Apparatus for measuring physical adsorption on intact supported porous membranes

Karl D. Hammond · Geoffrey A. Tompsett · Scott M. Auerbach · W. Curtis Conner

Abstract We present a non-destructive, reusable apparatus with which to measure physical adsorption isotherms of intact porous membranes. We developed a two-piece sample container to make reliable sorption measurements of porous membranes, the properties of which may differ from those of powders due to crystal intergrowth. This novel system employs a resealable container that can be immersed in a cryogenic bath, into which tubular, planar, or other porous membranes and films may be placed. Detailed sorption isotherms, including high-resolution adsorption in the low pressure (micropore-filling) region, are shown for MFI-type zeolite membranes grown on two types and configurations of α-alumina support.

Keywords Membrane · Adsorption · Porosity · Zeolite

1 Introduction

Zeolite membranes offer a microporous environment with which to achieve energy-efficient separations of mixtures that arise in the petrochemical and fine chemical industries [1, 2]. Optimizing these separations requires detailed knowledge of the adsorption properties of mixtures in the membrane micropores. Such adsorption measurements can also provide insight into structural defects in intergrown microporous [3–14], and mesoporous [15–18] membranes. Though measurements of physical adsorption on porous materials provide a standard method of characterizing porosity without damaging the material [19], most adsorption instruments are designed for experiments on powders, not larger objects such as membranes. As such, simulations and analyses of transport through zeolite membranes have often relied on adsorption measurements on powders [1, 2, 20, 21], possibly leading to erroneous interpretations of transport data. To address this, we have developed a new apparatus for measuring physical adsorption on intact supported membranes.

Most physical adsorption on powders is carried out using narrow-necked blown glass bulbs attached to a vacuum fitting. Powders fit relatively easily down the neck of such a tube, but an intact membrane a few centimeters in diameter and/or several centimeters long will not. A sample holder large enough to hold a membrane but with an appropriately sized neck is required to determine the adsorption properties of porous membranes in a nondestructive way.

Using larger-diameter glass tubing is not a good solution: controlling the temperature profile in the tube connected to the sample container (and thus the void, or dead, volume) becomes increasingly difficult as the diameter of the tube is increased. Several groups have attempted to solve this problem by using a 1/4″ glass cell and either scraping off the membrane and grinding it into a powder [4, 18, 22, 23] or cutting the membrane into smaller pieces that fit down the neck of the tube

K. D. Hammond · G. A. Tompsett · W. C. Conner (✉)
Department of Chemical Engineering, University of Massachusetts Amherst, 159 Goessmann Laboratory, Amherst, MA 01003, USA
e-mail: wconner@ecs.umass.edu

S. M. Auerbach
Department of Chemistry, University of Massachusetts Amherst, 701 Lederle Graduate Research Tower, Amherst, MA 01003, USA

[3, 6, 16]. These methods clearly make the membrane useless for any further experiments on the intact membrane, and also raise questions as to whether the process of pulverizing the material creates additional porosity—powdered samples have long been known to change their porosity after being ground or compacted [19]. Yet another method is to actually fuse a glass tube around the sample and then degas and analyze it [17]. While this preserves the macroscopic structure, the heat required to fuse the glass could damage the membranes [24] and the sample container must be destroyed to remove the sample at the end of the analysis. Some other containers have been assembled using two pieces of glass sealed by black wax or vacuum grease; these containers are not appropriate for zeolites, which must be degassed at high temperatures where the wax/grease will melt and/or infiltrate the zeolite pores (which would require calcination to remove). Typically, the exact handling procedure used to prepare membranes for adsorption is not reported [10–15, 25–28].

