups is pivotal in achieving high proton conductivity, presumably due to the formation of a more complete hydrogen bonded water network in the materials with many dangling −OH, and better water saturation inside the molecular sieves.

See the Supporting Information for detailed synthetic procedures. Aluminum reinsertion into S-PE-CIT-6 extracted with acetic acid at 60 and 80 °C is attempted using $Al(NO_3)_3 \cdot 9H_2O$ according to a previously published procedure.[25]

Samples are characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), ^{13}C CPMAS NMR, and ^{29}Si CPMAS NMR. See Supporting Information (Figures S3−S6) for spectra. Silicon and aluminum contents are obtained by energy dispersive spectroscopy (EDS). Samples are titrated to estimate acid loading with 0.01 N NaOH followed by back-titration with 0.01 N HCl.

From the EDS results, it is observed that aluminum has been incorporated into as-made and calcined nanocrystalline beta samples produced from aluminum containing gels (shown below for non-PE containing samples H-BEA-*X* and NH_4-BEA-*X*, but also true for PE containing samples prior to sulfuric acid treatment). While the SiO_2/Al_2O_3 ratio is greatly varied in the gels, a much narrower range is observed in the crystallized powders, and lower yields based on SiO_2 are observed with decreasing gel aluminum content. Treatment with sulfuric acid, however, removes aluminum from the framework, in addition to most of the TEA^+ (Supporting Information, Figure S6). Some residual TEA^+ exists and may be bound to framework defects. Treatment of the zincosilicate CIT-6 with acetic acid removes framework zinc,[25] and ^{27}Al MAS NMR indicates almost no reinsertion of aluminum into sulfonic acid functionalized CIT-6 (S-PE-CIT-6). We have yet to find a successful method for producing zeolite beta containing both organic sulfonic acids and framework aluminum (acid) sites.

Impedance spectroscopy is performed with a Solartron 1260 to measure the proton conductivity in an apparatus similar to that of Holmberg et al. (schematic shown in Supporting Information, Figure S2).[24,28] All samples are thoroughly washed and allowed to equilibrate with bulk water prior to measurement. Attempts were made to characterize free-standing pellets with evaporated gold contacts in a controlled temperature−humidity chamber, but the pellets lost mechanical integrity at elevated temperatures and humidities, even when held between gold, platinum, or stainless steel plates.

Proton conductivities, sample and gel SiO_2/Al_2O_3, and acid loadings from TGA and titration are presented in Table 1 for the investigated samples. For comparison, the

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conductivity of as-made samples (containing ~20 wt % SDA) are presented in Table S1 in the Supporting Information.

Acid site amounts from TGA and titration are in reasonable agreement, and the acid density from sample to sample and between synthesis methods is consistent. Samples with many hydroxyl groups show slightly higher loading by titration than by TGA (S-PE-BEA-*X*, S-PE-CIT-6_80AA, S-PE-MCM-41) when compared to samples with fewer hydroxyl groups (S-PE-PS-BEA, S-PE-CIT-6_135AA), possibly due to deprotonation of some of the hydroxyl groups.

Examining the results in Table 1, unfunctionalized samples that do not contain aluminum in the framework (PS-BEA, O-PS-BEA, BEA-*X*_80SA, MCM-41, O-MCM-41) exhibit a conductivity $\sim 10^{-5}$ S/cm, regardless of the hydrophilicity/hydrophobicity, as no proton donating sites exist. Treatment of MCM-41 and PS-BEA with oleum do not significantly affect the measured conductivity, nor does the small amount of residual SDA, as sulfuric acid treated samples (BEA-*X*_80SA) exhibit conductivities similar to that of calcined PS-BEA. Zeolite beta samples containing tetrahedrally coordinated aluminum counterbalanced by a proton (H-BEA-*X*) exhibit conductivity $\sim 5 \times 10^{-4}$ S/cm, and a slight trend of increasing conductivity with increasing aluminum content is observed as has been previously shown for ZSM-5.[29,30] Ammonium exchanged samples (NH_4-BEA-*X*) exhibit higher conductivity values ($1-2 \times 10^{-3}$ S/cm) than those in the proton form in accordance with other reports using impedance spectroscopy[30] and NMR.[31] Direct current electrochemical[32] and NMR[31] results suggest that ammonium ions move by vehicular motion (chemical diffusion) and that hydrated ammonium exchanged zeolites should exhibit greater conductivity than hydrated, proton exchanged zeolites.[31]

The incorporation of phenyl sulfonic acid groups into hydrophilic nanocrystalline zeolite beta (S-PE-BEA-*X*) further increases the proton conductivity to $\sim 5 \times 10^{-3}$ S/cm. Regardless of the aluminum content in the synthesis gel, no aluminum is detected by EDS in the sulfonated samples, and no significant difference in the measured conductivity values is observed among samples crystallized from synthesis gels containing differing amounts of aluminum. In attempts to study cooperativity, however, it is observed that phenyl sulfonic acid-containing pure-silica beta (S-PE-PE-BEA, synthesized out of fluoride containing media) exhibits proton conductivity an order of magnitude lower than phenyl sulfonic acid-containing beta synthesized from TEAOH containing gels even when their acid loadings are similar. This may be due to the hydrophobicity/hydrophilicity of the pores, as the formation of a hydrogen bonded water network is important for fast proton hopping by the Grotthüss mechanism. Pores with many hydroxyl defects hold more water than defect-free pores, leading to a more "complete" hydrogen bonding network available for proton hopping. Results using phenyl sulfonic acid-containing CIT-6 further strengthen this hypothesis. S-PE-CIT-6 treated with acetic acid at 80 °C exhibits a proton conductivity similar to that of S-PE-BEA-*X* ($X = 50, 100, 400, 1000$). S-PE-CIT-6 from the same synthesis batch treated with acetic acid at 135 °C, however, shows conductivity a factor of 5 lower than the S-PE-BEA-*X* samples and more closely resembles the conductivity of S-PE-PS-BEA. Additionally, phenyl sulfonic acid functionalized MCM-41 (S-PE-MCM-41) exhibits a conductivity value approximately that of S-PE-BEA-*X*. The acid loading by TGA and titration is slightly higher for S-PE-MCM-41, potentially leading to the slightly greater conductivity when compared to the S-PE-BEA-*X* samples.

In conclusion, it is shown that the incorporation of phenyl sulfonic acid groups into the pores of zeolite beta is more important for enhanced proton conductivity than framework alumina (in either the proton or the ammonium exchanged form) and that the conductivity observed in these samples does not arise from a cooperative effect between the bound organic sulfonic acid groups and the aluminum acid sites. Furthermore, the presence of framework hydroxyl groups is necessary for increasing the proton conductivity through the formation of a better hydrogen bonding water network in the pores leading to faster Grotthüss transport of the mobile protons.

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Supporting Information Available: Experimental details and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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