



## High-resolution physical adsorption on supported borosilicate MFI zeolite membranes: comparison with powdered samples

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### ABSTRACT

We have performed physical adsorption measurements to analyze the structure of intact MFI membranes with a nominal Si:B ratio of 12.5:1. Argon adsorption isotherms of membranes at 77 K are nearly identical to isotherms of corresponding zeolite powders throughout most of the domain of relative pressures, the exception being the micropore-filling region (between  $10^{-5}$  and  $10^{-4}$  relative pressure). The isotherm in the micropore-filling region is steeper by a factor of 4–5 for the borosilicate membranes than it is for a powder made under the same conditions, while the saturation loadings are found to be similar. This implies a difference in how the zeolite pores fill with argon – either thermodynamic or kinetic in origin – and that fluxes for argon permeation through such powder and membrane samples may differ. Our membrane adsorption measurements reveal no hysteresis and hence no mesoporosity in the zeolite membranes. This finding, from adsorption measurements, stands in contrast to recent alkane permeation measurements on these membranes, which suggest the presence of mesopores. We reaffirm the conclusion, found in previous work, that zeolite membranes can be approximated as a zeolite powder plus a support for the purposes of adsorption characterization.

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### 1. Introduction

Zeolites are crystalline silicates with regular arrays of nanometer-scale pores leading to a wide variety of important applications involving the separation or preferential reaction of small molecules of different sizes and shapes [1]. The MFI structure [2] in particular has been used both as a selective reaction environment, and as a molecular sieve for energy-efficient separations [1]. Separations are most easily performed when the zeolite is in the form of a membrane (a thin layer grown on a macroporous substrate). Design and optimization of such separations benefit from understanding and modeling permeation in zeolite membranes. This in turn requires accurate information about the adsorption properties of the membrane [3], and possibly those of the support as well [4]. It is, however, difficult to measure adsorption on membranes directly due to practical considerations such as

the rigid, high-aspect-ratio structure of membranes [5]. Adsorption analyses on intact membranes are nonetheless an important step in understanding the underlying permeation properties of the materials. To address this, we have previously reported adsorption studies [6] on intact membranes grown by secondary (seeded) methods popularized by Tsapatsis and coworkers [7]. In this study, we focus on zeolite membranes formed by primary (unseeded) growth [8]. We are particularly interested in exploring the importance of mesopore-sized defects in zeolite membranes prepared by these two methods.

Zeolite membranes are typically grown in one of two geometries when they are used in separations processes: planar and tubular. In the planar arrangement, permeation occurs normal to the plane and the mixture to be separated must be fed at the top or bottom of the supported membrane. In a tubular geometry, the zeolite is typically grown on the inside or outside of the support tube and the mixtures to be separated are fed to the interior of the tube. Permeation occurs in the radial direction. It is easier to grow membranes on a planar surface, but the tubular geometry is more often used in industrial applications because that geometry is more suitable to handling and scale-up [7], and because a tube has a higher surface-to-volume ratio than a disk. Membranes are usually grown on the

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inside surface of the tube to protect the membrane itself during handling. It should be noted, however, that the best geometry for industrial processes is a multi-channel self-standing structure or a hollow fiber; these geometries give the maximum surface area over the smallest volume. It is, however, much more difficult to grow membranes in these ways.

Zeolite membranes grown by unseeded techniques may contain defects (that is, non-zeolitic pores) due to imperfect crystal intergrowth. These defects may affect transport, as they may allow permeation through non-zeolitic pathways or preclude transport altogether through pore blocking. It has been shown that non-zeolitic pores can be blocked by adsorbed species and/or expansion of the lattice due to adsorbed species [9,10]. We expect that the size, quantity, and origin of these defects is different for membranes formed by primary growth than for membranes formed by secondary (seeded) growth that have a more ordered micron-scale structure [11]. Physical adsorption provides a relatively simple, non-destructive approach for quantifying defects less than 50 nm in diameter, and using small molecules such as nitrogen or argon should reveal the quantity and size of defects in the mesopore range (2–50 nm [12]).

Due to the relatively large size of many zeolite membranes, however, it has been difficult to perform physical adsorption experiments directly on intact membranes. Many methods utilized to date involve scraping, grinding, and/or cutting membranes by various methods [13–29] so that they can be analyzed by standard adsorption measurements developed for powdered samples. These methods destroy the membranes for future permeation studies and raise questions as to whether non-zeolitic porosity is created during the synthesis procedure or generated by the membrane-destruction procedure.