The consequences of using larger tubing are increased dead space (which means more sensitive instrumentation is required to measure the small differences in pressure which will result) and increased variability in the dead space. The variability in dead space volume can be estimated by the following equations:

$$V_{DS} = \frac{\pi D^2}{4}(\ell - h) + \left(V_{bulb} + \frac{\pi D^2 h}{4}\right)\frac{T_r}{T_b} \quad (1)$$

OR

$$\frac{\partial V_{DS}}{\partial h} = \frac{\pi D^2}{4}\left(\frac{T_r}{T_b} - 1\right) \quad (2)$$

where h is the height of the bath with respect to the top of the sample bulb, ℓ is the total length of the tube, V_{DS} is the dead space volume, V_{bulb} is the volume of the bulb (the widened portion at the bottom of the tube, which contains the sample; this volume is completely immersed in the cryogenic bath), D is the inner diameter of the tube, T_r is the room temperature, and T_b is the bath temperature. As should be clear from the equations, the dead space and the variability in it with bath height increases with the *square* of the inner diameter of the tube, or with the difference in the squares of the inner diameter and the diameter of the insert, in the case where an insert is employed.

Some examples of how the dead space varies due to a change in the bath height of 2 mm from its initial position (h_0) for $T_r = 298$ K, $T_b = 77$ K, $\ell = 25$ cm, $h_0 = 5$ cm, and $V_{bulb} = 20$ cm^3 (approximately the size of a cylinder 5 cm deep and wide enough to hold membranes 2 cm in diameter) for values of D used in 1/4″ capillary tubing, standard 1/4″ tubing, two sizes of tubing (with and without inserts) currently employed in commercial adsorption equipment, and two more diameters large enough to simply slide a 22 mm disc and a 45 mm disc inside (with and without inserts, where the insert diameter is estimated to be about 1 mm smaller than the outer tube's inner diameter) are included in Table 1. Please note that the values in this table rest on the assumption of a completely flat temperature profile, which is of course an invalid assumption even for low-pressure gases. In the case of a glass insert, this is even more of a problem, and in fact the temperature profile inside the glass would not be expected to be flat and in fact would probably change significantly throughout the experiment—it is for this reason that we do not recommend the use of large-diameter glass tubes with inserts for these experiments.

Larger diameter tubing does have advantages in that it decreases the time required to depressurize the vessel (the mechanism of molecular diffusion, which ultimately drives gases at very low pressures, changes from Knudsen to bulk diffusion as the diameter increases). It also means mechanical equilibrium takes less time to happen because of the same mechanism change. These

Table 1 Dead space volume variability with shaft inner diameter

D_t/D_i (mm)	V_{DS}(cm^3), $h = h_0$	% Change	Relative change[a]
1.0/0[b]	77.45	0.0058	0.066
4.0/0[c]	82.08	0.087	1.0
6.93/0[d]	91.98	0.23	2.7
6.93/5.94[d]	81.08	0.071	0.81
9.86/0[d]	107.1	0.41	4.7
9.86/8.99[d]	82.24	0.089	1.0
16.7/0[d]	163.1	0.77	8.8
16.7/1.58[d]	86.05	0.15	1.7
25/0	270.0	1.04	11.9
25/24[e]	92.26	0.24	2.7
50/0	848.5	1.32	15
50/49	107.7	0.41	4.7

D_t is inner diameter of the tube; D_i is the outer diameter of an insert (if applicable)

[a] Percent change in V_{DS} divided by the percent change in V_{DS} for standard 1/4 in tubing (4 mm inner diameter)

[b] 1/4 in capillary tubing

[c] Standard 1/4 in tubing

[d] These diameters were measured from commercially available equipment in use in many adsorption systems today [29]

[e] This diameter corresponds to the most accurate value in the table that would still be capable of measuring adsorption on the planar membranes we present as an example *without* employing a container such as that which we have developed

trade-offs, which increase experiment time, must be weighed against the dead space considerations, which increase experimental accuracy. If the former is more important, we recommend using 1/4″ tubing instead of capillary tubing, which is typically the standard size employed anyway. However, it is important to consider that *thermal* equilibrium (or, more accurately, heat transfer) is the limiting factor in experiment time; mass transfer in most cases is still relatively rapid in comparison. Note that these errors become amplified by the fact that the dead space volume is calculated by taking the difference between two large numbers and is subsequently used in similar calculations, so the absolute error also becomes significant.

