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Organosulfonic acid functionalized zeolite ZSM-5 as temperature tolerant proton conducting material

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ABSTRACT

Organosulfonic acid functionalized zeolite ZSM-5 materials namely sulfonated polystyrene ZSM-5, phenylsulfonic acid functionalized ZSM-5 and propylsulfonic acid functionalized ZSM-5, were successfully synthesized in this study. Characterization by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectrometers indicate that the functionalized zeolites comprise of the organosulfonic acid groups attached onto the surface of zeolites. Impedance spectroscopy results showed that the proton conductivities of zeolites in the operating temperature range of 24–100 °C were enhanced significantly to higher values (about 1–3 orders of magnitude) by loading of sulfonic acids onto the surface of zeolite. Proton conductivities were correlated with the concentration of sulfonic acid groups and increased as follows: sulfonated polystyrene ZSM-5 > phenylsulfonic acid functionalized ZSM-5 > propylsulfonic acid functionalized ZSM-5 which is in line with the ion-exchange capacity, acidity and water uptake analysis. The high proton conductivity of sulfonated polystyrene ZSM-5 might be explained by using surface diffusion mechanism.

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1. Introduction

Proton exchange membrane fuel cells (PEMFC) have been identified as promising power sources for vehicular transportation and for other applications requiring clean, quiet, and portable power [1]. However, despite the promising achievements and prospects of PEMFCs, the remaining problems mean that it is still a long way before they can successfully and economically replace the various traditional energy systems. There are three main challenges that are common including a stable supply of high-purity hydrogen, cost reduction of the

system and various technological problems associated with the low performances at high temperature (over 100 °C) and low humidity [2]. Since proton conducting membranes are the key-components in PEMFCs, therefore, greater emphasis on research aimed at reducing the cost of proton conducting membranes and overcoming some of the technical problems remaining in a PEMFC system (water management, thermal management and control of CO poisoning of the platinum anode electro catalysts) have been carried out [3].

Conventional PEMFCs typically operate with Nafion[®] membranes [4,5]. Over the last 40 years, Nafion[®] properties

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have become a benchmark for comparison with other materials. Currently, development of organic-inorganic composite membranes as alternative to Nafion[®] has been an active area in the field. The following are some examples of organic-inorganic composites that were reported in the literature, vinyltrimethoxysilane-modified ZSM-5 [6], silicalite-1/SPEEK [7] and ZSM-5/Nafion composites [8–10].

Although hydrophilic, silica particles are not proton conductors, inclusion of the hygroscopic silica particles in composite solid electrolytes is primarily single-functional, i.e. for water retention. Clearly, bifunctional particles, being both hydrophilic and proton conducting are preferred to be used as proton conducting material. Thus, zeolite could be one of the suitable materials with the preferred properties due to its crystalline aluminosilicate with a uniform pore size. Zeolite is a moderate proton conductor and also hydrophilic which retains more water for efficient proton conduction in the membrane. Because of zeolites microporosity (<10 Å), zeolites can maintain hydration at very low relative humidity. This feature may be especially helpful for high temperature applications [11]. In addition, molecular sieving capabilities and high surface area of zeolite may be effective at reducing methanol permeability in the case of direct methanol fuel cell. Therefore, zeolite is expected to be a much better material than silica particles for the application considered here.

Initial attempts to apply zeolite in the preparation of proton conducting membranes include Zeolon 100H (the protonated form of mordenite) [12], natural zeolite such a chabazite and clinoptilolite [13], and mesoporous molecular sieves (MCM-41) [14]. These new solid proton conductors were developed based on zeolite loading with heteropolyacids (HPA) or zeolite-polymer composites. However, these efforts for using heteropolyacids as a solid electrolyte suffer from some drawbacks due to their high solubility in water and alcohols. As a result, the problem of high leaching of HPA was found detrimental to

long-term use of the composite membranes. One of the promising approaches to overcome this problem is by surface functionalization of zeolite by sulfonic acid [15].

Along this line, here, we reported the preparation of various organosulfonic acid functionalized ZSM-5 and testing of their proton conductivities. As shown in Fig. 1, three kinds of organosulfonic acid functionalized ZSM-5 have been prepared, namely sulfonated polystyrene ZSM-5, phenylsulfonic acid functionalized ZSM-5 and propylsulfonic acid functionalized ZSM-5. Zeolite ZSM-5 is chosen for this study because of a few reasons. First, this zeolite is usually synthesized as a high silica zeolite, and is known for its resilience in strong acid environments. Second, ZSM-5 is a hydrophilic zeolite which can help to retain more water by hydrogen bonding with its silanol groups. Third, the well-known high solid acidity of zeolite ZSM-5 could also be used to contribute to the overall proton conductivity of the hybrid material.

2. Experimental

2.1. Synthesis of zeolite ZSM-5

Solution I (the aluminum source) was prepared by adding Al₂O₃ (0.30 g) with NaOH (0.11 g) and double distilled water (10 ml). The mixture was stirred until all components were dissolved. After that, NaOH (2.95 g) and double distilled water (15 ml) were added into the mixture and stirred until a clear solution was obtained. Solution II was prepared by adding double distilled water (50 ml) with 96% H₂SO₄ (3.1 g) and tetrapropyl ammonium bromide (TPABr) (4.0 g) and stirred until all TPABr was dissolved. Solution I and Solution II were mixed with rice husk ash (9 g) and double distilled water (21 g) and shaken for 5 min. The mixture was then stirred for 30 min before crystallization at 170 °C for 2 days in a stainless steel autoclave. Zeolite ZSM-5