Using recently developed techniques that employ a bolted stainless steel cup with a copper seal [5], we have previously examined the adsorption properties of thin silicalite (Si-MFI) membranes on thick alumina supports formed by secondary (seeded) growth [30] while leaving the membranes intact [6]. One would expect the presence of mesopores in these membranes, as their existence can be inferred from other methods [10,31,32]. However, we found that the regions of the adsorption isotherm associated with surface coverage and mesopore-filling are virtually identical for the corresponding samples of powder and membrane for these zeolites. We have thus previously reported for the seeded zeolite membranes that: (i) mesoporosity is not evident in our adsorption measurements, and (ii) these supported zeolite membranes can be well approximated as zeolite powder plus support for the purpose of understanding adsorption [6].

We now turn our attention to MFI membranes that are different from the previously studied membranes in four ways: (i) formed by unseeded growth rather than seeded, secondary growth; (ii) composed of borosilica (nominal Si:B = 12.5:1) rather than pure silica; (iii) relatively thick membranes (the membrane thickness is closer to that of the support); and (iv) tubular rather than planar geometry. In the present article, we explore whether our previously reported conclusions remain valid for these MFI membranes, i.e., (i) do these membranes exhibit mesoporosity in their adsorption isotherms? (ii) can these supported B-ZSM-5 membranes be viewed as equivalent to B-ZSM-5 powder plus support for the purpose of adsorption characterization? Below, we report that our previous conclusions remain largely valid for these relatively thick B-ZSM-5 membranes, except for a measurable difference between supported membrane and powder in the micropore-filling region of the isotherm. We then discuss origins for this difference, and we also discuss recent permeation measurements on these B-ZSM-5 membranes [9,10] that do suggest the presence of mesoporosity.

**Table 1**

Weight change after each procedure for membrane BZ1

Procedure	Gross weight (g)	Weight gain (g)	Membrane weight (g)
Bare support	5.5185		
First layer	5.6992	0.1807	0.1807
Second layer	5.8662	0.167	0.3477
Third layer	6.0759	0.2097	0.5574
First calcinations	6.0007	−0.0752	0.4822
Fourth layer	6.2416	0.2409	0.7231
Fifth layer	6.4151	0.1735	0.8966
Second calcinations	6.3976	−0.0175	<b>0.8791</b>

Numbers in boldface denote the mass of the zeolite membranes used to normalize the quantity adsorbed.

The next section of this article details the preparation of our zeolite membranes and the methods used to measure the adsorption isotherms. In Section 3, we present and interpret our results, and in Section 4 we summarize our findings.

## 2. Experiments

### 2.1. Zeolite membranes

Samples used in these experiments are borosilicate MFI (B-ZSM-5) membranes grown on the inner surfaces of tubular, asymmetric supports. The supports, manufactured by Pall Corporation, are composed of  $\alpha$ -alumina with an inner layer containing 200 nm pores with a void fraction of 0.35. The two ends of the supports were sealed with a glaze (Duncan, IN1001) as described by Lin et al. [33]. The glaze was then fired at increasing temperature with a final hold at 900 °C for 30 min. with a heating and cooling rate of 0.02 °C/s.

The membranes were grown on the inner surface of the tube by *in situ* crystallization as described by Tuan and coworkers [34] (this procedure is also called *unseeded growth* or *primary growth*, referring to the fact that seed crystals are not used). The gel composition for making the membranes was 4.44 TPAOH:19.46 SiO<sub>2</sub>:1.55 B(OH)<sub>3</sub>:500 H<sub>2</sub>O, where Ludox (AS40, Aldrich) was used as the silica source, boric acid (99.999%, Aldrich) was used as the boron source, and tetrapropylammonium hydroxide (TPAOH, 1 M aqueous solution, Aldrich) was used as the structure-directing agent. The membranes were grown using several growth periods to reduce the likelihood of the formation of pin-hole defects, i.e., defects that go all the way through the membrane. They consequently consist of several layers.

We tested membranes grown by two synthesis procedures. The synthesis procedure for sample BZ1 consists of growing three layers, calcining, growing two more layers, and calcining again. The two calcinations were performed at 480 °C for 8 h with heating and cooling rates of 0.01 and 0.018 °C/s, respectively. The weight change after each synthesis procedure is listed in Table 1.