In addition to increasing the variability of the calculated dead space volume with height, a wider tube increases the dead space volume itself (as can be seen from Table 1), leading to decreased resolution. Therefore, more sample is required to obtain a measurement with sufficient precision to generate an adsorption isotherm repeatably. In the case of some of the silicalite membranes we studied, which have a membrane approximately 5 μm thick and 22 mm in diameter, we were required to use four or five samples at the same time to provide sufficient material and thus a sufficient signal to measure the adsorption isotherm. This problem would be exacerbated for a container with a larger stem volume.

The problems with all the other methods we are aware of are circumvented by the sample container we have designed. No additional fittings are required—the tube is standard 1/4″ glass tubing (another size could easily be installed in order to be compatible with existing equipment), and the container uses no inserts to provide uncertainty in dead space.

2 Materials and methods

2.1 Sample container

To measure physical adsorption on intact macroscopic materials, we have designed a new adsorption sample container that satisfies all of the following criteria:

– Holds pressure between $< 10^{-9}$ atm and > 2 atm over a 600°C range: between –196°C (liquid nitrogen temperature) and 300–400°C (degassing temperature ranges)
– Shaft must fit into 1/4″ and/or 9 mm UltraTorr® fittings on existing sorption equipment
– Shaft itself should have a small inner diameter ($< 1/4$″) and be made of glass or another poor heat

conductor to allow for better control of the dead space volume (see Equation 1)
– Cell should be reusable and relatively versatile to accommodate various sizes of samples with only minor modifications to the apparatus.

Our sample container consists of an MDC Vacuum Products Del-Seal flange and Del-Seal CF half-nipple flange [30], an oxygen-free copper gasket, a 1/4″ Kovar metal-to-glass seal, and a long, 1/4″-outer-diameter glass capillary tube (inner diameter approximately 1 mm). The copper seal and flanges are held together by several bolts, the bottom of the cup is sealed by welding a piece of stainless steel plate to the base, and the glass-to-metal seal is secured to the upper flange with silver solder. The glass tube was annealed after being attached to the soldered glass-to-metal seal to undo any weakening of the glass that occurred during the soldering process. The CF flanges are made from 304 stainless steel and are rated to a temperature range of –200°C–450°C and pressures as low as 10^{-13} Torr ($\sim 10^{-16}$ atm $\sim 10^{-11}$ Pa) [30]. The glass tube is made thick-walled to reduce heat conduction and thereby minimize dead space errors. The container is diagrammed in Fig. 1. The flanges we used in these experiments have an outer tube diameter of one inch
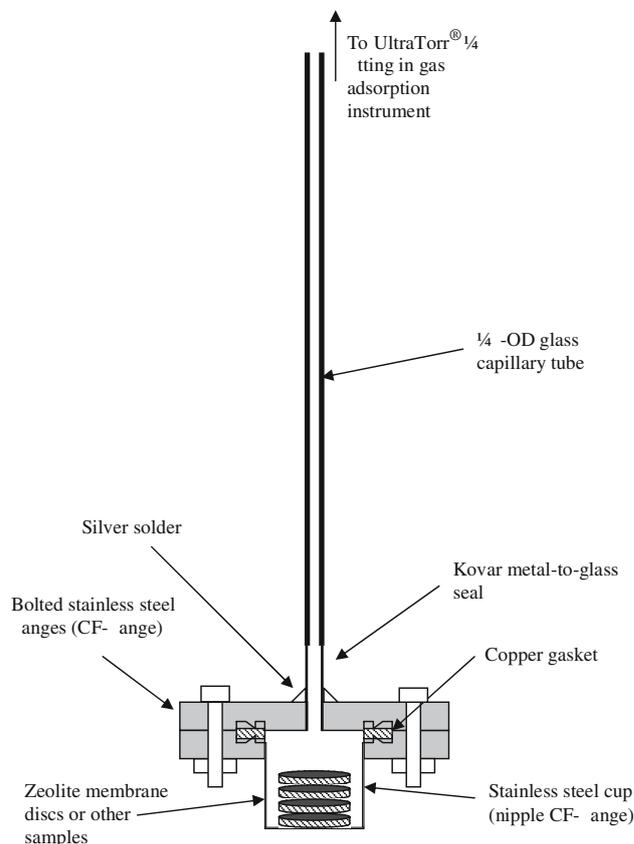
Fig. 1 Diagram of flange-based adsorption cell

