



# Pore structure characterization of supported polycrystalline zeolite membranes by positron annihilation spectroscopy



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## ABSTRACT

It is important to characterize the pore structure of supported polycrystalline zeolite membranes but it has remained a major challenge in studying microporous inorganic membranes. This paper reports the use of positron annihilation spectroscopy including positron annihilation lifetime spectroscopy and Doppler broadening energy spectroscopy to non-destructively characterize the pore structure of four MFI zeolite membranes of different microstructures on alumina supports. Positron annihilation lifetime spectroscopy analysis reveals a bimodal pore structure consisting of intracrystalline zeolitic micropores of around 0.6 nm in diameter and irregular intercrystalline micropores of 1.4–1.8 nm in size for the four MFI zeolite membranes studied. Distributions of the micropores along the membrane thickness direction can be inferred from Doppler broadening energy spectroscopy results, illustrating development of intercrystalline gaps during the growth of the zeolite layer. The amount and size of the intercrystalline micropores of the zeolite membranes vary with the synthesis method, and are the smallest for the randomly oriented MFI zeolite membrane synthesized without template and the largest for the *c*-oriented MFI zeolite membrane synthesized with the template. The *c*-oriented membrane has an asymmetrical distribution of intercrystalline pores along the film growth direction as compared to the uniform distribution of the bimodal structure for the other three membranes. The pore structure data obtained by positron annihilation spectroscopy are consistent with the xylene isomer separation performance of these membranes.

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## 1. Introduction

Polycrystalline zeolite membranes offer many attractive properties, such as excellent separation capability and high structural stability, for separation and catalytic membrane reactor applications [1–3]. The separation properties and stability of the zeolite membranes are derived from their unique crystalline pore structure, pore surface chemistry and bulk inorganic material characteristics [4–6]. However, polycrystalline zeolite membranes contain grain-boundary or intercrystalline gaps, which, if larger than the zeolitic pores, provide non-selective pathways for mass transport, degrading the overall performance of the membrane [7,8]. Researchers have tried to minimize or eliminate these intercrystalline defects through manipulation of crystal orientation [9], template-free secondary growth [10], template removal by rapid calcination [11], and post-synthesis defect repairing [12]. It is expected that the intercrystalline pore structure of the polycrystalline zeolite membrane depends on the synthesis methods, so a good understanding of the microstructure of

polycrystalline zeolite membrane is key to ensure synthesis of high quality zeolite membranes. However, it is difficult to directly characterize the intercrystalline gaps of supported zeolite membranes and the effectiveness of a synthesis or post-treatment method to prepare zeolite membranes with intercrystalline pores minimized or eliminated. As a result, the research on synthesis of high quality zeolite membranes was largely performed in trial-and-error fashion.

Direct observation of the complex hierarchical microporous structure of polycrystalline zeolite membranes remains a major challenge in the membrane community, because the intercrystalline pores are in micropore range (< 2 nm) and of highly irregular topological structure [13]. Nitrogen adsorption porosimetry is a destructive means to characterize the pore structure of the zeolite membranes by measuring the powdery samples of the zeolite membrane layer scratched off from the support [14]. Permporometry uses condensable gas-like water or hexane in the process, both of which could induce microstructure change by strong adsorption and affect the measurement accuracy [15]. Molecular probing method relies on the permeance cutoff of a series of probing gases (or liquids) with different molecular sizes to estimate the critical pore size of the membrane [16]. All these methods could not provide information of the hierarchical pore structure of the supported polycrystalline zeolite membranes.

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Positron annihilation spectroscopy (PAS), based principally on the annihilation phenomena of positron and positronium due to pickoff in open-volume defects, is an emerging nondestructive technique to probe the pore structure of various materials [17]. Among the many PAS techniques, positron annihilation lifetime spectroscopy (PALS) has proven to be effective in quantifying the free-volume in polymers [18,19], micro/mesopores in silica [20], and cage and cavity size in zeolite crystals [21,22]. Recently, Yan and co-workers reported the use of PALS to obtain pore size and pore connectivity information in zeolite low-k films [23]. Duke and co-workers reported the use of PALS to characterize the pore structure of MFI zeolite powders [24,25]. The results revealed a hierarchical trimodal porous structure of the MFI zeolite powders containing intrinsic zeolite crystalline pores, intercrystalline micropores and interparticle mesopores [24,25]. The work shows promise of using the PAS technique to study the pore structure of the supported zeolite membranes.