The synthesis procedure for sample BZ5, which consists of two layers followed by calcination, is similar to that of BZ1 except that the membrane is only two layers thick, the outside of the support was wrapped with Teflon tape, and the autoclave was completely filled with the synthesis gel. The autoclave was horizontal and

**Table 2**

Weight change after each procedure for membrane BZ5

Procedure	Gross weight (g)	Weight gain (g)	Membrane weight (g)
Bare support	5.4941		
First layer	6.6463	1.1522	1.1522
Second layer	7.4383	0.792	1.9442
Calcination	7.2109	−0.2274	<b>1.7168</b>

Numbers in boldface denote the mass of the zeolite membranes used to normalize the quantity adsorbed.

rotated at about 120 rpm during synthesis. The membrane was calcined at 480 °C for 8 h with heating and cooling rates of 0.01 and 0.018 °C/s. The membrane weight gain is shown in Table 2.

## 2.2. Adsorption equipment

Prior to characterization by physical adsorption, samples were placed in an adsorption vessel as described in Ref. [5], which employs a resealable stainless steel container large enough to hold the sample without having to cut or otherwise damage it. The container was sealed with a copper gasket and evacuated using a turbomolecular pump. Samples were heated gradually over the course of about 4–5 h to 300 °C. Each sample was maintained at this temperature for 24 h or more, then cooled to room temperature over the course of 4–5 more hours. The container was then cooled below –100 °C very slowly by placing the nitrogen bath under the sample such that the sample was cooled by the air over the bath. Once the container had cooled as much as possible in this manner, the sample container was immersed in the nitrogen bath to its final temperature (–196 °C). We used this slow cooling procedure to minimize damage to the membranes caused by rapid changes in temperature.

Adsorption and desorption isotherms were measured at the boiling point of nitrogen (77 K) using adsorption equipment as described in Ref. [35], which employs a volumetric dosing system and two pressure transducers with ranges of 0–1000 Torr and 0–2 Torr on the adsorption manifold. Nitrogen and argon were used as adsorbates, and a constant level of the liquid nitrogen bath was maintained during all measurements. Dead space measurements were conducted using helium; saturation pressures were determined by condensing or subliming adsorbate in the sample container at the end of the experiment. All gases used in the experiments are ultra-high purity (Merriam–Graves Corporation; Charlestown, New Hampshire).

## 2.3. X-ray diffraction

We analyzed the X-ray diffraction pattern of membrane sample BZ5 after adsorption analysis by scoring and breaking the tube, filing the zeolite to obtain a smooth surface, and placing the fragment in the spectrometer. The spectrometer is a Philips X'Pert Professional model with a wavelength of 1.64 Å. A slit width of 0.5° on the source and detector was used to obtain scans from  $2\theta = 5^\circ$  to  $50^\circ$  using an accelerator.

## 3. Results and discussion

### 3.1. X-ray diffraction

The X-ray diffraction pattern of borosilicate ZSM-5 powder is shown in Fig. 1, and the pattern from the membrane sample is shown in Fig. 2. The similarity of these diffraction patterns to each other and to MFI standards [2] indicates that the membranes are indeed ZSM-5 and that the crystals have no preferred orientation. This serves as confirmation of the results from scanning electron micrographs [36] which showed micrometer-scale crystals with little or no preferred orientation for membranes made by the same procedure. These patterns are characteristic of the *orthorhombic* symmetry phase of the MFI crystal structure [2]. Scanning electron micrographs (not shown) indicate a broad range of powder particle sizes with a mean of 0.4 μm and a standard deviation of 0.3 μm. It is essentially impossible to extract a surface area from microporous materials – powder or membrane – as the classic BET analysis [37] is inapplicable [38].

