Final Report:

Multicomponent Transport through Realistic Zeolite Membranes: Characterization & Transport in Nanoporous Networks

DE-FG02-94ER14485

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OBJECTIVES (from the proposal)

Considerable progress is being made in the synthesis of novel nanoporous solids for use in catalysis, storage and separations. At the same time, experimental and computational capabilities are being developed to study and to characterize transport/sorption of individual fluids within solids of uniform nanoporous dimensions.

However, the diffusion of pure fluids through nanoporous solids is not of practical significance; rather, it is multicomponent transport that must be understood. Furthermore, permeation through defect-free single-crystal membranes is not relevant, because present-day membranes are riddled with polycrystallinity, porosity on many length scales, and defects of many varieties. The focus of this proposal is the development and application of experiment and simulation to understand how mixtures of guests and mixtures of pore sizes conspire to produce observable transport properties.

This research involves a direct collaboration between laboratories involved in synthesis, characterization, measurement and simulation of transport within nanoporous networks to understand the application of these new catalytic solids.

The nanoporous solids we will are study are: 1- silicalite (ZSM-5) or faujasite (X or Y) zeolites as crystals and formed into membranes by intergrowth; 2- SBA-15 (or related mesoporous solids) that exhibit microporosity, probably within the surfaces that form the mesoporosity. A broader spectrum of solid samples will be (and already have been) studied to calibrate the characterization techniques employed (e.g., other zeolites), but not formed into membranes. We will also, as needed, study sorption and transport of smaller molecules that are employed in characterization of pore structure (e.g., N2, Ar, Kr or ...) and those whose changes in diffusive rates are measurable and will be employed as a probe of the network structure.

SIUMMARY

These research studies focused on the characterization and transport for porous solids which comprise both microporosity and mesoporosity. Such materials represent membranes made from zeolites as well as for many new nanoporous solids. Several analytical sorption techniques were developed and evaluated by which these multi-dimensional porous solids could be quantitatively characterized. Notably an approach by which intact membranes could be studied was developed and applied to plate-like and tubular supported zeolitic membranes. Transport processes were studied experimentally and theoretically based on the characterization studies.

Approach (Summary of accomplishments in the two years of this grant):

Two new students have joined this research: Eunyoung You, who just defended her masters thesis on this research and Karl Hammond who is currently finishing his PhD.

The Research Accomplishments

- 1. We have developed a technique to measure supported intact zeolite membranes, the first such study.
- We developed a simulation based on the textural characterization of plate-like membranes employing Maxwell-Stefan diffusion coefficients. The significance of diffusion through the support was surprisingly demonstrated.
- 3. We refined the force field in molecular dynamic simulations of for Benzene diffusion in NaX membranes. These now agree with other techniques such as pulse field gradient NMR and quasi-elastic neutron scattering data.
- 4. We applied the above technique to the characterization of several types of MFI membranes (on support plates or tubes). In these cases, the support and zeolite sorption processes behave independently.
- 5. We have synthesized multiple SBA-15 samples and discovered that the presence of microporosity depends on specific synthesis conditions and heating method.
- 6. We have developed a general correlation for microporous dimensions from Ar and N_2 high resolution adsorption (HRADS) by studying a series of zeolites with 1D channels. This then enabled us to estimate the microporous dimensions in SBA-15.
- 7. We developed and employed preadsorption to separate sorption in the micropores from the mesopores in SBA-15 and in zeolites. We discovered the profound influence that the combined isotherms exhibit in terms of the calculated surface area(s), they do not behave independently.
- 8. We studied the stability within the hysteresis loop for sorption in mesoporous solids by reversing the sorption processes and thereby scanning within the loop. Several distinct behaviors were evident in the data which represent different physical processes.
- 9. We studied the stability within the sorption hysteresis loop to thermal and mechanical perturbations. These "metastable" points were stable to mechanical perturbances but moved toward the sorption or desorption branches under thermal changes.
- 10. We have developed a variable angle attenuated total reflectance approach to measure the relative concentrations at different positions across a supported zeolite membrane. This was applied to MFI membranes.