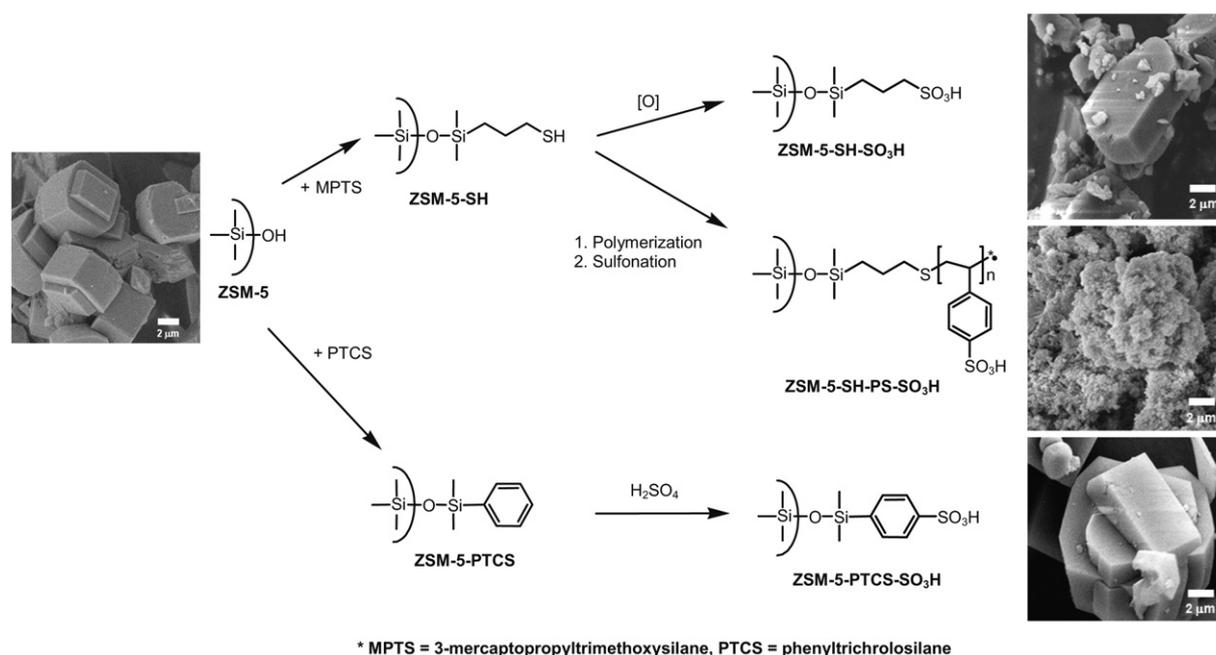


Fig. 1 – SEM images and schematic diagram of preparation of organosulfonic acid functionalized zeolite ZSM-5.

in Na⁺ form obtained was then filtered and washed with double distilled water before drying at 100 °C overnight and calcined in air at 550 °C at the rate of 3 °C min⁻¹ for 5 h. Calcined ZSM-5 (5.0 g) in Na⁺ form was protonated by ion-exchange of Na⁺ with NH₄⁺ in 1.0 M NH₄Cl solution (250 ml) stirred at 60 °C for 16 h. The solid (ZSM-5 in NH₄⁺ form) was filtered, washed with distilled water and dried at 100 °C overnight. The solid powder was then calcined at 550 °C at the rate of 2 °C min⁻¹ for 2 h in order to remove NH₃ for the generation of ZSM-5 in H⁺ form. The sample is labeled as ZSM-5. The silicon-to-aluminum molar ratio of the ZSM-5 obtained was 20.

2.2. Preparation of propylsulfonic acid functionalized zeolite

The grafting procedure was carried out by reaction of ZSM-5 (2.0 g) with 3-mercaptopropyltrimethoxysilane (MPTS) (2 ml) in 4 ml of toluene under stirring at 60 °C for 6 h. The mixture was then filtered and washed with toluene and double distilled water before drying at 100 °C. The oxidation was carried out by contacting the sample (1.0 g) with a solution of hydrogen peroxide (33 wt%; solid/liquid ratio of 1/10, w/v) at room temperature and stirred for 12 h [16]. The solid was then filtered, washed abundantly with distilled water, following by drying at 100 °C for overnight. The mercaptopropyl and propylsulfonic acid functionalized zeolite are labeled as ZSM-5-SH and ZSM-5-SH-SO₃H respectively.

2.3. Preparation of sulfonated polystyrene-zeolite composites

The zeolite surface was first silylated by using (MPTS) followed by grafting polymerization of styrene and divinylbenzene on the modified zeolite surface. Mercaptopropyl functionalized zeolite prepared in section 2.2 (ZSM-5-SH) (0.5 g) and potassium persulphate (0.5 g) were added into distilled water (40 ml). The mixture was stirred at room temperature until all the potassium persulphate was dissolved in the water. Then, styrene (2 ml) and divinylbenzene (1 ml) were added into the mixture while stirring vigorously to form an emulsion [17]. The reaction mixture was stirred at 80 °C for 6 h and the polystyrene-zeolite composite obtained was washed with distilled water and dried in air.

Acetyl sulfate was prepared by mixing dichloroethane (4 ml) and acetic anhydride (0.765 ml). 96% sulfuric acid (280 μl) was then added slowly to form a clear solution of acetyl sulfate. The sulfonation reaction was performed in a round bottom flask by pouring the acetyl sulfate solution into polystyrene-zeolite composite (0.2 g) which was pre-dissolved in 4.9 ml of dichloroethane and heated at 80 °C for 6 h under stirring [18]. The reaction was stopped by adding methanol to the mixture, and then rinsed the surface with methanol and dried in air at room temperature. The sulfonated polystyrene ZSM-5 composite is labeled as ZSM-5-SH-PS-SO₃H.

2.4. Preparation of phenylsulfonic acid functionalized zeolite

Grafting was carried out by reaction of the ZSM-5 (2.0 g) and phenyltrichlorosilane (PTCS) (2 ml) in 4 ml of toluene in

a centrifuge tube. The mixture was shaken vigorously for 15 min and then centrifuged to separate the phenyl functionalized ZSM-5 from the reaction solution. The upper layer was discarded. Phenyl functionalized ZSM-5 was washed with toluene by pouring 2 ml of toluene into the centrifuge tube and shaken again for 15 min. The mixture was centrifuged and the upper layer was discarded. The washing procedure was repeated 3 times. The resulting phenyl functionalized ZSM-5 was dried overnight at 100 °C.