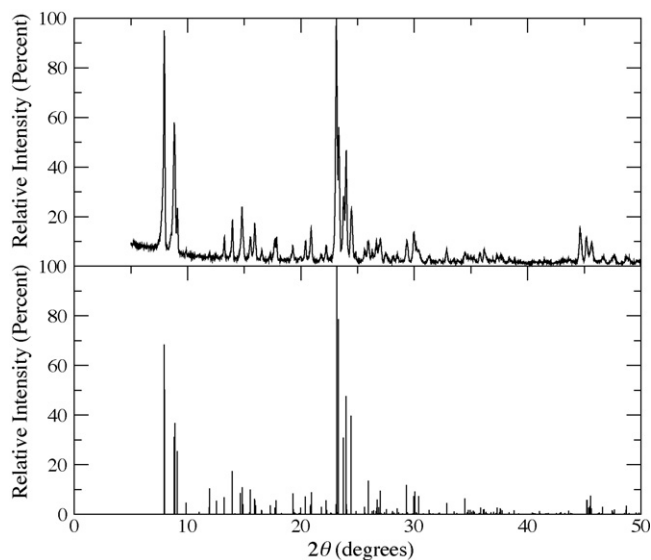


Fig. 1. X-ray diffraction pattern of calcined B-ZSM-5 powder (top) and orthorhombic MFI (bottom, from Ref. [2]).

### 3.2. Adsorption

Adsorption isotherms of zeolite powder prepared under the same conditions are overlaid with the isotherm of the membranes in Fig. 3. The mass of the zeolite in the membrane is determined by the weight gain during the synthesis procedure.

The support's surface area is so low that almost no gas adsorbs on it compared to the amount adsorbed on the zeolite (Fig. 4). Furthermore, the pores in the support (~200 nm) do not fill until relative pressures of 0.995 or greater. Experimental error at  $P/P_0 > 0.995$  precludes accurate measurements of pore sizes greater than 50 nm. The extremely low amount adsorbed by the support and the large size of the pores in the support mean that surface diffusion is wholly controlled by the zeolite layer. This result is in contrast to our study of very thin seeded-growth membranes on planar supports [6], where we found that the support dominated the quantity adsorbed at moderate to high pressures and was therefore presumed to be

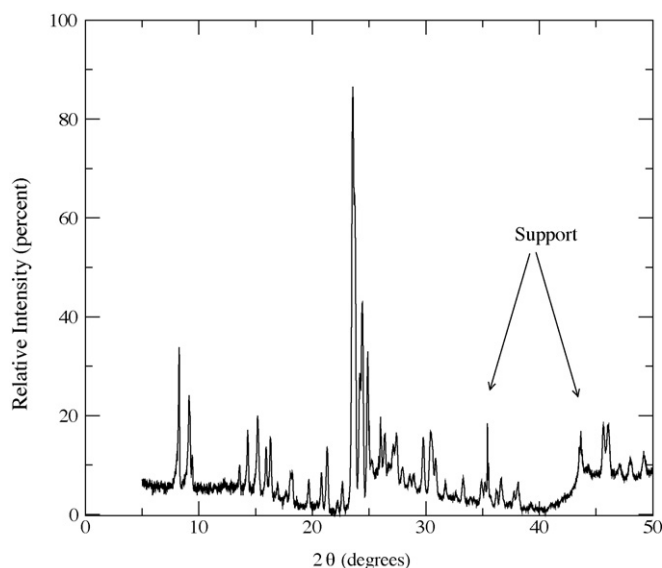
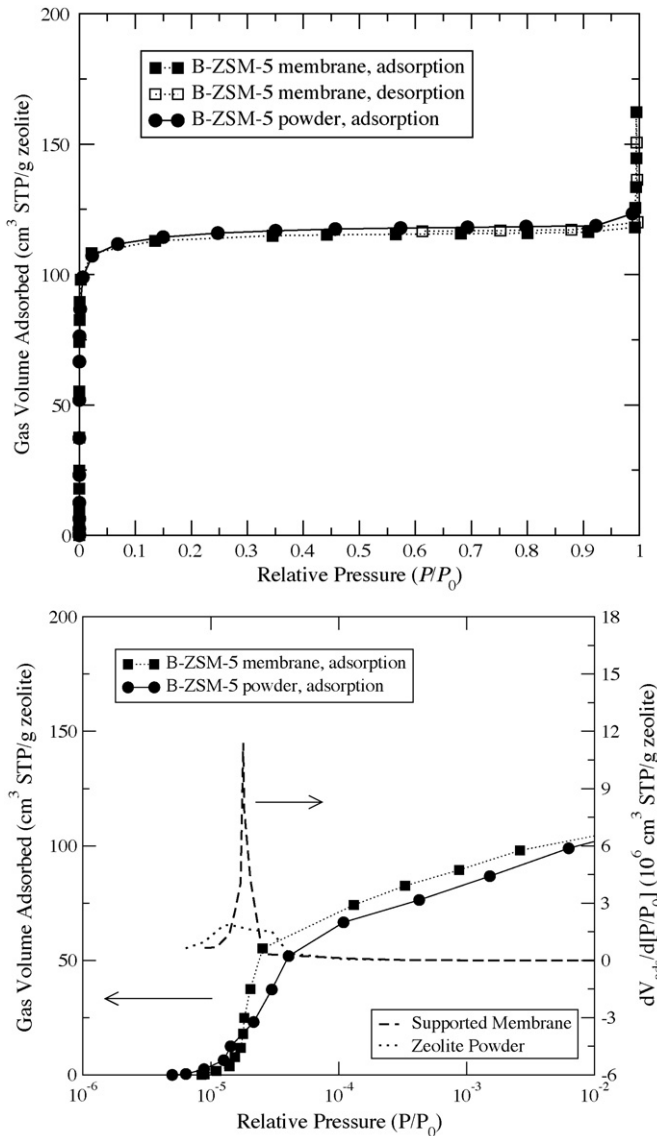