(2.54 cm) and an outer flange diameter of 2 1/8 inches (5.40 cm; MDC part numbers 401001 and 110005, respectively [30]). However, any of the other sizes of flange could be employed in this system to accommodate larger objects, though the torques described below should be readjusted for a different size flange.

To test the container, we measured isotherms of silicalite powder in a standard glass adsorption cell and in the new container. The resulting adsorption isotherms (not shown) were identical.

2.2 Membrane sample preparation

The calcined membrane samples were placed in the adsorption cell (Fig. 1), and a seal was formed by tightening the bolts on the flanges uniformly in increments of 10 inch-pounds (1.1 N · m) to a total torque of about 60 inch-pounds (6.7 N · m) using a torque wrench. This gradual tightening procedure is crucial so that the copper gasket seals uniformly around the flanges—this gasket has to withstand a 600°C difference in temperature while maintaining a vacuum seal. The sample container was then connected to an UltraTorr® (Swagelok) fitting on the adsorption system and evacuated over the course of several minutes. We employed two springs secured between the housing of the adsorption system and a metal ring under the bottom of the cell to support some of the weight of the sample container; without these springs for support, the steel flanges may be heavy enough to pull the glass tube out of the fitting. The entire setup with springs attached is shown in Fig. 2.

The sample container was evacuated gradually by a dual-pump system with a roughing pump and a turbomolecular pump to the rated residual pressure of 10^{-9} Torr (10^{-7} Pa or 10^{-12} atm). The sample cell was heated under vacuum over the course of at least 5 h (target ramp rate of one to two degrees per minute) to 300°C. The sample was maintained at 300°C under vacuum for 24–96 h to allow for complete desorption of water and other adsorbed species. The sample was then cooled to room temperature over the course of at least 5 h, and then down to the bath temperature ($\approx$77 K) over the course of 3–4 more hours (same target ramp rate) while maintaining vacuum.

The thermal properties of porous membranes should also be considered when preparing materials for physisorption analysis. Dong et al. [24] noted that randomly oriented MFI-structure zeolite membranes are usually less mechanically stressed than oriented membranes because expansion along the *b*-axis during heating can offset contraction along the *a*- and *c*-axes of adjacent crystals. While their emphasis was on crack formation,

Fig. 2 Complete adsorption cell attached to system valve and supported by springs. The entire cell is immersed in the Dewar (left) until the level of the cryogenic bath is up to the bottom of the black tape

the problem of unequal thermal expansion persists for sorption measurements as well: when the membrane is heated during calcination (removal and/or oxidation of occluded template molecules) or degassing (removal of existing adsorbed material), the membrane could expand at a different rate than the support, and indeed at a different rate from other areas of the membrane. A similar process occurs when the membrane and support are cooled down to the temperature of the bath. To minimize this type of unequal thermal expansion, one must employ a slow heating and cooling procedure in order to minimize thermal variations from one part of the material to another. It should be noted that many procedures for automated physical adsorption measurement ignore thermal shock issues (as these are unimportant in powder samples), so extra care must be taken when measuring sorption in membranes. Thermal expansion, especially the anisotropic expansion–contraction of zeolite crystals within membranes, is unvoidable, but a procedure involving differential heating such as that described herein helps to combat such effects.