Phenyl groups attached on the surface of ZSM-5 was sulfonated by contacting the phenyl functionalized ZSM-5 sample (1.0 g) with concentrated sulfuric acid (2 ml) and stirring for 1 h at 80 °C. The solid was then filtered, washed abundantly with distilled water, followed by drying overnight at 100 °C. The phenyl and phenylsulfonic acid functionalized zeolite are labeled as ZSM-5-PTCS and ZSM-5-PTCS-SO₃H, respectively.

2.5. Characterization of zeolite and composite obtained

In this study, X-ray diffraction (XRD) measurements were done on a Bruker Advance D8 using Siemens 5000 diffractometer with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 40 mA). The powder samples were ground and spread on a sample holder. The samples were scanned in the range from $2\theta = 2^\circ - 50^\circ$ with a step size of 0.05°.

Infrared spectra were acquired by using a Perkin Elmer Spectrum One FTIR spectrometer with a 4 cm⁻¹ resolution and 10 scans in the mid IR region (400–4000 cm⁻¹). KBr pellet method was used in which the solid samples were finely pulverized with dry KBr in the ratio of 1:100 and the mixture was pressed in a hydraulic press (5000 psi) to form a transparent pellet. The pellet was put in a sample holder and the spectrum of the pellet was measured. The sample image was display via FESEM (JSM-6701F) with accelerating voltage of 15 kV. The sample was coated with a conducting layer of gold.

For acidity evaluation, the wafer of the sample (10–12 mg) was prepared and locked in the cell equipped with CaF₂ windows and evacuated at 150 °C under vacuum condition (10⁻⁶ mbar) for 2 h before adsorbing an excess of pyridine at room temperature, followed by desorption at 150 °C. Infrared spectra of the samples were recorded at room temperature in the hydroxyl region of 4000–3000 cm⁻¹ and pyridine vibration region at 1700–1300 cm⁻¹.

The thermogravimetric analysis (TGA) measurements were carried out on Perkin Elmer's Pyris Diamond Thermogravimetric/Differential Thermal Analyzer under N₂ atmosphere with a flow rate of 20 ml min⁻¹ using ca. 10 mg of the sample. The sample was heated in the temperature range 50–900 °C with a heating rate of 10 °C min⁻¹.

2.6. Water uptake test

Samples were dried at 100 °C overnight prior to the measurements. After measuring the weight of the dried samples, they were put in an air-tight desiccator and exposed to moisture at ambient temperature. The samples with adsorbed moisture for an increasing period were weighed in order to calculate the water uptake.

2.7. Ion-exchange capacity measurement

The samples were placed in 0.1 M NaCl solutions and stirred overnight to exchange all the H^+ with Na^+ . The proton content in the salt solution was determined by titration with 0.01 M NaOH solution using phenolphthalein as the endpoint indicator. The protons released in the solution were calculated from the volume of NaOH consumed in the titration. The ion-exchange capacity (IEC) is given by:

$$IEC = \frac{H^+ \text{ mmol}}{W_{\text{dry}}} \quad (1)$$

2.8. Proton conductivity testing

Pellets were prepared by placing sufficient amount of sample (50 mg) in a steel die measuring 13 mm in diameter, and a pressure of 5 tons were applied and held for 30 s. The thickness of pellets were 3.31, 3.35, 3.30, 3.15, 3.28 and 3.29 mm for ZSM-5, ZSM-5-SH, ZSM-5-SH-SO₃H, ZSM-5-SH-PS-SO₃H, ZSM-5-PTCS and ZSM-5-PTCS-SO₃H, respectively. The electric properties of the membrane prepared were measured by ac impedance spectroscopy using frequency response analyzer (Autolab PGSTAT 30) in the frequency range from 0.01 Hz to 1 MHz with an applied voltage of 10 mV under controlled temperature and humidity condition. The impedance data were fitted by GPES software. The measurement was performed by sandwiching the pellet between two circular copper electrodes. Generally, measurements were made from 24 °C to 100 °C with 2 min stabilization time.

3. Results and discussion

3.1. Physical properties

The SEM images of ZSM-5 in Fig. 1 showed typical hexagonal prismatic ZSM-5 crystals. In general, the morphology of phenylsulfonic acid functionalized ZSM-5 (ZSM-5-PTCS-SO₃H) and propylsulfonic acid functionalized ZSM-5 (ZSM-5-SH-SO₃H) samples are similar to that of the starting zeolites with non-uniform aggregates of particles located on the external surface of the zeolites. As shown in Fig. 1, almost all the external surface of sulfonated polystyrene ZSM-5 composite (ZSM-5-SH-PS-SO₃H) was covered by the monodispersed polystyrene particles.

The XRD patterns of ZSM-5, ZSM-5-SH, ZSM-5-SH-SO₃H, ZSM-5-SH-PS-SO₃H, ZSM-5-PTCS and ZSM-5-PTCS-SO₃H samples obtained are depicted in Fig. 2. XRD diffractograms of all the samples synthesized show characteristic patterns for zeolite ZSM-5. Except for ZSM-5 containing polymer (ZSM-5-SH-PS-SO₃H), all the samples are pure and highly crystalline as proven by intense and narrow peaks without elevated baseline and extra peaks. However, the polymer-zeolite composites (ZSM-5-SH-PS-SO₃H) still show characteristic patterns for ZSM-5, which indicates that ZSM-5 is stable during the polymerization and sulfonation process. A broad hump appears in the XRD pattern of ZSM-5-SH-PS-SO₃H is due to the presence of polystyrene in the sample. There is no appreciable change in the framework structure of the zeolites

