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TRANSPORT ACROSS SUB-NANOMETER ZEOLITE PORES FOR WATER DESALINATION

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ABSTRACT

The molecular sieving capability of zeolites, aluminosilicate minerals with 3-8 Å diameter pores, promises an efficient method to remove salt from seawater. In this work, we synthesized and characterized MFI zeolites with a nominal pore diameter of 5.6 Å with varying Si/Al ratio from 23 to infinity to alter the wetting properties. We subsequently performed pressure infiltration tests with the synthesized zeolites suspended in water to investigate the effect of wetting properties on water transport in the pores. Water sorption isotherms were obtained that show distinct infiltration stages of water transport. For MFI zeolites, pressures of over 100 MPa were needed to fill the pore volume. The insight gained from this work is a first step towards designing zeolite-based membranes for the active layer of a reverse osmosis membranes. This work will be further developed in future work to understand ion transport through zeolites.

INTRODUCTION

Reverse osmosis (RO) using polymeric, thin film composite membranes is the state-of-the-art large-scale seawater desalination system, accounting for nearly 50% of the world's desalination capacity [1, 2]. While most new RO plants operate near the theoretical minimum energy required to desalinate seawater (~2.5 kWh/m³ for current generation RO plants compared to the minimum energy required of ~0.8 kWh/m³ with 35% recovery), challenges limit the potential of RO. Water transport across RO membranes relies on diffusion across a semi-permeable active layer, so that the water flux is limited. Therefore, achieving a sufficient amount of clean water requires a large active membrane area.

Membranes with selective sub-nanometer pores promise an order of magnitude increase in water flux for RO [5-7]. For example, such pores allow water molecules, which have an effective diameter of 3.3 Å, to transport through, while rejecting the passage of larger solvated salt ions, which have an effective diameter of 6 – 8 Å [8, 9]. Furthermore, in addition to steric-based (size) exclusion, electrostatic and Donnan equilibrium effects may also contribute to salt rejection [10].

Zeolites, aluminosilicate minerals with pore diameters ranging from 3-8 Å, can be ideal molecular sieves for desalination [11]. Molecular dynamics simulations have demonstrated that ZK4-type zeolites with 4.4 Å diameter pores perfectly rejected solvated salt ions due to steric exclusion effects, while still allowing water molecules to pass through the pores [12, 13]. This result has motivated researchers to fabricate zeolite-based membranes for water desalination [14-16]. However, these membranes had limited performance due to challenges with fabrication, in which water and salt permeated around the zeolites or through intercrystalline defects. Currently, there are limited experiments demonstrating the understanding of transport of water and exclusion of ions across zeolites, which is a necessary step towards tailoring zeolites for efficient RO membranes. The infiltration of water in zeolite pores was recently investigated, but the work focused on using such materials for energy recovery systems, which has different requirements than RO [17, 18].

In this work, we investigated the effect of wetting properties of various zeolites on water transport, which is the first step in providing insight into the transport mechanisms. We synthesized and characterized MFI zeolites with pore diameters of 5.6 Å with varying silicon to aluminum (Si/Al) ratios. We subsequently performed pressure infiltration experiments. These results aid in determining the type of MFI zeolites for eventual integration into the active layer for RO membranes.

EXPERIMENTAL PROCEDURE

Zeolite Synthesis:

All chemicals were used as received. Tetraorthosilicate (TEOS, 98%), tetrapropylammonium hydroxide (TPAOH, 1M in H₂O), aluminum isopropylate (Al(Pro)₃, 98%), and sodium hydroxide (NaOH, 99.995%) were used in the zeolite synthesis.

MFI 1: Silicate-1 (MFI, Si/Al - ∞) was synthesized from a gel containing a molar ratio of 5 TEOS:1 TPAOH:500 H₂O [19]. 5 g of TEOS was introduced into a solution containing 4.9 g of TPAOH along with 39.3 g of de-ionized H₂O. This solution was vigorously stirred for 12 hours. The resulting solution was

then filtered and transferred to a PTFE-lined stainless steel autoclave (Parr, Inc). To obtain an average particle size of $0.5 \times 0.5 \times 0.2 \mu\text{m}^3$, the autoclave was heated in a furnace at 150°C for 5 hours. The resulting solution was then washed with excess de-ionized water, separated through centrifugation and dried at 60°C . The zeolites were then calcined at 450°C for 6 hours to remove the precursor so that the zeolites pores were opened.