In this paper, we report, for the first time, the use of two PAS techniques, PALS and Doppler broadening energy spectroscopy (DBES), to characterize non-destructively the hierarchical micro-porous structure of polycrystalline zeolite membranes on inorganic supports. The membrane model system chosen in our study is MFI type zeolite membrane, one of the most studied zeolite membranes in the literature because of its industrial importance. DBES was used to detect the free-volume variation and the multilayer structure of composite polymer membranes [26–28], but it has never been used to characterize zeolite membranes. Such structure information is important to guide the membrane synthesis and to explain the separation performance of the zeolite membranes. The objectives of this paper are to demonstrate that PALS and DBES are effective in revealing the complex hierarchical structure of zeolite membranes composed of both intra- and inter-crystalline micropores and the use of these techniques to help determine the synthesis-structure-properties relationship of polycrystalline zeolite membranes.

## 2. Experimental

### 2.1. Membrane synthesis and characterization

The following four supported MFI zeolite membranes of different microstructures, as summarized in Table 1, were synthesized on macroporous  $\alpha$ -alumina support by the seeded secondary growth methods under different conditions as reported in the respective literature: (a) randomly oriented MFI zeolite membrane (TR) prepared with the use of a TPABr template in the secondary growth step [29]; (b) randomly oriented MFI zeolite membrane (TFR) prepared without an organic template in the secondary growth step (template-free method) [30]; (c) *h0h*-oriented MFI zeolite membrane (TH) prepared with a template by performing sequential secondary growth at a moderate temperature of 130 °C [31]; and (d) *c*-oriented MFI zeolite membrane (TC) prepared with a template at a high secondary growth temperature of 175 °C [32].

The disk supports were pressed from A16 powders (Almatis), and then sintered at 1150 °C for 30 h in air. One side of the disk was polished using SiC sandpaper (#500, #800 and #1200) to smoothen the surface. Silicalite seeds were prepared by hydrothermal synthesis at 120 °C for 12 h using a synthesis solution of 10 SiO<sub>2</sub>:2.4 TPAOH:1 NaOH:110 H<sub>2</sub>O. Silicalite seed layers were dip-coated onto the polished side of  $\alpha$ -alumina supports, dried in a humid oven at 40 °C for 2 days and then calcined at 550 °C in air for 8 h to strengthen the bonding between the seed layer and support.

The secondary growth solution for three templated membranes had a molar composition of 1 KOH:1 TPABr:4.5 SiO<sub>2</sub>:16 C<sub>2</sub>H<sub>5</sub>O:1000 H<sub>2</sub>O. The composition of the synthesis solution for template-free secondary growth was 5 g SiO<sub>2</sub>:60 g H<sub>2</sub>O:1.15 g NaOH: 0.65 g Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18H<sub>2</sub>O. The solution and seeded supports were transferred to a Teflon-lined stainless steel autoclave and hydrothermally treated at different conditions as listed in Table 1. After synthesis, the membranes were washed with de-ionized water several times and dried at room temperature for one day. The TR, TH, TC membranes synthesized using the templated method were calcined at 550 °C in air for 8 h to remove the templates trapped inside the zeolite pores. The template-free synthesized membrane (TFR) was dried at 200 °C for 8 h to remove any adsorbed water and other impurities in the membranes.

The surface and cross-section of the membranes were characterized by scanning electron microscopy (SEM) (Philips, XL 30) to evaluate the morphology and to estimate the thickness of the membranes. X-ray diffraction (XRD) (Bruker AXS-D8, Cu K $\alpha$  radiation) was used to analyze the crystal structure, especially the orientation of the membranes.

### 2.2. Membrane separation performance measurement

The xylene isomers' separation performance was measured using a home-made pervaporation setup [13]. The MFI zeolite membrane was placed in the stainless steel pervaporation cell with the membrane layer facing up to the feed reservoir, which was filled with pure *p*-xylene (99%, Sigma-Aldrich) or *o*-xylene (99%, Sigma-Aldrich). The permeate side or downstream side was evacuated by a vacuum pump, and the permeated vapors were collected by a cold trap placed in liquid nitrogen. The duration of each run was kept at 4 h. The flux of each component was calculated by

$$J = \frac{w}{At} \quad (1)$$

where  $w$  is the weight of the collected sample (kg),  $A$  is the permeation area (m<sup>2</sup>), and  $t$  is the total time for the run (h). The ideal selectivity was determined by the ratio of the *p*-xylene flux to the *o*-xylene flux.

### 2.3. Positron annihilation spectroscopy

Two PAS techniques, positron annihilation lifetime spectroscopy (PALS) and Doppler broadening energy spectroscopy (DBES), were

**Table 1**  
Secondary growth conditions for MFI zeolite membranes.

Membrane type	Structure and synthesis method	Secondary growth conditions		
		Temperature (°C)	Duration (h)	Number of growths
TR	Randomly oriented with template	175	4	1
TFR	Randomly oriented without template	175	24	1
TH	<i>h0h</i> -oriented with template	130	24	2
TC	<i>c</i> -Oriented with template	175	24	2

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