Fig. 2. X-ray diffraction pattern of calcined B-ZSM-5 membrane BZ5.



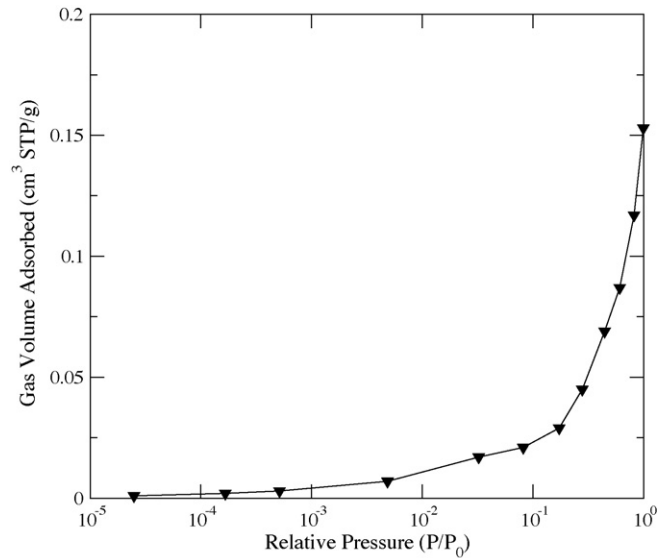
**Fig. 3.** Argon adsorption isotherms at 77 K of B-ZSM-5 powder and the intact supported membrane BZ1 using argon as the adsorbate. A logarithmic pressure scale is used in the bottom figure to show the micropore-filling region, and the derivative (using centered finite differences) of the isotherm is plotted on the right-hand vertical axis to illustrate the difference in slope.

much more important to surface diffusion. Knudsen and bulk diffusion are believed to be important in the support, however, so the overall diffusion resistance in the support should be modeled by a non-surface mechanism such as that employed in Ref. [39].

### 3.2.1. Argon isotherms

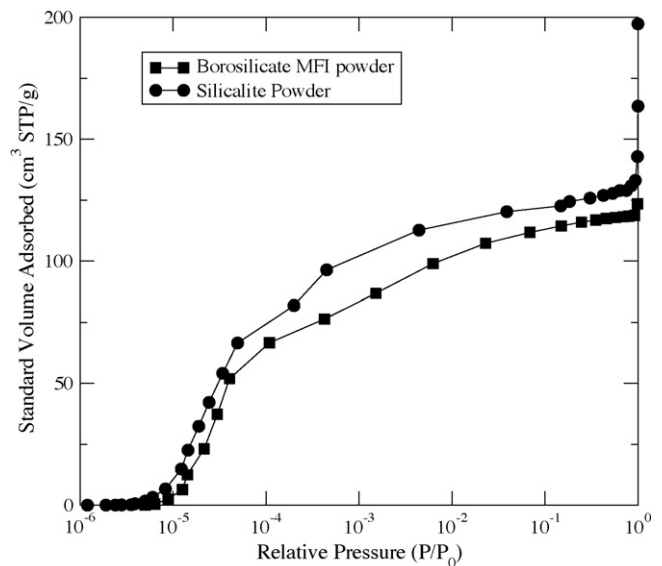
The powder isotherms (Figs. 3 and 5) are in broad agreement with that reported by Borghard and coworkers [40] for argon on ZSM-5 at 77 K; the isotherm slopes gradually upwards as  $P/P_0$  increases between  $10^{-5}$  and  $10^{-4}$ . Similar physical adsorption behavior is also observed for silicalite (pure-silica MFI) [6]. Fig. 5 shows that the slope at each value of the relative pressure is approximately the same between the all-silica and boro-silica powders.