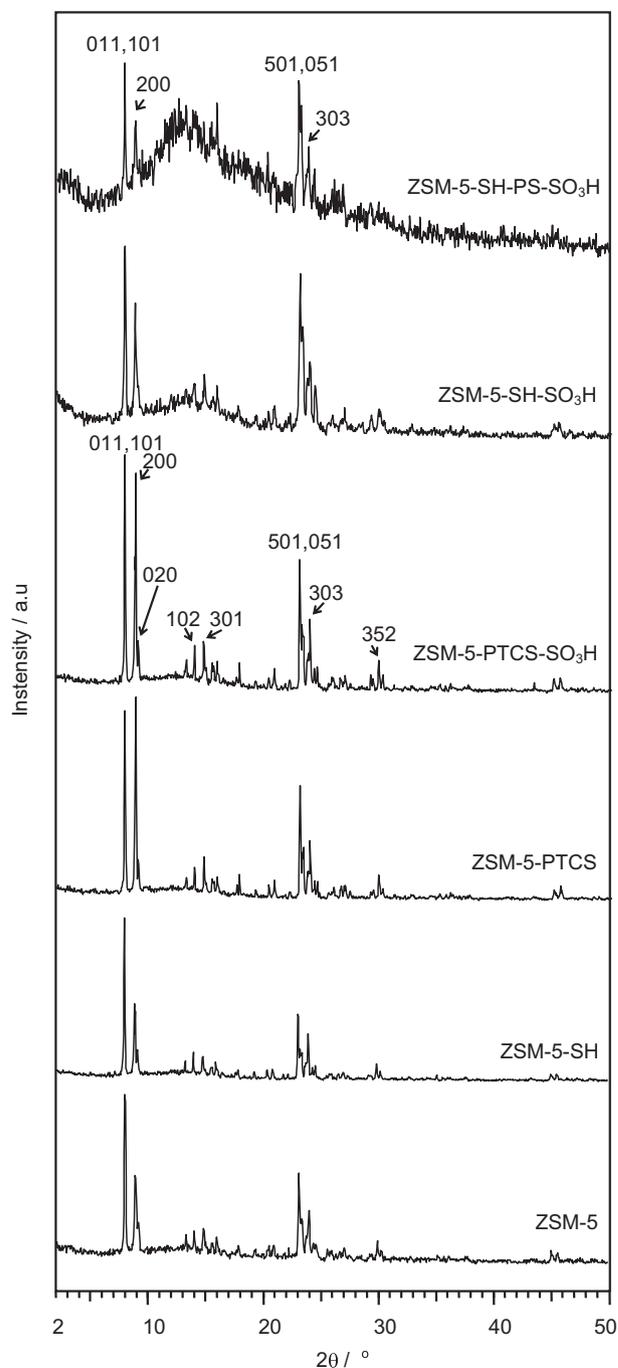


Fig. 2 – X-ray diffractograms of ZSM-5 and organosulfonic acid functionalized zeolite ZSM-5.

even after modification. The distribution of crystallite sizes of ZSM-5 calculated by Scherrer's formula was in the range of 0.4–1.0 μm .

Fig. 3 showed the FTIR spectra of polystyrene, ZSM-5 and organosulfonic acid functionalized zeolite ZSM-5. It indicates that all the samples, except for polystyrene, show six similar bands at around 3440, 1635, 1223, 1091, 792, 543 and 451 cm^{-1} . The broad peak around 3440 cm^{-1} is due to O–H stretching of water absorbed in the cavities and channels of zeolites while the peak at around 1635 cm^{-1} corresponds to the bending

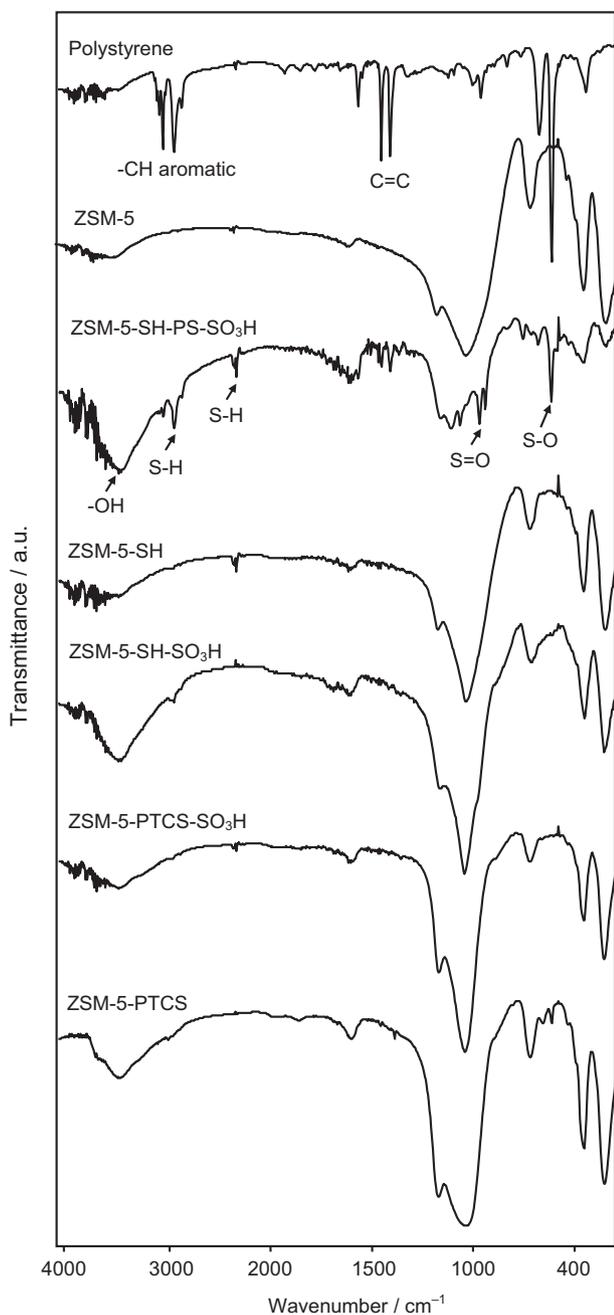


Fig. 3 – FTIR spectra of polystyrene, ZSM-5 and organosulfonic acid functionalized zeolite ZSM-5.

mode of O–H of water [19]. Besides that, the broad band at around 1091 cm^{-1} , the most prominent in the IR spectra, corresponds to asymmetric stretching of the internal vibration bands of SiO_4 or AlO_4 while the small bands observed at around 1223 cm^{-1} is assigned to asymmetric stretching of the external vibration bands of SiO_4 or AlO_4 [20]. On the other hand, the bands at around 792 cm^{-1} and 543 cm^{-1} are due to the symmetric stretching of SiO_4 or AlO_4 and double ring vibration respectively. The small band observed at around 451 cm^{-1} is assigned to Si–O–Si bending modes [19].