Each of these accomplishments are discussed in more detail below as are the state of the resultant publications and presentations:

1. SORPTION CHARACTERIZING OF INTACT ZEOLITE MEMBRANES

IN PRESS J. POROUS MATERIAL

Apparatus for Measuring Physical Adsorption on Intact Supported Porous Membranes

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

Abstract

In this publication (*J. Porous Mater.*, 2007, in press, DOI 10.1007/s10934–006–9034–x), we presented a non-destructive, reusable apparatus with which to measure physical adsorption on macroscopic objects such as supported zeolite membranes. The measurement cell employs a copper sealed reusable metal container and a metal-to-glass seal; the entire apparatus can be immersed into a cryogenic bath. The apparatus is intended to preserve the advantages of traditional glass tubing such as low conductivity and low dead volume; the bottom of the container is removable so as to be usable for objects which do not fit down the neck.

Motivation

This work was motivated by research on zeolite membranes, in particular the confocal microscopy experiments of Tsapatsis and coworkers, 1,2 which indicate that zeolite membranes possess some quantity of non-zeolitic porosity. This porosity has an impact on the adsorption and transport properties of zeolite membranes, both of which are important in membrane-based separation processes. However, adsorption on membranes themselves has been difficult for practical reasons: standard adsorption equipment is designed for powders and other preparations that fit easily down the neck of a glass tube. Using narrow tubes to measure adsorption is necessary in order to reduce experimental error. The fact that membrane porosity as well as the support are neglected in the analysis means that the adsorption capacity is underestimated and diffusion coefficients are overestimated in the supported membrane.

Most adsorption characterization of powders is carried out with narrow-necked glass tubing attached to a high-vacuum fitting. Powders fit down the neck, but clearly most membranes will not. Using larger-diameter tubing is not sufficient to overcome this limitation: as the diameter of the tube increases, the dead volume increases and the experimental error correspondingly increases. The larger the cross-section that spans the bath, the more significant the changes in pressure that result from minor variations (less than a millimeter) in the height of the cryogenic bath or the temperature profile of the upper tube to due to boil-off of the cryogenic bath.

Some groups have attempted to solve the problems associated with adsorption on membranes by cutting or grinding their samples prior to analysis. This procedure allows the membranes to be analyzed with standard glass tubing, but it destroys the membranes for future use for their intended purposes that require intact membranes. Another technique is to scrape the membrane off the support, which suffers from the same problem. Another method we are aware of is fusing the glass tube into place around the membranes; this solves the dead space problem, but requires rapid and uneven heating of the sample in order to fuse the glass. Our new apparatus solves all of these problems by creating a container that seals at room temperature via a series of bolts and a disposable copper gasket.

Results

Our adsorption apparatus satisfies all of the following requirements:

- The cell holds pressure between rated pressures of 10⁻⁹ atm and at least 2 atm over a pressure range of -196°C to 400°C (liquid nitrogen and degassing temperatures, respectively)
- The shaft has a small inner diameter and is made of glass (a poor heat conductor) to reduce dead space errors
- The shaft end fits into standard fittings on existing adsorption equipment
- The apparatus is reusable and versatile enough to accommodate several geometries of zeolite membrane

We used the membrane adsorption apparatus (Fig. 1) to generate high-resolution adsorption isotherms on silicalite powders and membranes as a test of our apparatus.

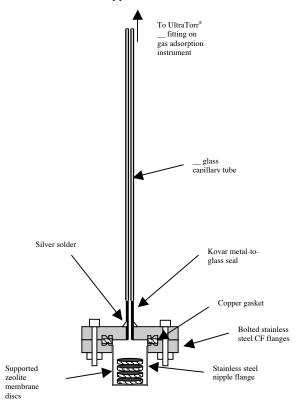


Figure 1. Diagram of flange-based adsorption system.