The strong similarity of the powder and membrane isotherms in the pressure domain of  $0.05 < P/P_0 < 1$  (Fig. 3a) indicates that the zeolite in the membrane is nearly identical to the powder for the purposes of external (non-micropore) surface area. The lack



**Fig. 4.** Adsorption isotherm (logarithmic pressure scale) at 77 K of a bare support using argon as the adsorbate. The very small quantity adsorbed means that the contribution from the support to the adsorption isotherm is negligible for these supported membranes.

of hysteresis in the membrane isotherms suggests that very few mesopores (pores 2–50 nm across) were created by the growth procedure. This conclusion is supported by the pore size distributions (not shown) that were extracted from the adsorption isotherms. This indicates that any mesopores present are very few in number. These observations are similar to those for the seeded-growth membranes discussed in our earlier publication [6]. However, recent permeation studies have shown that such mesopores – despite their sparse distribution – may have measurable impacts on permeation and can even be opened and closed by filling or emptying the zeolite pores [9,10]. This observation also raises the issue of whether the presence of non-zeolitic porosity is influenced by the cryogenic temperatures under which adsorption isotherms are measured.



**Fig. 5.** Comparison of silicalite powder and borosilicate ZSM-5 powder for argon adsorption at 77 K. Note the similarity in slope despite the slightly increased volume adsorbed per gram zeolite in silicalite.

In the low-pressure region ( $P/P_0 < 10^{-4}$ ) of the isotherm, however, we observe clear differences in the slope of the adsorption isotherm between the membrane and powder isotherms. This increased steepness in the membrane isotherm translates to a smaller increase in pressure for a given change in concentration. If we express the Fick diffusion coefficient  $D_F$  as  $D_F = D_{MS} \partial \log P / \partial \log C$ , where  $D_{MS}$  is the Maxwell–Stefan diffusion coefficient [3,41], the increased steepness of the isotherm translates to a smaller Fick diffusion coefficient for argon. In particular, the slope of the membrane isotherm in the micropore-filling region is four to five times greater than that for B-ZSM-5 powder. A similar effect was observed for argon adsorption on one variety of planar silicalite membranes [6], though the effect was less pronounced than the one observed here.

The observed increase in isotherm steepness for these membranes could be due to several factors. One is structural flexibility (or lack thereof) of the membrane crystals relative to those in the powder. In a powder, crystals filled with adsorbate may expand or contract more than they can in membranes due to the empty spaces between the powder grains. This flexibility may cause the local host–guest interactions to change as a function of how much is adsorbed. A flexible structure would adjust to the presence of higher levels of adsorbate – as the pressure increases, the tendency of the adsorbate to densify in the pores is partially offset by expansion of the adsorbent (in this case, the zeolite). In a more rigid structure, such as an incipient-growth membrane where the crystals are touching one another, the structure may not flex as much to offset an increase in adsorbate density. This means the effective distribution of pores is narrower (since there is no room for expansion), and therefore the quantity adsorbed would increase more abruptly with pressure. The hypothesis that lattice expansion influences the phase transition in silicalite was also put forth by Pellenq and Nicholson [42], who concluded that “a small expansion of the adsorbent would enable further molecules to squeeze into the cavities, the increase in lattice energy being compensated by a reduction in adsorbate energy. In some cases, distortion of the framework does not lower the overall free energy and its structure is not modified at high loading.” Douquet and coworkers [43] noted that the zeolite framework seems to be affected similarly by adsorbed argon at 77 K and *p*-xylene at room temperature. They also noted a “striking analogy” between adsorption isotherms for argon at 77 K and *p*-xylene at 195 K, and noted the fact that adsorption of methane at 77 K and cyclohexane at 300 K did not present stepped isotherms and did not alter the zeolite structure. We similarly conclude that argon interacts sufficiently with the zeolite to be affected by lattice (in)flexibility. This is not to say that the lattice is completely inflexible in these membranes, however. Indeed, we have previously demonstrated [9] that the framework is flexible in MFI membranes grown by a similar technique. *In situ* NMR spectroscopy and/or X-ray and neutron scattering could, in principle, be used to test whether decreased lattice flexibility is correlated with increased steepness of the isotherms.