In Fig. 3, there are extra new peaks at around 2974 cm^{-1} and 2550 cm^{-1} for sample ZSM-5-SH, which is assigned to

alkyl groups stretching and stretching band of thiol groups (–SH) respectively [20]. While the peaks at around 1465 cm^{-1} are due to $-\text{CH}_2$ bending band [20]. These show that the modification of zeolite with MPTS was successful but the attachment of propylthiol groups was low as the –SH and alkyl stretching bands are not apparent.

After oxidation of thiols groups to form sulfonic acids, extra new peaks at around 1050 cm^{-1} and 650 cm^{-1} which is assigned to S=O symmetric stretching and S–O stretching respectively [20] were found in ZSM-5-SH-SO₃H, ZSM-5-SH-PS-SO₃H, and ZSM-5-PTCS-SO₃H samples. As shown in Fig. 3, grafting of polystyrene on thiols functionalized zeolite ZSM-5 was confirmed by the presence of benzene ring features in ZSM-5-SH-PS-SO₃H: C–H aromatic symmetric stretching vibrations at 3025 and 2922 cm^{-1} and skeletal C=C in plate-stretching vibrations at 1493 and 1601 cm^{-1} [20]. It can also be seen that the prominent peaks at 756 and 697 cm^{-1} in polystyrene-zeolite composite are due to –C–H out of plane bending [20]. As compared with polystyrene, the characteristics peaks of zeolite ZSM-5 at 442 , 550 , 801 , 1112 and 1229 cm^{-1} , which are due to Si–O/Al–O bending, double ring vibration, symmetric stretching of $\text{SiO}_4/\text{AlO}_4$, asymmetric stretching of the internal vibration bands of $\text{SiO}_4/\text{AlO}_4$, and asymmetric stretching of the external vibration bands of $\text{SiO}_4/\text{AlO}_4$ respectively, are observed. These prove that the attachment of polymer into thiol functionalized ZSM-5 was successful.

Fig. 4 shows the FTIR spectra of the organofunctionalized zeolite ZSM-5 samples after evacuation at 150°C for 2 h under

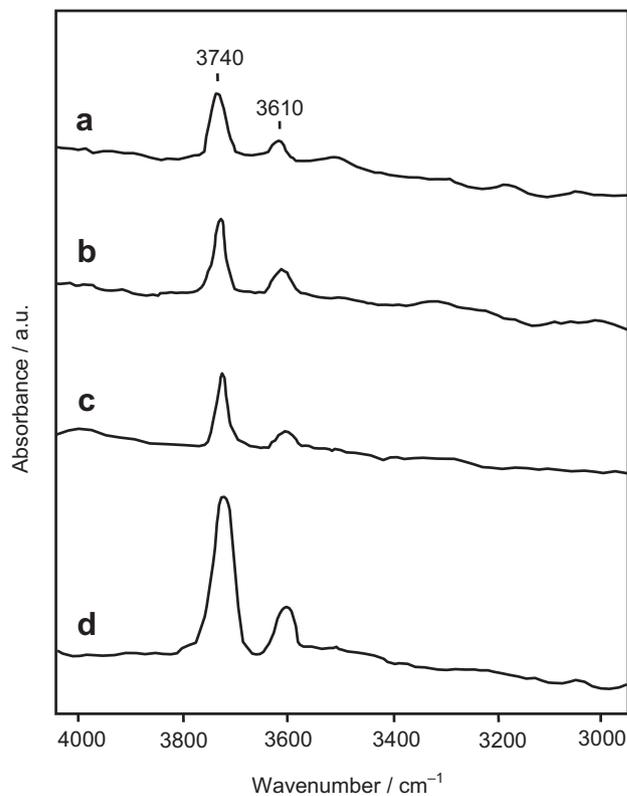


Fig. 4 – The FTIR spectra of hydroxyl group of (a) ZSM-5-SH-PS-SO₃H, (b) ZSM-5-SH-SO₃H, (c) ZSM-5-PTCS-SO₃H and (d) ZSM-5.

vacuum. In the region of hydroxyl groups, two bands were observed at 3610 and 3740 cm^{-1} . The former had been assigned to acidic bridging OH from the Si–O(H)–Al band while the latter is attributed to the defect sites and terminal Si–OH [21]. Both bands at 3610 and 3740 cm^{-1} can be clearly seen in all samples. As shown in Fig. 4, it is clearly observed that decreasing the peak area at 3610 and 3740 cm^{-1} in ZSM-5-SH-PS-SO₃H (Fig. 4a), ZSM-5-SH-SO₃H (Fig. 4b), and ZSM-5-PTCS-SO₃H (Fig. 4c) compared to that of original ZSM-5 (Fig. 4d). This indicated that the functionalization of ZSM-5 occurred via bonding between Si–OH with 3-mercaptopropyltrimethoxysilane (MPTS) and also phenyl-trichlorosilane (PTC).