MFI 2: ZSM-5 type zeolites (MFI, Si/Al – 50) were synthesized from a gel containing 0.3 NaOH:0.5 Al_2O_3 :50 SiO_2 :12 TPAOH:1600 H_2O [20]. A solution with this molar ratio contained 0.016 g sodium hydroxide, 22.28 mL of de-ionized H_2O , 15 mL of TPAOH, 0.437g of aluminum isopropylate, and 14.2 mL of TEOS. This solution was vigorously stirred for 12 hours, filtered, and then transferred to a PTFE lined autoclave and synthesized at 140°C for 6 hours. The resulting solution was then washed with excess de-ionized water, separated through centrifugation and dried at 60°C . The zeolites were then calcined at 450°C for 6 hours to remove the precursor so that the zeolites pores were opened. The resulting ZSM-5 aggregates varied in size from 500 nm to $10 \mu\text{m}$ in width.

MFI 3: ZSM-5 type zeolites (MFI, Si/Al – 23) were commercially obtained (CBV 2314, Zeolyst, Inc).

Note that ZSM-5 and Silicate-1 zeolites are both MFI type zeolites, and therefore the available pore volume is also the same.

Characterization:

Powder X-ray diffraction analysis (XRD) was performed using a Phillips X'Pert Pro diffractometer using a $\text{CuK}\alpha_1$ incident beam monochromator and an X'Celerator Detector. The XRD patterns of the various calcined zeolite samples are shown in Figure 1. The measured patterns match the diffraction pattern of the known MFI-type zeolites. There is no distinguishable difference among any of the zeolites, which is expected since the Si/Al ratio should not affect the microstructure and pore size of the zeolites. Further XRD was also performed after the infiltration experiments and no changes were observed. These results ensured that the pressure infiltration experiments did not cause a large-scale change in order or structure of the zeolites.

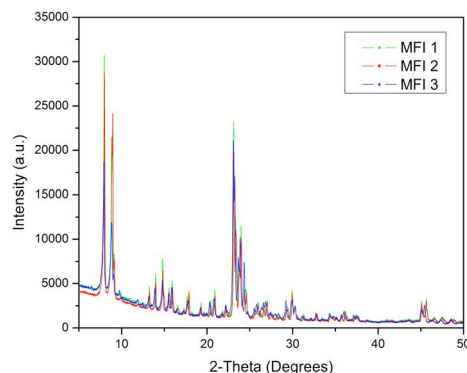


Figure 1. X-ray diffraction patterns for MFI 1 (green), MFI 2 (green), and MFI 3 (blue).

The Si/Al ratio of the zeolites was determined *via* powder X-ray photoelectric spectroscopy (XPS) using a Kratos AXIS Ultra Imaging X-Ray Photoelectron Spectrometer. Analysis was performed and the Si/Al ratio of the three samples, MFI 1, MFI 2, and MFI 3, are infinite, 50, and 23, respectively.

Scanning electron microscopy (SEM) images were obtained using a Phillips XL30 ESEM and are shown in Figure 2. Samples were typically coated with a 10 nm gold film prior to viewing. The morphology of the various zeolites was examined. MFI 1 crystals have an average size of $0.5 \times 0.5 \times 0.2 \mu\text{m}^3$. The structure of the zeolites is very well defined, as nearly all of the particles have a typical ‘disk-type’ shape as has been reported in similar syntheses [21]. As the Si/Al changes and decreases from infinity, the ‘disk-type’ structure no longer occurs. Instead, aggregates of zeolites were observed ranging in size from 200 nm to over $10 \mu\text{m}$ in width. Although the particle structure is not uniform and seems to be disordered, the MFI type pore structure remains (as the XRD analysis confirmed).