Another possible explanation of the steepness discrepancy is kinetic. We are operating under the assumption that the isotherms shown are indeed equilibrium curves. It is possible, however, that the observed curves are in fact metastable or even non-equilibrium phenomena. The latter would occur if the rate of diffusion of adsorbate through the zeolite membrane at 77 K is very slow, such that the pressure change due to adsorption/densification of additional material in the micropores was too small to be detected by the instrumentation on the time scale of the experiment. For points in the micropore adsorption region, this amounts to a decrease of about 0.0005 Torr over the course of 15 min (a point is only taken if the pressure has been constant within the precision of the measurement for at least 15 min in the low-pressure region). Such diffusion limitations could delay the apparent onset of the increase

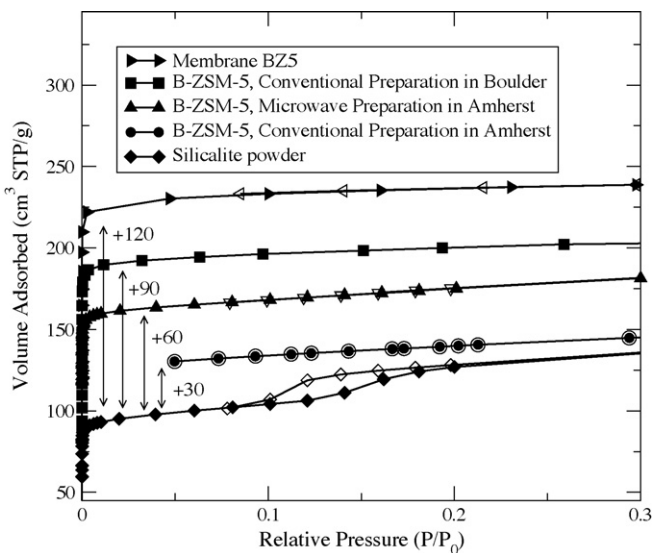
in quantity adsorbed, making the isotherm steeper since thermal and chemical equilibria are established much faster at higher pressures. A reasonable estimate of the characteristic time is  $L^2/(6D)$ , where  $D$  is the diffusion coefficient and  $L$  is the characteristic length. Assuming the diffusion coefficient for condensed phases in zeolite pores is on the order of  $10^{-7}$  m<sup>2</sup>/s [44], then for powders with particle sizes on the order of 0.4 μm the characteristic time is on the order of  $10^{-7}$  s. For a membrane 1 mm thick, the characteristic time increases to on the order of 1 s. The fact that these numbers differ by a factor of a million may indicate that diffusion limitations are much more significant in the membrane, though both of these times are still far less than the time scale of the experiment where the time between data is on the order of 1 h. Testing whether measured isotherms are in fact equilibrium curves can be difficult. If the isotherm ever sloped *backwards*, it would indicate equilibrium had not been established, but this behavior is not evident in our experiments. The fact that the shape is repeatable means that any non-equilibrium behavior is consistent from one experiment to another, though this is also insufficient to ensure equilibrium.

One might test for *metastability* by measuring a desorption isotherm in the micropore-filling region. If the resulting desorption isotherm returned to the original (adsorption) isotherm, it would indicate that equilibrium was probably established. If, however, hysteresis occurs, it would indicate that long-lived non-equilibrium or metastable states may be responsible for the difference. Unfortunately, desorption in micropores is in general very slow – *much* slower than adsorption – due to the heat required to desorb. This problem is made worse at low densities, where heat and mass transfer are slow. In addition, dosing at low pressures is very difficult because the maximum change in pressure for a dose is the actual value of the pressure (0.01 Torr or below in this region). For all of these reasons, high-resolution desorption isotherms are rarely if ever performed. With the information available to us, we conclude that the resulting isotherms indicate a difference in lattice flexibility. The rigidity of the membrane-bound zeolite crystals imposed by the physical contact between them causes a more precipitous change in the amount adsorbed as a function of pressure.