2.3 Adsorption-desorption system

Nitrogen and argon adsorption isotherms were measured at the boiling point of nitrogen ($\approx$77 K) using

either a volumetric valve-based dosing system similar to that described in Ref. 31 or an AUTOSORB®-1-C (Quantachrome Instruments) gas adsorption analyzer [29]. A constant level of the liquid nitrogen bath was maintained during measurements to minimize errors in calculations (see Eq. 1 as well as Refs. 32 and 33). Dead space measurements were conducted using helium gas.

Saturation pressures (P_0) for the experiments were determined by condensing (in the case of nitrogen) or subliming (in the case of argon) adsorbate in the vessel at the end of the experiment or by measuring the barometric pressure (in the case of a few nitrogen isotherms at the normal boiling point, 77 K). It should be noted that the most accurate method of determining saturation pressures is to use a dedicated empty glass vessel in which adsorbate is condensed and the pressure measured at various intervals throughout the experiment—this alleviates problems with the saturation pressure changing by small amounts due to changes in barometer (especially if a storm blows in over the course of the experiment) or due to changes in the bath temperature due to oxygen or argon from the air dissolving in the bath. We also note that the latter effect also changes the dead space volume (cf. Eq. 1), and these effects are likely to be a significant contribution to the error in an isotherm.

Pore size distributions can be determined from nitrogen isotherms at 77 K by standard methods [34, 38]. The exact thermodynamic state of argon in the adsorbed phase at 77 K is not certain [19], but some work has been done to extract pore size distributions from argon data at 77 K [39] as well. Some work has also been done to compare measurements at 77 K to measurements at 87 K (liquid argon temperature), with the recommendation being that neither one is strongly preferred over the other [40]. Because liquid nitrogen is generally cheaper and more readily available than liquid argon, it is often chosen as a cryogenic coolant despite the uncertainty in physical state.

2.4 Samples

Powder and membrane samples in this paper are the MFI zeolite structure (silicalite, ZSM-5) grown on alumina substrates [41]. Powder samples are silicalite (Union Carbide lot 961884061002–S), calcined at 500°C. The disc-like supported membranes consist of silicalite grown by a secondary (seeded) growth procedure as described by Xomeritakis et al. [42], with primary crystal orientations along the *c*-axis in one case and the *h0h* crystal faces in the other. The rod-like membranes are borosilicate MFI synthesized on the

inner surfaces of tubular, asymmetric α-alumina supports using a 4.44 TPAOH : 19.46 SiO_2 : 1.55 $B(OH)_3$: 500 H_2O solution [43] as described by Coronas and coworkers [44]. Powders and membranes were calcined at > 500°C; a slow ramp rate of 1–2°C per minute was used for the membrane samples to avoid thermal damage.

In many cases (including our MFI membranes on disc-like supports), the membranes are so thin (~ 1–100 μm) that there is too little material on one membrane to measure using standard physical adsorption. In that case, we recommend stacking more than one membrane in the sample container to ensure that enough mass is present that experimental error does not become extreme. This type of analysis provides an averaged set of adsorption data for the membranes.

3 Results: Adsorption isotherms

We compared the isotherms of silicalite powder with those of two types of MFI membrane as described in the previous paragraph. Examples of these isotherms are shown in Figs. 3–5. The adsorption isotherms of these membranes show all features expected from adsorbing nitrogen or argon into the micropores of an MFI-structure zeolite. We show both standard ($P/P_0 \in [0.01–1)$, linear scale) adsorption and desorption as well as high-resolution ($P/P_0 \in (0, 1)$, logarithmic scale) adsorption for powders and membranes. The membranes isotherms were scaled such that the quantity adsorbed at $P/P_0 \sim 8 \times 10^{-6}$ (nitrogen) and $P/P_0 \sim 6 \times 10^{-5}$ (argon) was the same for powder and membrane alike. This rests on the assumption that the micropores fill at about the same pressure in both membrane and powder samples, which both have the same micropore structure as determined by X-ray crystallography (spectra not shown). Scaling the isotherms in this manner allows us to estimate the mass of the zeolite in the membrane based solely on the adsorption isotherm. Another method would be to compare the weight of the membrane before and after synthesis; the method used here works when the pre-synthesis weight is unknown, and also accounts for the possibility that not all material deposited during the synthesis procedure is actually crystalline. Figs. 3–5 demonstrate that this apparatus can be used for both conventional and high-resolution (low-pressure) adsorption measurements on both planar and cylindrical membranes.

