



## Adsorption-induced expansion of defects in MFI membranes

Justin B. Lee, Hans H. Funke, Richard D. Noble, John L. Falconer\*

Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO 80309-0424, United States

### ARTICLE INFO

#### Article history:

Received 9 June 2008

Received in revised form 13 May 2009

Accepted 7 June 2009

Available online 12 June 2009

#### Keywords:

Defect expansion  
MFI zeolite membrane  
Permporometry  
MFI crystal shrinking  
i-Butane  
p-Xylene  
Benzene

### ABSTRACT

Adsorption of i-butane, p-xylene, and benzene shrinks the size of MFI crystals in polycrystalline MFI membranes at room temperature. The crystal shrinkage, which is over different loading ranges for the three molecules, increases the sizes of the defects (gaps between the crystals). Two membranes, one with 90% of its helium flux through defects, and one with 9% were studied in detail. For the membrane with 90% of its helium flow through defects, the flux through the defects increased by as much as 44%, depending on the permeating molecule. The defect sizes increased for p-xylene loadings below 4 molec./u.c. and for i-butane loading between 3 and 8 molec./u.c. At higher loadings (7 molec./u.c. for p-xylene and 9 molec./u.c. for i-butane) p-xylene and i-butane expanded MFI crystals and shrank the defect sizes so that the helium flow through defects decreased by as much as two orders of magnitude. Benzene did not significantly change the flux through defects at loadings below 8 molec./u.c. Near a loading of 8 benzene molec./u.c. the flux through the defects increased by approximately 18% for one membrane.

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### 1. Introduction

Zeolite membranes are of interest for separations [1–6], chemical sensors [7–9], and corrosion protective coatings [10–12]. Their molecular-sized pores and adsorption properties govern how molecules permeate through them, and their high thermal and chemical stability indicate their potential for numerous applications. The most widely studied zeolite membranes are composed of MFI crystals because their 0.6-nm pores are similar in size to many small organic molecules, and thus they have been used to separate mixtures of hydrocarbon isomers [3,13,14]. The separation ability of these polycrystalline membranes is strongly affected by the size and number of defects (or non-zeolitic pores). These intercrystalline pathways, many of which are larger than the MFI pores, lower separations selectivities, and thus understanding their properties and how they are affected by adsorption in the MFI crystals is important for improving zeolite membrane separations.

In our recent studies [15–18], permeation measurements showed that C<sub>3</sub>–C<sub>8</sub> n-alkanes and SF<sub>6</sub> expanded the size of MFI crystals, and this expansion decreased the size of defects in MFI membranes. The expansion was only approximately 0.5% in a given

direction (based on XRD data [19,20]), but when the defects were small enough, this expansion had a dramatic effect on the permeation behavior. For a MFI membrane in which 90% of the helium flux at room temperature was estimated to be through defects (as determined by permporometry with benzene), n-hexane adsorption in the MFI pores decreased the helium flux by almost three orders of magnitude. This decrease in flux was seen at a n-hexane activity below 0.0002, and thus was not due to capillary condensation. Similar behavior was seen with the other n-alkanes and with SF<sub>6</sub>, but not with benzene because benzene did not expand the crystals. These adsorbate-induced expansions took place well below saturation loadings, and the number of molecules per unit cell (molec./u.c.) required to decrease the flux through defects significantly increased as the n-alkane became smaller. These results are of interest because most techniques for characterizing MFI membranes have used one of these molecules in permporometry (also referred to as permporosimetry), single-gas permeance ratios, or separations [3,5,13,21–36]. The same conclusions about adsorbate-induced expansion were reached for a number of MFI membranes by a combination of permporometry, vapor permeation, pervaporation of molecules too large to adsorb in the MFI pores, single-gas and mixture permeation, and temperature-programmed desorption [15–18,37,38].

In these previous studies, although a number of molecules expanded MFI crystals, some molecules did not. Pervaporation measurements indicated that benzene at saturation loadings did not expand the crystals. The single-component pervaporation fluxes of molecules larger than n-hexane, such as benzene and

\* Corresponding author at: Department of Chemical and Biological Engineering, University of Colorado, Box 424, Boulder, CO 80309-0424, United States. Tel.: +1 303 492 8005; fax: +1 303 492 4341.

E-mail address: [john.falconer@colorado.edu](mailto:john.falconer@colorado.edu) (J.L. Falconer).

2,2-dimethylbutane (DMB), were 1–2 orders of higher than the n-hexane flux for several membranes. Note that DMB was too large to adsorb in the MFI pores under these conditions, and thus only transported through defects. The low fluxes of n-hexane relative to DMB and benzene were attributed to n-hexane-induced expansion of MFI crystals; the expansion shrank the defects. When 1.6 mol% n-hexane was added to benzene during pervaporation, the benzene flux dropped by almost 2 orders of magnitude due to crystal expansion. Since benzene is small enough to adsorb into the MFI pores, but does not cause the MFI crystals to expand, it was used in permoporometry to determine the percentage of helium flux through defects.

The objective of the current study is to show that some molecules, when adsorbed in MFI crystals, shrink the size of MFI crystals and *increase* the flux through MFI membranes. This behavior has significant implications for MFI membrane characterizations since many studies have used i-butane and p-xylene permeation to characterize MFI membranes. Others have also shown that the MFI framework is flexible in the presence of xylene isomers [39–41]. Two MFI membranes, which were used in the previous study to show that n-alkanes and SF<sub>6</sub> expand MFI crystals and decrease the flux through defects [15], were used. For one membrane, the flux through defects increased by 44%. Benzene, i-butane, and p-xylene all increased the flux through defects for some concentration (or activity) range. Measurements in two flow systems demonstrated that the flux through defects increased. Permoporometry was used by measuring the helium flux as a function of the activity of a molecule added to the feed. Helium permeates through both MFI pores and defects, and the permoporometry measurements showed that the helium flux increased for some loadings in the MFI pores. In a second system, the flux of isooctane vapor, which only diffuses through defects because it is too large to adsorb in the MFI pores [42,43], was measured as a function of the activity of i-butane or p-xylene. These measurements showed directly that the flux of isooctane through the defects increased when these molecules adsorbed in MFI pores.