The acidity of the sulfonic acid functionalized ZSM-5 was further monitored by FTIR using pyridine as a probe molecule. The purpose of this experiment is to determine the amount and type of acid in the material. Fig. 5 shows the IR spectra of samples after the adsorption of pyridine. The band at 1452 cm^{-1} in the spectra is attributed to adsorbed pyridine bound coordinative with Lewis acid sites [21]. The absorption bands at 1538 cm^{-1} correspond to pyridine interacting with Brønsted acid sites [21]. The presence of these bands for all samples indicates that all samples contain both Brønsted and Lewis acid sites. As can be seen in Fig. 5, the results show the trend of the amount of acid sites in ZSM-5 and sulfonic acid functionalized ZSM-5 in decreasing order as follows: ZSM-5-SH-PS-SO₃H (most acidic) > ZSM-5-SH-SO₃H > ZSM-5-PTCS-SO₃H > ZSM-5 (least acidic).

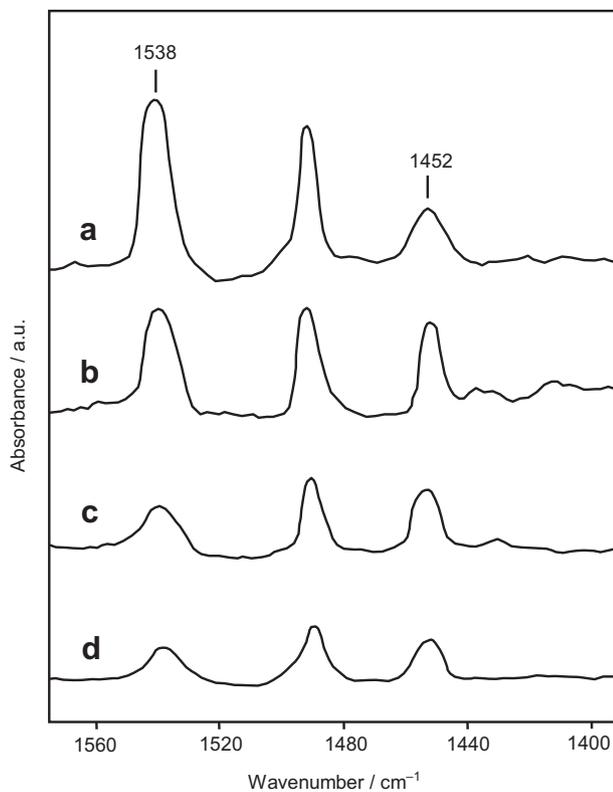


Fig. 5 – The FTIR spectra of pyridine adsorbed on (a) ZSM-5-SH-PS-SO₃H, (b) ZSM-5-SH-SO₃H, (c) ZSM-5-PTCS-SO₃H and (d) ZSM-5.

3.2. Ion exchange capacity

Ion exchange capacity test provides a semi-quantitative analysis of the proton concentration (especially from –SO₃H groups) in the synthesized samples and the values are shown in Table 1. The ion-exchange capacities in Table 1 are averages of three measurements of each sample. It should be noted that the ion-exchange capacities obtained in this study are subject to small uncertainties because not all of the amount of protons in the synthesized samples could be released into the salt solution during ion exchange process. In general, the ion capacities of the samples increase as follow: ZSM-5-SH-PS-SO₃H > ZSM-5-SH-SO₃H > ZSM-5-PTCS-SO₃H > ZSM-5 ≈ ZSM-5-SH ≈ ZSM-5-PTCS. This trend is in agreement with pyridine adsorption experiment (see Fig. 5).

3.3. Water uptake test

Fig. 6 demonstrates the water adsorption capacity of all the samples investigated in this study. The samples were exposed for increasing periods to a moist atmosphere at ambient temperature. It is very important to characterize the behavior of proton conducting membranes in contact with water, since the presence of water in the membrane is a prerequisite for reaching high proton conductivity.

Zeolites have internal and external surfaces. The water uptake in the internal surface is well-defined and should be a maximum for the parent zeolite. The water uptake decreases for steric reasons, if a functionalization took place in the pore of the aquaphilic zeolite. However, there is no space for the functional group in a crossing channel of ZSM-5 zeolite. This fact account for no significant increase of water uptake upon functionalization with –SH group, in which –SH functionalization on the external ZSM-5 surface formed only slightly influenced by functionalization. In addition, the outer surface of a ZSM-5 with a silicon-to-aluminum molar ratio of about 20 should be aquaphilic for both.

As can be seen in Fig. 6, ZSM-5-SH-PS-SO₃H showed the highest water adsorption capacity followed by ZSM-5-SH-

Table 1 – Ion-exchange capacities and amount of the functional group of ZSM-5 and organosulfonic acid functionalized zeolite ZSM-5.

Sample	Ion-exchange capacity (mmol H ⁺ g ⁻¹) ^a	Amount of the functional group on ZSM-5 surface (wt%) ^b
ZSM-5	0.01	0
ZSM-5-SH	0.02	2
ZSM-5-SH-SO ₃ H	0.25	15
ZSM-5-SH-PS-SO ₃ H	1.00	65
ZSM-5-PTCS	0.02	7
ZSM-5-PTCS-SO ₃ H	0.10	10

^a The ion-exchange capacity was determined by titration method (see section 2.7).

^b The percent weight of functional group attached on ZSM-5 surface was calculated from the weight loss in thermogravimetric analysis (see section 2.5).

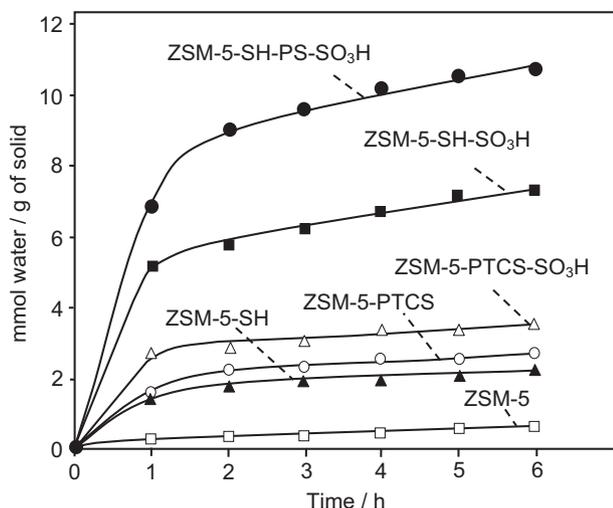


Fig. 6 – Water uptake capacity of ZSM-5 and organosulfonic acid functionalized zeolite ZSM-5.