### 3.2.2. Nitrogen isotherms

Nitrogen isotherms of the borosilicate membranes examined here show remarkably little difference from those of a boron-MFI powder synthesized under the same conditions (Fig. 6) and to the adsorption isotherms on B-ZSM-5 powders published by Ruren and Wenqin [45]. This supports the conclusion drawn above of negligible mesoporosity in these materials, at least with respect to adsorption characterization at 77 K.

The one thing that is remarkably absent from the nitrogen isotherm is hysteresis between relative pressures of 0.1 and 0.2 (see Fig. 6). This loop is usually observed in adsorption on MFI powders [46–49], and is indeed seen in Fig. 6 for the silicalite powder sample. This loop is not linked to pore filling in the traditional sense. It has been attributed instead to phase transitions either in the adsorbed phase (from liquid-like to solid-like [50]) or in the adsorbent (from a crystal with monoclinic symmetry to one with orthorhombic symmetry [50,51]). The loop's shape is affected by Si:Al ratio [47,52], and to a lesser extent by crystal size [47]. Kyriakou and Theocharis [48] also found that the loop's presence or absence is influenced by cation exchange for the MFI samples (Si:Al = 120:1) they studied. Mentzen and coworkers [53] found that the orthorhombic–monoclinic phase transition has a lower enthalpy change at low Si/Al ratios, and a survey of various reports of adsorption on ZSM-5 and silicalite indicates that the loop disappears when the Si:Al ratio drops below 30:1 [46,47,52,54–56]. We presume that a similar trend holds for the Si:B ratio as well. As such, the absence of this loop in the membranes analyzed here



**Fig. 6.** Nitrogen isotherms at 77 K on B-ZSM-5 powders and membranes. Filled symbols represent adsorption points and empty symbols represent desorption points. The vertical axes for all samples except silicalite powder have been shifted by 30 cm<sup>3</sup>/g increments for clarity. It should be noted that samples represented by circles and upward triangles were prepared from the same solution.

(Si:B = 12.5:1 from synthesis conditions, which has been shown to produce a similar ratio in the zeolite itself by elemental analysis [34]) is not entirely surprising. The question of why this loop is absent in other membranes and self-supporting silicalite structures [6,22–24] that contain only trace amounts of either aluminum or boron remains a mystery.

#### 4. Summary and conclusions

We measured the nitrogen and argon adsorption isotherms on intact supported B-ZSM-5 membranes. We found that the adsorption isotherms are nearly identical to those of zeolite powders throughout most of the adsorption isotherm. This means that for most regions of the isotherm, using powder adsorption data to model membrane permeation is a good approximation. The only differences we find are differences in the slope of the argon adsorption isotherm in the micropore-filling region, indicating that there may be subtle differences in how the pores fill with argon. Due to equipment precision, it remains unclear whether this effect exists in the nitrogen isotherms as well. This may indicate a change in lattice flexibility from powders to membranes, or a difference in the samples' structure between room temperature and the temperature at which measurements are taken (77 K). The isotherms reveal no hysteresis and hence no mesoporosity in the membrane or support—at least, no mesoporosity at volumes high enough for detection by physical adsorption at 77 K.

In contrast to our adsorption studies that find no evidence of mesoporosity in these supported B-ZSM-5 membranes, previous permeation studies [9,10] on membranes made by the same techniques exhibit mixture permeation behavior consistent with the presence of mesopores. This intriguing discrepancy suggests a useful model of the Fick diffusion coefficient ( $D_F$ ), which can be expressed [41] as a product of the Maxwell–Stefan diffusion coefficient ( $D_{MS}$ ) and a thermodynamic factor ( $\Gamma = \partial \log P / \partial \log C$ ) controlled solely by adsorption. Evidently, a small number of mesopores in a zeolite membrane can influence the Maxwell–Stefan diffusion coefficient in a measurable way, but the same mesopores may have no measurable effect on the thermodynamic factor. This conclusion applies to both primary and secondary growth tech-

niques, and to both the thin and thick membranes we have studied (cf. Ref. [6]). The only modification for thin membranes is that the support must be taken into account when determining the adsorption capacity of the supported membrane. Future studies on other kinds of membranes with multiscale porosity are required to determine whether this picture is generally applicable.

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