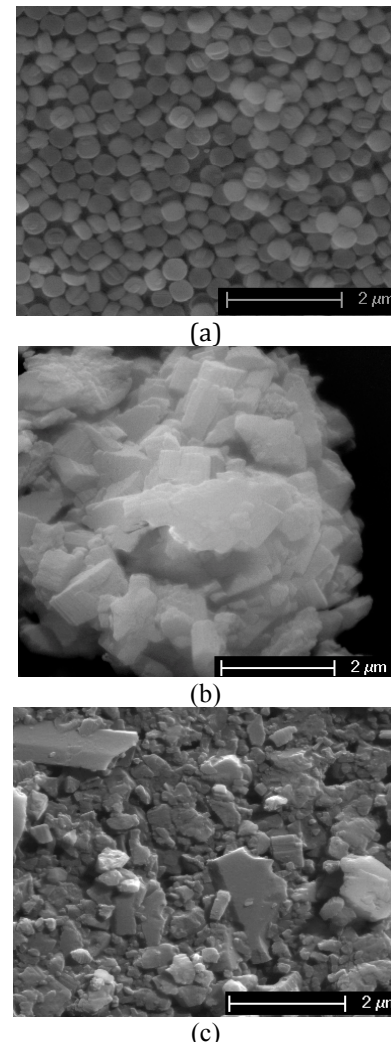


Figure 2. Scanning electron microscope images of zeolites. a) MFI 1 (Si/Al – ∞) b) MFI 2 (Si/Al – 50) c) MFI 3 (Si/Al – 23).

Pressure Infiltration Experiments:

The water infiltration experiments were performed at room temperature using a custom pressure vessel with a mobile piston (Figure 3). The cross-sectional area of the piston is 71 mm^2 . A load was applied and the piston displacement was measured using an Instron testing apparatus. The applied force ranged from 0 to 9500 N, which corresponds to a maximum applied pressure of 134 MPa. The piston displacement rate used was 1 mm/min. Experiments were carried out using a suspension of 0.2-0.7 g of zeolite in 6 g of water. The zeolites were heated in an oven at 150°C for 24 hours prior to the experiments to dry the samples. Volume change was calculated by multiplying the displacement collected from the Instron by the cross sectional area of the piston. The specific infiltration volume was obtained by subtracting out the volume change corresponding with the compressibility of pure water from each infiltration experiment.

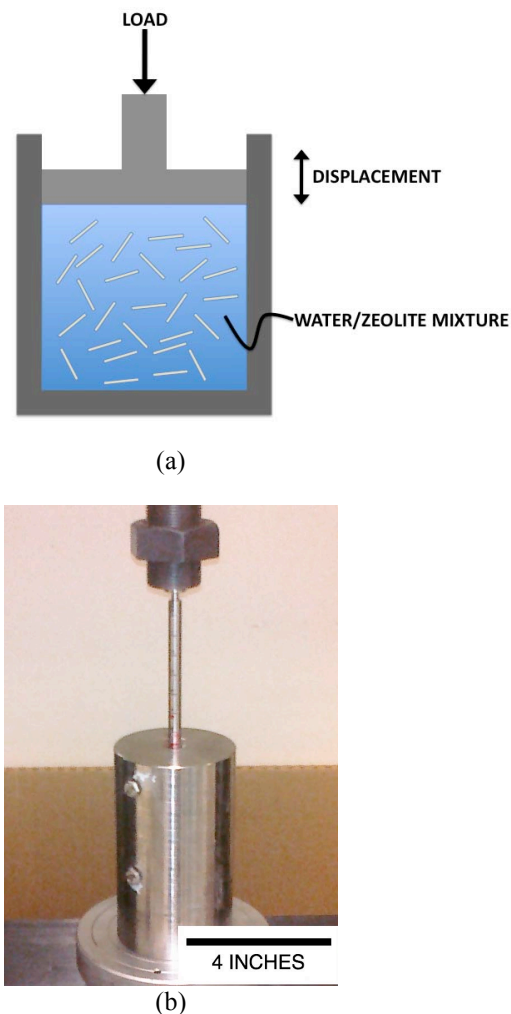


Figure 3. Custom pressure vessel. a) Schematic and b) image of pressure vessel for infiltration experiments