SO_3H , ZSM-5-PTCS- SO_3H , ZSM-5-PTCS, \approx ZSM-5-SH and ZSM-5. These indicate that water sorption increased with sulfonic acid content due to the strong hydrophilicity of the sulfonate groups [22–24]. Sulfonic acid in this context is capable to increase the hydrophilicity of the membranes. As tabulated in Table 1, it is clearly observed that the water adsorption and ion-exchange capacities of modified ZSM-5 are strongly correlated with the amount of the functional group as analyzed by thermogravimetric analyzer. It is found that the ZSM-5-SH-PS- SO_3H sample has the most number of functional group (65 wt%) and therefore, had the highest ion-exchange ($1.0 \text{ mmol H}^+ \text{ g}^{-1}$) and water adsorption capacities (see Fig. 9). Unmodified ZSM-5 showed the lowest ion-exchange capacity and water uptake since no functional groups presence in the sample. This suggests that the functional groups play an important role to increase the ion-exchange capacity and water uptake. The water molecules

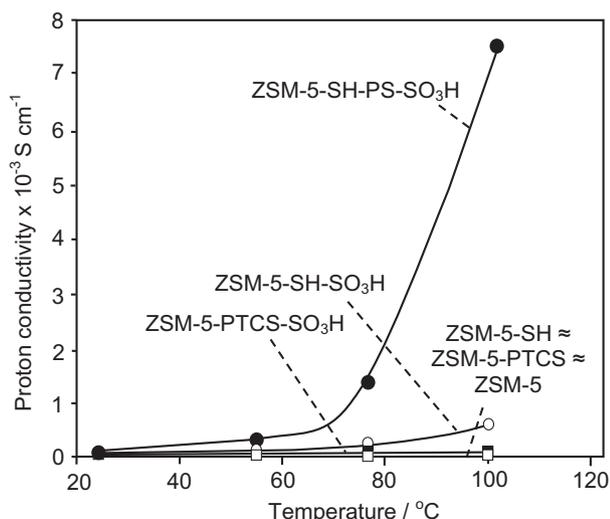


Fig. 7 – Proton conductivity of ZSM-5 and organosulfonic acid functionalized zeolite ZSM-5.

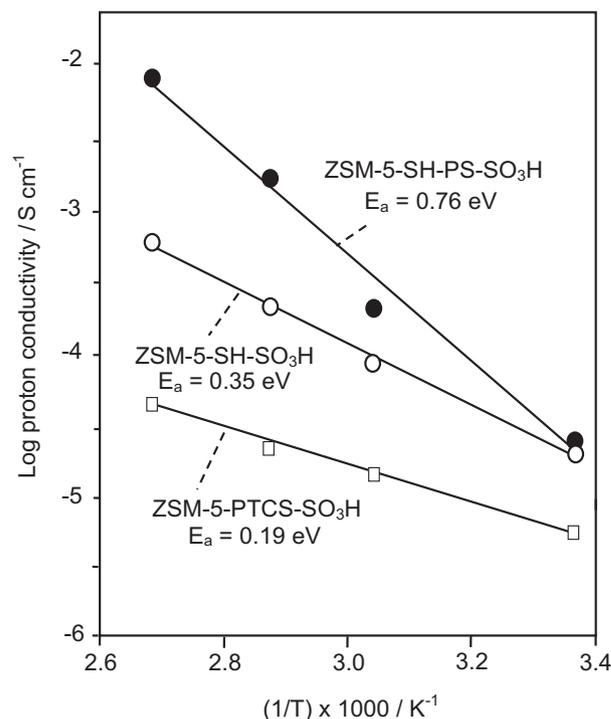


Fig. 8 – Proton conductivity of organosulfonic acid functionalized zeolite ZSM-5 versus the reciprocal of the temperature.

penetrate the polymer matrix by hydrophilic interaction with $-\text{SO}_3\text{H}$. Based on these results, one suggests that the contribution of framework structure of ZSM-5 for water adsorption is much smaller than that of the functional group ($-\text{SO}_3\text{H}$) attached on the external surface of ZSM-5, especially for ZSM-5-SH-PS- SO_3H .

3.4. Proton conductivity

In Fig. 7, it is observed that sulfonated polystyrene-zeolite composites give the highest proton conductivity (2.3×10^{-5} – $7.5 \times 10^{-3} \text{ S cm}^{-1}$) followed by propylsulfonic acid functionalized ZSM-5 (3.4×10^{-5} – $5.8 \times 10^{-4} \text{ S cm}^{-1}$) and phenylsulfonic acid functionalized ZSM-5 (8.7×10^{-6} – $4.3 \times 10^{-5} \text{ S cm}^{-1}$). It is shown that proton conductivity correlates with the concentration of sulfonic acid groups and the concentration of sulfonic acid decreases as follows: ZSM-5-SH-PS- SO_3H > ZSM-5-SH- SO_3H > ZSM-5-PTCS- SO_3H . Thus, the highest proton conductivities of sulfonated polystyrene-zeolite composites resulted from the systems having the highest carrier (proton) concentration of sulfonic acid groups.