One membrane (boron-substituted ZSM-5) had 90% of its helium flux through defects at room temperature, but the defects were small enough so that they were essentially closed off by crystal swelling when n-alkanes or SF<sub>6</sub> adsorbed. This membrane had high ideal and separation selectivities in the presence of these molecules, in spite of the large fraction of helium flow through defects. Its benzene and DMB fluxes were two orders of magnitude higher than its n-hexane flux because n-hexane shrank the defects, but benzene and DMB did not. The n-hexane/DMB vapor separation selectivity at room temperature, for an isomer feed pressure of 0.8 kPa, was 260. The H<sub>2</sub>/SF<sub>6</sub> ideal selectivity at room temperature and a feed pressure of 360 kPa was 260 because SF<sub>6</sub> swelled the MFI crystals and thus decreased its flux through the defects.

The other membrane (silicalite-1) had only 9% of its helium flux through defects, but the defects were larger, and thus they were not closed off by molecules that swelled the crystals. The normalized helium flux through this membrane during permoporometry only decreased to about 6% when n-hexane was adsorbed. Its H<sub>2</sub>/SF<sub>6</sub> ideal selectivity at room temperature and a feed pressure of 360 kPa was 45. The n-hexane/DMB separation selectivity was 60 at room temperature (293 K) and an isomer feed pressure of 0.8 kPa. The ideal and separation selectivities were lower in the silicalite-1 membrane than the B-ZSM-5 membrane, even though it had an order of magnitude smaller fraction of its helium flux through defects. Three other membranes were used to demonstrate that the behavior seen is general. Since defects can shrink in the presence of certain molecules and expand in the presence of others, changes in defect sizes must be taken into account in interpreting MFI membrane separations and characterization.

## 2. Experimental methods

### 2.1. Membrane preparation

The silicalite-1 membrane was prepared by hydrothermal synthesis onto the interior of porous stainless steel tubes (0.8- $\mu$ m pores, Pall Corp.). The permeate area was approximately 7.8 cm<sup>2</sup>. The synthesis procedure is similar to that described previously [21]. The supports were soaked in synthesis gel overnight at room temperature prior to synthesis. The synthesis gel composition was 1.0 TPAOH: 19.5 SiO<sub>2</sub>: 438 H<sub>2</sub>O. The outside of the support was wrapped with Teflon tape, and the autoclave was filled with the gel during the first synthesis. The membrane was then washed and dried. Three synthesis steps were required to make the membrane impermeable to N<sub>2</sub> at room temperature before calcination. The first hydrothermal synthesis was carried out at 458 K for 48 h. The subsequent synthesis steps were conducted at 458 K for 24 h using the same procedure, but only the inner part of the support was filled with the synthesis gel. After synthesis, the membrane was washed in distilled water and dried. It was calcined in air to remove the template with heating and cooling rates of 0.8 and 0.9 K/min, respectively. The maximum calcination temperature was 753 K, and the membrane was held there for 8 h and then stored at 383 K under vacuum.

The B-ZSM-5 membranes contained boron isomorphously substituted in the framework and was synthesized by *in situ* crystallization onto the inside of a tubular  $\alpha$ -alumina support (0.2- $\mu$ m pores, Pall Corp.). The synthesis gel had a molar composition of 4.44 TPAOH: 19.5 SiO<sub>2</sub>: 1.55 B(OH)<sub>3</sub>: 500 H<sub>2</sub>O. The synthesis was similar to that described previously [44]. The resulting gel was aged at room temperature for at least 6 h. One end of the support tube was wrapped with Teflon tape and plugged with a Teflon cap, and the inside of the support was filled with about 2 mL of the synthesis gel. The other end was then plugged with a Teflon cap and left overnight at room temperature while the porous support soaked up most of the gel. The tube was again filled with synthesis gel, plugged with a Teflon cap, and put into an autoclave for hydrothermal synthesis at 458 K for 24 h. The membrane was then brushed, washed with DI water, and dried. The same synthesis procedure was repeated, except that the tube was not soaked overnight, and the membrane's vertical orientation in the autoclave was switched. The membrane was impermeable to N<sub>2</sub> at room temperature. It was calcined at 700 K for 8 h, with heating and cooling rates of 0.6 and 0.9 K/min, respectively. An XRD pattern for crystals collected from the bottom of the autoclave confirmed the MFI structure.

### 2.2. Permoporometry

Adsorption branch porosimetry or permoporometry [26,28] at room temperature was used to measure the helium flux as a function of the activity of a second condensable gas or vapor in the gas stream. The membranes were sealed in a stainless steel module with Viton o-rings. At low activities, adsorption blocks the helium flux through MFI pores. The remaining helium flux is through defects.

Permoporometry experiments were performed using either i-butane (99.5% Airgas and 99.995% Matheson-Trigas), benzene (>99.9% Sigma-Aldrich), or p-xylene (>99%, Sigma-Aldrich) as the condensable species. The helium and i-butane flows were adjusted with mass flow controllers, and the two streams were mixed to achieve the desired i-butane activity. The activities of benzene, and p-xylene were adjusted by saturating a helium stream with the hydrocarbon using two temperature-controlled liquid bubblers in series and then mixing the saturated stream with a pure helium stream. The hydrocarbon activities were changed by adjusting the temperature of the bubblers and the ratio of the two helium

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