The resulting adsorption isotherms (Fig. 2) show additional adsorption in the membranes that is not present in the powders. We have already used this apparatus to measure adsorption isotherms on intact samples of (1) supported silicalite (MFI zeolite) membranes in a planar geometry, (2) supported B-ZSM-5 (MFI zeolite) membranes in a cylindrical geometry, (3) planar titania films supported on stainless steel, (4) planar gold films on silicon substrates, and (5) planar polymeric films on glass substrates. These samples could not have been analyzed by traditional methods.

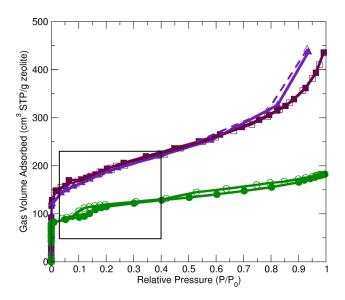


Figure 2. Nitrogen isotherms at 77 K of silicalite powder (green circles), and two types of oriented silicalite membranes (red circles and purple triangles). Note that the low-pressure hysteresis characteristic of MFI is absent for the silicalite membranes.

Conclusions

We concluded that this adsorption vessel is an effective and useful way to extend adsorption characterization to intact membranes. This will allow for characterization of materials that would otherwise have to be destroyed in order to be analyzed. This also allows us to test the assumption—up to this point, a necessary one—that zeolite membranes can be treated like zeolite powders for the purposes of interpreting separation experiments.

Significance

The established method of pore-size characterization by adsorption of small, chemically inactive vapors such as nitrogen and argon are applicable to complex systems such as zeolite membranes. This allowed us to determine the pore structure of zeolite membranes and other thin films in a non-destructive fashion. Such an analysis will make it possible to study such materials with greater structural insight, which in turn will allow the materials to be further developed for use in catalysis, separations, and other applications.

2. CHARACTERIZATION OF MEMBRANES BY SORPTION

Langmuir 23 (16): 8371-8384, 2007

Physical Adsorption Analysis of Intact Supported MFI Zeolite Membranes Karl D. Hammond, Geoffrey A. Tompsett, Scott M. Auerbach, and W. Curtis Conner, Jr.

Abstract

In this article (*Langmuir* 23 (16): 8371–8384, 2007, DOI 10.1021/la063256c), we compared the adsorption isotherms of intact supported silicalite membranes with those of zeolite powder and a comparable amount of support. We attempt to disentangle the contributions of the zeolite from those of the support, and

examine the effects of each region on the predicted transport properties. The support is, contrary to popular intuition, very important to the adsorption isotherms and transport properties because of its relative thickness. The lack of hysteresis in the resulting isotherms indicates little if any of the mesoporosity we anticipated. In fact, the adsorption isotherm of the powder plus the support is so close to the adsorption isotherm of the supported membrane that we find no reason to make a distinction for these membranes. The support should, however, be considered in the interpretation of transport experiments.

Motivation

Zeolite membranes promise energy-efficient mixture separations due to their shape-selective network of micropores. Modeling and interpreting transport through zeolite membranes requires accurate information about the pore sizes and equilibrium properties of real membranes. Specifically, it requires information about any defects—especially mesoporous defects—that exist in the zeolite layer due to the incomplete intergrowth of zeolite crystals. Defects in the size range of 2–50 nm should be detectable by physical adsorption analysis.

Previous studies of adsorption on membranes³ have shown that self-supporting membranes can exhibit hysteresis in the nitrogen isotherms, implying the existence of mesopores. These mesopores would have a dramatic impact on transport, as both the magnitude and loading dependence of the diffusion coefficients would be affected by the larger pores. It is not clear, however, whether the handling procedure used to analyzed the membrane samples used in other studies created additional mesoporosity due to grinding. Our goal in this study was to measure adsorption isotherms on intact membranes, compare them to those of zeolite powders, and incorporate any differences in the isotherms into models of transport.

Results

We divided both the transport domain and the adsorption isotherms into two regions, corresponding to the support and the zeolite. The adsorption isotherms are typically scaled according to the mass of the adsorbent; since there are *two* adsorbents in this case (zeolite and support), we normalized the isotherm by the mass of the zeolite alone. This mass was determined by matching the isotherm of the supported membrane to that of the zeolite powder at the knee in the micropore-filling region (near 10⁻⁴ relative pressure). This region was selected because the adsorbate does not interact significantly with the support at that pressure, and all adsorption occurs in the micropores of the zeolite.