The differences between membrane and powder samples are primarily at high pressures, where surface area and/or pores in the support become significant to
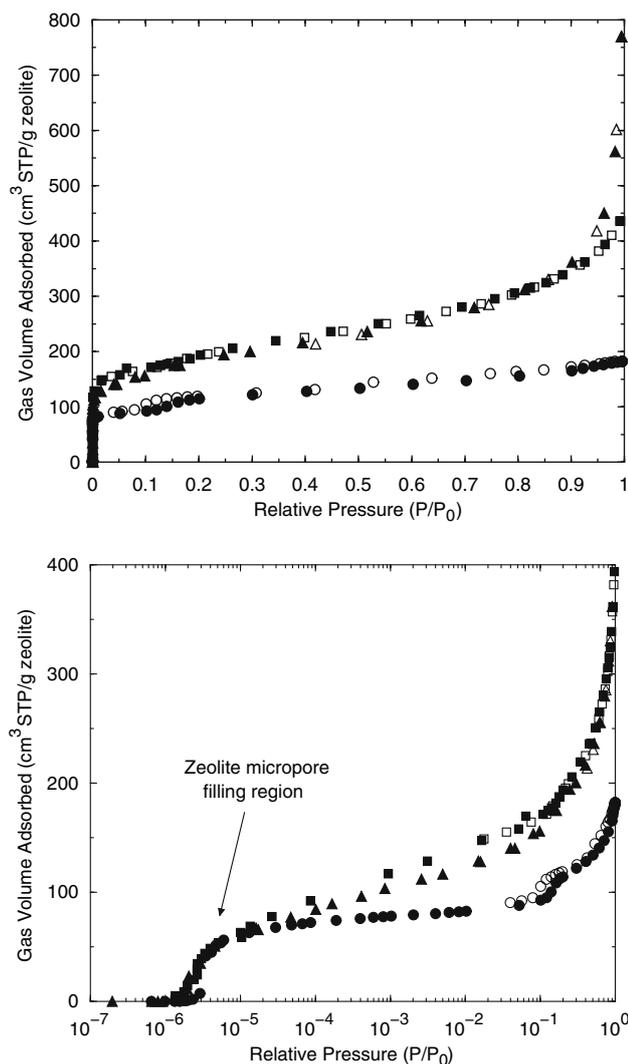
Fig. 3 Nitrogen sorption isotherms at 77 K of silicalite powder (○) and seeded-growth silicalite membranes on disc-shaped α-alumina supports oriented along the c-axis (□) and $h0h$ crystal faces (△). Filled symbols represent adsorption, empty symbols desorption. A linear pressure scale is used in the top figure, while a logarithmic scale is used in the bottom figure (high-resolution region). The sharp increase in the volume adsorbed near $P/P_0 = 10^{-6}$ is due to filling of the micropores

Fig. 4 Argon sorption isotherms at 77 K of silicalite powder (○), and seeded-growth silicalite membranes on disc-shaped α-alumina supports oriented along the c-axis (□) and $h0h$ crystal faces (△). Filled symbols represent adsorption, empty symbols desorption. A linear pressure scale is used in the top figure, while a logarithmic scale is used in the bottom figure (high-resolution region). The sharp increase in the volume adsorbed near $P/P_0 = 10^{-5}$ is due to filling of the micropores

the adsorption isotherm. The system introduced here allows us to determine mesoporosity in the sample without concern over whether we have created new porosity by processing the material before the analysis. Please note also that there is a significant contribution to the sorption from the support (due to its relatively large mass) in the case of the disc-shaped membranes; the adsorption attributable to the supports used for the cylindrical membranes, however, is negligible. The contribution of the support to the adsorption isotherm and its overall significance is a subject of our future research.