RESULTS AND DISCUSSION

The results of the pressure infiltration experiments are shown in Figure 4. The infiltration isotherms are shown for DI water, DI water/MFI 1 (Si/Al - ∞), DI water/MFI 2 (Si/Al - 50), and DI water/MFI 3 (Si/Al - 23). According to the framework density of an MFI-type zeolite, the available pore volume is $0.11 \text{ cm}^3/\text{g}$ [22] which should be equal to the total volume displacement measured in these experiments, if water is initially absent from the pores. The results show that for completely hydrophobic MFI 1 zeolites, the infiltration volume is indeed $0.11 \text{ cm}^3/\text{g}$. However, in the case of both MFI 2 and MFI 3 zeolites, water has already infiltrated into the pores prior to the experiments, which is due to the decrease in Si/Al ratio. In the cases of MFI 2 and MFI 3, we estimate that the amount of water inside of the pores before the infiltration experiments to be $\sim 0.05 \text{ g}$ ($\sim 45\%$ of the available volume) and $\sim 0.1 \text{ g}$ ($\sim 90\%$ of the available volume), respectively.

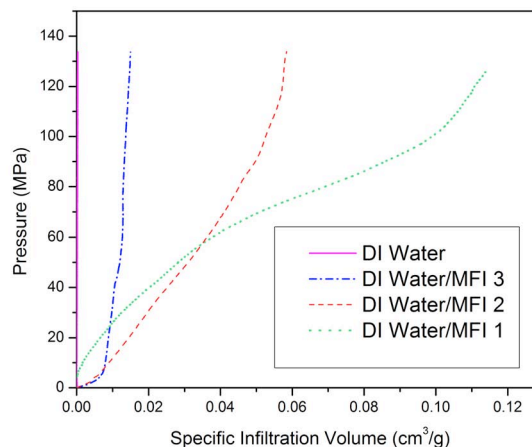


Figure 4. Water sorption isotherms showing infiltration pressures for DI water, DI water/MFI 1, DI water/MFI 2, and DI water/MFI 3. The specific infiltration volume is expressed in cm^3 per gram of calcined zeolite.

The shape of the infiltration curve changes with the Si/Al ratio. For the completely hydrophobic zeolite (MFI 1), we observed three ‘infiltration stages’ [18]. During the first stage, water gradually infiltrates the pores until the applied pressure reaches $\sim 60 \text{ MPa}$. In the second stage, which occurs between 60 and 100 MPa , a majority of the available pore volume ($\sim 60\%$ or $0.7 \text{ cm}^3/\text{g}$) is infiltrated by water. Finally, as the pressure exceeds 100 MPa , the available pore volume is nearly filled and only a small amount of water continues to fill the pore. The slope of the isotherm approaches infinity as the available pore volume approaches zero. However, as the Si/Al ratio of the zeolites decreases, the infiltration isotherms seem to only capture the latter infiltration stages, where a majority of the pore volume is already filled with water. From the experiments, we observed that the slope of the specific infiltration isotherms for MFI 2 and MFI 3 zeolites approaches infinity at $\sim 0.06 \text{ cm}^3$ and $\sim 0.01 \text{ cm}^3$, respectively, due to the amount of water initially in the pores before the pressure

infiltration experiments. Further insights will be obtained by performing experiments on additional zeolites with varying Si/Al ratios and pore sizes.

CONCLUSIONS AND FUTURE WORK

We investigated the effect of the silicon to aluminum ratio on water infiltration and transport in sub-nanometer MFI pores. We synthesized and characterized zeolites with Si/Al ratios varying from 23 to infinity. Through pressure infiltration tests, we obtained water sorption isotherms that indicate the role of Si/Al ratio on water infiltration characteristics. A substantial pressure was required to fill a majority of the available pore volume with water (~100 MPa) for MFI 1 zeolites. As the Si/Al ratio of the zeolite decreases, the pressure to fill a majority of the pores substantially decreases.

Our future work seeks to provide more quantitative insight into pressure infiltration and subsequently transport properties across zeolites. We plan to perform more detailed experiments with additional zeolites with varying Si/Al ratios (80 and 300) and varying pore sizes (Linde Type A - 4.4 Å and Faujasite - 7.4). We will also simultaneously use MD simulations to guide our understanding of the experiments.

The overall goal of the work is to determine the type of zeolite that would optimally serve as a water-selective active layer for an RO membrane. An initial criterion for zeolite selection is that water should be able to infiltrate the zeolite pores at pressures that RO systems operate (<5.5 MPa). Currently, only the ZSM-5 zeolites with a Si/Al ratio of <50 appear to be suitable.

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