

MASS TRANSPORT THROUGH ZEOLITE MEMBRANES: INVESTIGATING FRAMEWORK POLARITY

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Introduction

Zeolites are microporous crystalline aluminosilicates which have uniform, molecular-sized pores. Zeolites can be used as membrane material to separate gaseous or liquid mixtures based on difference in molecular size and/or adsorption and diffusion properties. The polarity of the zeolite is an important parameter determining the separation properties of the membrane. This study focuses on the systematic investigation of the influence of membrane polarity on the mechanism of transport.

Zeolite polarity

The polarity of permeating components strongly determines the transport through inorganic membranes [1]. Most research on dewatering of organic solvents has been done using highly hydrophilic membranes [2,3]. These highly polar membranes exhibit a strong interaction between zeolite host and the permeating guest molecules. This results in a high loading of the zeolite, however, the strong interaction also results in a low diffusivity. Figure 1 shows the saturation loading, and the self diffusivity of water in several zeolite types, plotted against the silica to alumina ratio (Si/Al). Lower Si/Al means a more polar membrane. From this figure it is evident that there is a trade-off between adsorption and diffusion. Tuning the zeolite polarity would enable the optimization of membrane processes.

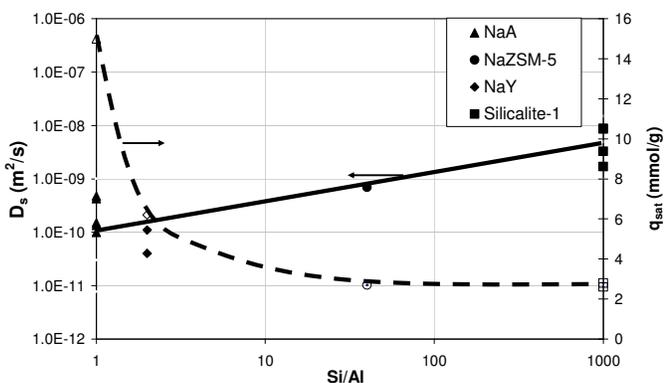


Figure 1: Self diffusion (D_s , closed symbols), and saturation loading (q_{sat} , open symbols) of water in zeolites (compiled from literature, both experimental and computational data)

Methods and Results

In principle there are several ways of modifying the zeolite polarity. The polarity is determined by: the silica to alumina ratio, the cation type, the pore configuration and the amount of silanol groups

Zeolite crystals can contain defects in the crystal structure. When a Si-O-Si bond is broken, a Si-OH group can be formed. These silanol groups are present in every real zeolite, and provide a certain amount of polarity. At high temperatures the silanol groups are removed through a condensation reaction [4], and the zeolite becomes more hydrophobic. After introducing these silanol groups, the polarity can be tuned by post synthesis calcination at different temperatures, leaving different amounts of silanol groups [5].

De Ruiter et al. have shown that when [B]MFI crystals are calcined under ammonia atmosphere, the template is removed, but the boron remains in the zeolite framework. The boron can then be easily removed subsequently, leaving silanol nests [6]. Up to five

boron molecules per unit cell can be isomorphically substituted in an MFI zeolite [4]. We have synthesized [B]-ZSM5 membranes and crystals with a Si/B ratio of 50. The figure below shows a FTIR plot of the deboronated crystals. From Figure 2 it is evident that increasing the calcination temperature decreases the amount of silanol groups within the framework. Also ^{29}Si -NMR confirms this, as shown in the figure below.

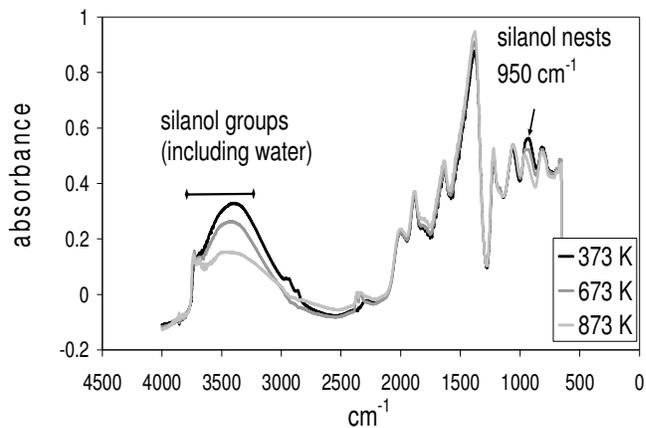


Figure 2: FTIR of [B]ZSM5 crystals taken at room temperature after calcination at 373, 673 and 873 K.