4 Conclusions

We have presented a reusable adsorption vessel that is capable of measuring conventional and high-resolution adsorption/desorption isotherms on intact supported porous membranes with two geometries of support. It should be possible to measure the adsorption isotherm of any sample of reasonable dimensions using the apparatus (or a suitable modification thereof) described in this paper and shown in Figs. 1 and 2. The procedure causes no damage to the material being analyzed, provided an appropriate procedure is used
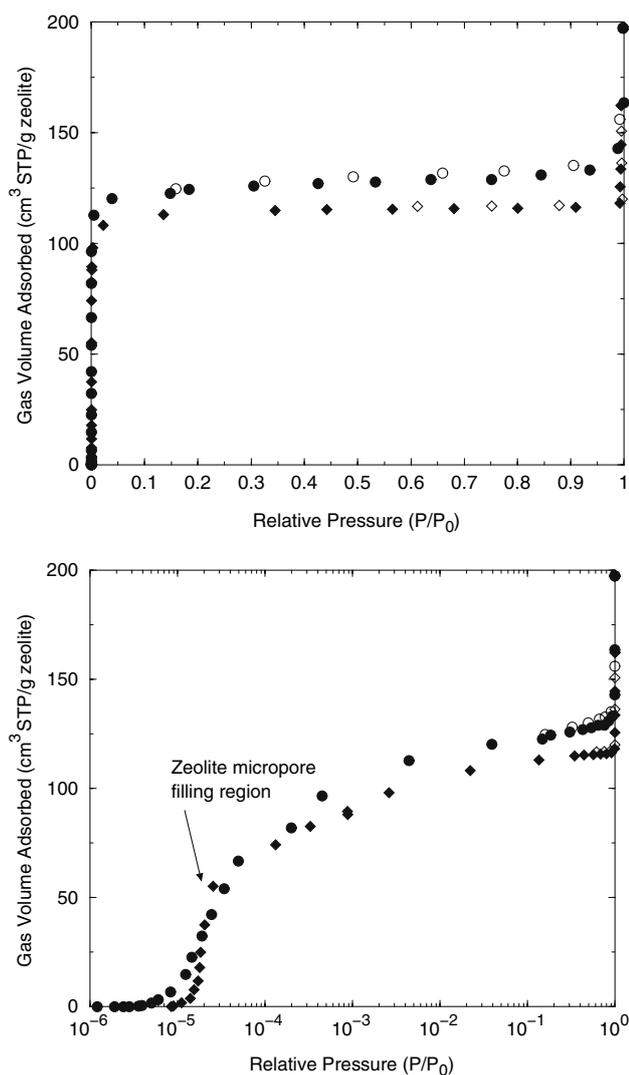
Fig. 5 Argon adsorption isotherms at 77 K of silicalite powder (◯) and supported boron-MFI membranes on rod-shaped α-alumina supports (◇). Filled symbols represent adsorption, empty symbols desorption points. A linear pressure scale is used in the top figure, while a logarithmic scale is used in the bottom figure (high-resolution region). The sharp increase in the volume adsorbed near $P/P_0 = 10^{-5}$ is due to filling of the micropores

for heating and cooling the sample so as to avoid damage to the membrane(s) due to thermal gradients. Our results show that one can use this apparatus for both conventional and high-resolution adsorption. We also note that this technique is not limited to zeolitic membranes such as those we analyze here: we have also used this apparatus to measure adsorption on non-porous films and polymeric membranes.

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