As clearly shown in Fig. 7, the proton conductivities of organosulfonic acid functionalized ZSM-5 zeolite were increased significantly due to the presence of sulfonic acid groups in the composite because of a few reasons related to their proton conduction mechanisms. In all cases, proton transfer is obviously associated with acid sites (sulfonic acid groups) bound to the support materials. In the hydrated state, the electrostatic force between the cations and the lattice is weakened due to solvation [25]. Hydration allows the bridging

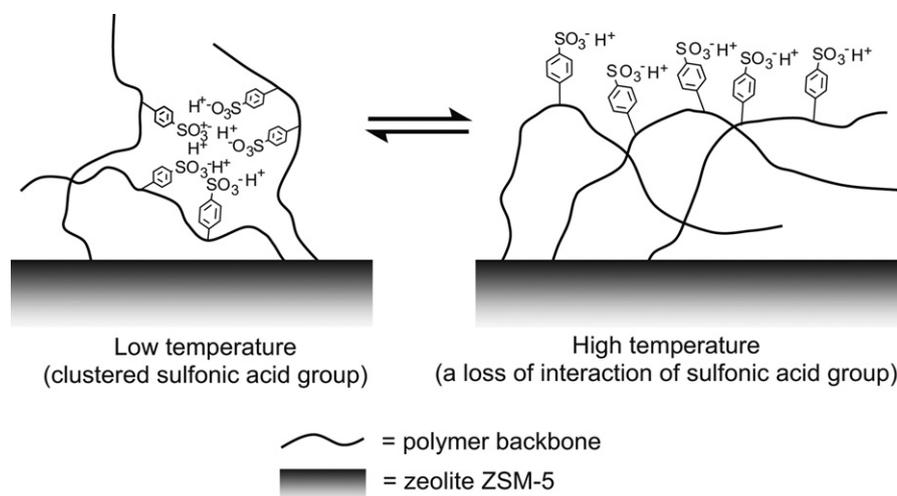


Fig. 9 – Effect of temperature on the arrangement of sulfonate group of the sulfonated polystyrene attached on the surface zeolite ZSM-5.

acidic sites to assist in ion hopping and provide additional charge carriers as the sulfonic acid groups dissociate into SO_3^- (fixed charge) and H^+ (mobile charge) upon the addition of water. The protons, which are responsible for the ion conductivity, thus, encounter a lower resistance to hop from one water molecule to the next or from one cluster of water molecules to the next under a potential gradient. Thus, this more effectively help the protons to hop from its host lattice throughout the membranes.

Fig. 8 shows the proton conductivity of sulfonated polystyrene ZSM-5 versus the reciprocal of temperature. An Arrhenius-like dependence with temperature is observed in Fig. 8. The value of the activation energy (E_a) was obtained by linear regression of the Arrhenius equation $\sigma = \sigma_0 \exp(-E_a/KT)$, where σ , σ_0 , K are proton conductivity, a pre-exponential parameter and the Boltzmann's constant, respectively. The activation energy was calculated from the determination the slope value shown in Fig. 8. The calculated value is 0.76 eV. The high activation energy and sudden change in proton conductivity at ca. 80 °C of sulfonated polystyrene ZSM-5 (Fig. 7) might be explained by using surface diffusion mechanism [26].

A sudden change in proton conductivity of ZSM-5-SH-PS- SO_3H about 80 °C could be related to the glass transition temperature (T_g) of sulfonated polystyrene. It has been reported that T_g of sulfonated polystyrene is 104 ± 4 °C [27]. On the basis of these results, a model of the arrangement of sulfonate group of the sulfonated polystyrene attached on the surface zeolite ZSM-5 at low and high temperatures is proposed (see Fig. 9). One suggests that the polar sulfonic acid groups may cluster together to form a closed structure at low temperature. As the temperature increase, the ionic groups will lose their interaction for each other, and the chains will move freely. This movement allows the sulfonic acid functional group projected outward on the polystyrene backbone to form an open structure at its glass transition temperature (ca. 100 °C).

The increase of proton conductivity with temperature could also be related to kinetic energy of hydronium ion and the increased mobility of hydronium with temperature [26,28].

The synergetic effect between sulfonate group rearrangement and mobility of water connected proton ($\text{H}^+(\text{H}_2\text{O})_x$) play an important role in proton conduction of sulfonated polystyrene. The excess proton diffuses through water in form of high mobility water connected proton ($\text{H}^+(\text{H}_2\text{O})_x$) such as (H_9O_4^+) or Zündel ions (H_5O_2^+) and jump with the help of surfaced projected outward sulfonate groups [29].

Apart from the hopping mechanism helped by the presence of sulfonic acid groups, zeolite ZSM-5 in this context plays a significant role in the diffusion of the hydronium ions formed. Generally, zeolite is known to be capable of retaining water molecules in their cavities especially at relatively high temperature. Thus, the proton attached to a water molecule may be transmitted through a chain of water molecules from one electrode to the other, providing a fast route for conductivity, corresponding to a low specific resistance of the membranes.

By introducing silane coupling agents, which create strong covalent bonds between the polymer and zeolite, a good interfacial adhesion between ZSM-5 particles and polystyrene is achieved. Therefore, chemically bonded sulfated polystyrene-ZSM-5 provides a direct contact between the sulfonic acid groups of polystyrene and zeolite particles. As a result, protons can move more continuously which lead to higher proton conductivity.

4. Conclusions

The enhancement of proton conductivity of sulfonated polystyrene ZSM-5 can be considered by the following properties of organic-zeolite composite, i.e., the concentration of sulfonic acid groups and the ability of ZSM-5 to retain water molecules in their cavities especially at relatively high temperature. The spectroscopic analysis by using XRD and FTIR, and supported by the ion-exchange capacity and water uptake analysis indicate that the type of the organosulfonic acid groups (phenylsulfonic acid, phenylsulfonic acid, or sulfonated polystyrene) attached on the surface of zeolite plays an important role in proton conductivities of

organosulfonic acid functionalized zeolite ZSM-5. It is observed that sulfonated polystyrene ZSM-5 gives the highest proton conductivity compared to that of phenylsulfonic acid functionalized ZSM-5 and propylsulfonic acid functionalized ZSM-5. Based on the value of the activation energy was obtained by linear regression of the Arrhenius equation, the drastic increase in proton conductivity in sulfonated polystyrene ZSM-5 at ca. 80 °C might be explained by using surface diffusion mechanism. One concludes that proton conductive zeolite ZSM-5 may be prepared by surface functionalization by attachment of sulfonated polystyrene on the surface of ZSM-5 particles.

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