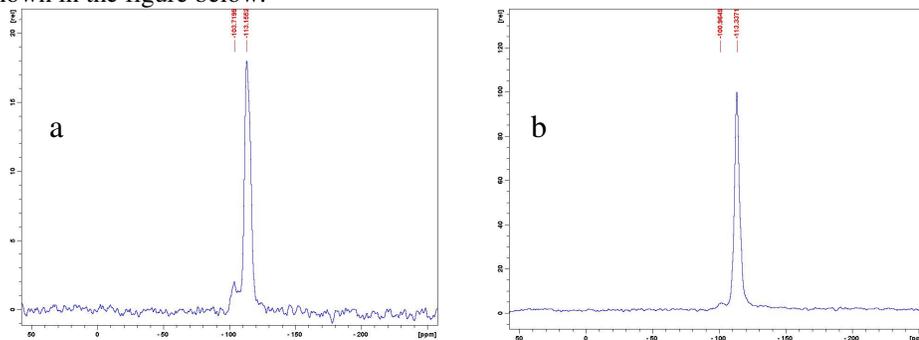


Figure 3: ^{29}Si -NMR spectra of deboronated [B]ZSM-5 (a) and silicalite-1 calcined at 773 K (b)

The membranes are synthesized on α -alumina disks (Pervatech AKP30, 80nm pore size, 2mm thick, 25mm diameter, polished) according to the synthesis developed by Tuan et al.[7] and de Ruiter et al. [6]. [B]ZSM5 membranes, with a thickness of about 15 μm and a nitrogen permeance after calcination, of $10^{-7} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ have been synthesized. The membranes have a Si/B ratio of 50. The boron content before and after calcination is equal showing the calcination procedure developed by de Ruiter et al. [6] works.

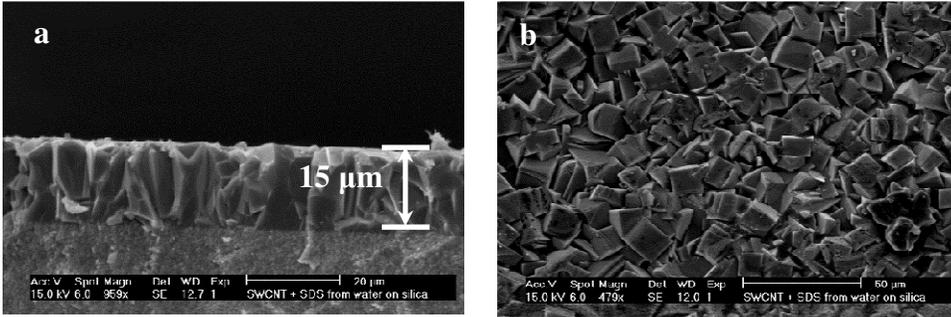


Figure 4: SEM pictures of [B]ZSM5 membrane (a) cross section, and (b) top view. Synthesized according to reference [7].

The boron content is determined by ICP OES analysis, this analysis indicated there is no dissolved aluminium from the support incorporated in the zeolite. To characterize the influence of the polarity on the transport through the membrane, pure water pervaporation tests are conducted. First the water flux through the as-synthesized membrane is measured, after the test the membrane is calcined, and the flux is measured again. In this way a single membrane can be used, changing the amount of silanol groups, but keeping the membrane thickness and amount of defects constant. The membrane is deboronated by treating it in a HCl solution (pH=1,5) at 373K for 24 hours. After pervaporation measurements the membrane is calcined at 673K and finally at 873 K. The preliminary results indicate there is an optimum in the amount of silanol groups. The flux after the first calcination step is substantially higher than before calcination and than after the subsequent calcination step. The influence on the membrane selectivity still needs to be investigated.

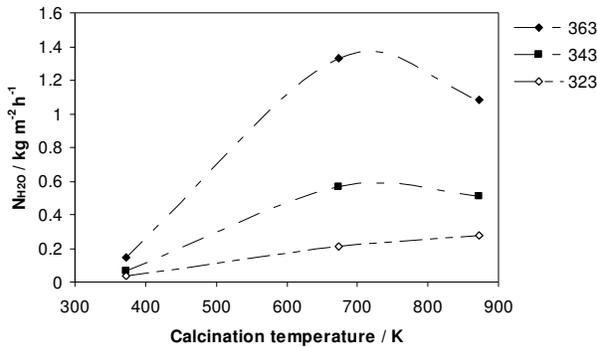


Figure 5: Water flux through deboronated [B]ZSM5 membrane at different temperatures, after calcination steps

Conclusions

A method to systematically investigate the influence of zeolite polarity on the transport characteristics has been developed. Boron containing zeolite membranes have been synthesized with a thickness of 15 μm , and a Si/B ratio of 50. After deboronation, leaving silanol nests, the polarity can be tuned by subsequent calcination steps at which part of the silanol groups are condensed. The water flux under pervaporation conditions is measured for the a single membrane after deboronation, and after calcination at 673K and 873K. A decreasing polarity will decrease the water-zeolite interaction, therewith decreasing the adsorption onto the zeolite, but increasing the diffusivity. The results indeed show a maximum in water flux after calcination at 673K, which indicates the trade-off between adsorption and diffusion, although the results need to be regarded as preliminary until verified in more measurement series.

Outlook

The pervaporation measurements on the deboronated [B]ZSM5 membrane have, so far, only been conducted on a single membrane. To verify the results the experiments need to be repeated. Adsorption measurements of water on deboronated [B]ZSM5 will be conducted as well as pervaporation with water/alcohol mixtures. We are planning to further optimizing the synthesis procedure, increasing the boron content in the zeolite framework, and thus the amount of silanol nests in the deboronated zeolite. Although ICP OES analysis have shown there is no aluminium present in the zeolite crystals, laser ablation ICP HRMS analysis will be conducted to verify there is no dissolution of the γ -alumina support in the zeolite. By means of molecular dynamics simulations we will investigate the influence of the presence of the silanol groups on an atomistic scale.

Acknowledgements

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