The resulting powder and supported membrane adsorption isotherms look quite similar until a relative pressure of about 10^{-3} , at which point the support begins adsorbing significantly (Fig. 3). However, comparing the adsorption isotherms of the powder added to the support—weighted by mass—yields very similar isotherms to those observed for the supported membranes. This indicates two things: first, there is very little mesoporosity in the membrane or support; and second, the isotherm of a supported membrane is not qualitatively different from a "supported powder" (a powder plus a support).

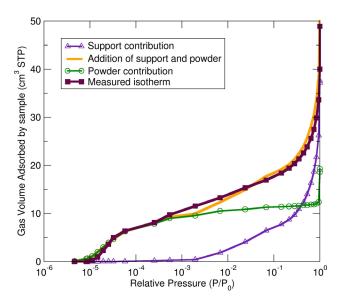


Figure 3. Argon adsorption at 77 K on silicalite membranes. The high-resolution pressure axis shows the micropore-filling region and demonstrates how little the support adsorbs at low pressures. The vertical axis is not scaled; it represents the total amount adsorbed on all membranes being analyzed.

There are subtle differences between the powder and membrane isotherms of some samples at low pressures. To verify the effects of this, we performed flux calculations using a finite differencing numerical solution; the results (Fig. 4) indicate that the differences in the isotherm have only minor effects on the loading dependence of the diffusion coefficient.

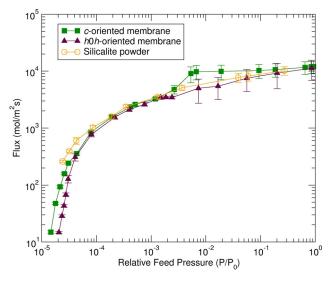


Figure 4. Result of flux calculations using a constant Maxwell–Stefan diffusion coefficient in the zeolite with the remaining loading dependence determined from the argon adsorption isotherms. The support has been ignored here; it was included in other calculations.

Conclusions

We found that silicalite membranes—as synthesized by the same means as the ones we study—can be reasonably approximated as a zeolite powder deposited on a support for the purposes of adsorption

characterization. No mesoporosity was detected, indicating all defects are either smaller than 2 nm and very low in concentration or larger than about 30–50 nm and thus beyond the range of detection by adsorption.

Another conclusion reached during this study is that the support—contrary to conventional wisdom—is potentially *very* important to permeation. We suggest that including the support in the interpretation of permeation experiments is very important and should be done. Including membrane-layer defects appears to be less significant, as these defects do not manifest themselves in the adsorption isotherms and thus the concentration of defects relative to support and zeolite porosity is very low.

3. BENZENE DIFFUSION IN NAX MEMBRANES

Publications:

- H. Ramanan, M., Tsapatsis and S. M. Auerbach,
- 1. "Beyond Lattice Models of Activated Transport in Zeolites: High-temperature Molecular Dynamics of Selfand Cooperative-Diffusion of Benzene in NaX,"
- J. Phys. Chem. B 108, 17171-17178 (2004).
- 2. "Predicting Benzene Fluxes in NaX Membranes from Atomistic Simulations of Cooperative Diffusivities,"
- J. Phys. Chem. B 108, 17179-17187 (2004).

ZEOLITE MEMBRANE PERMEATION: IDEAL MODELS OF BENZENE IN NAX MEMBRANES

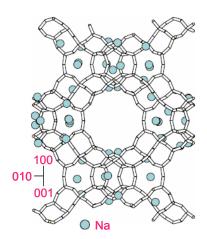
SUMMARY

We employed high-temperature molecular dynamics to investigate self and cooperative transport of benzene in NaX (Si:Al = 1.2)⁴. The atomic unit cell structure and membrane SEM micrograph are shown below in Fig. 5. We refined the benzene-NaX forcefield for use with our previously developed framework forcefield for alumino-silicates, which explicitly distinguishes Si and Al atoms in the frame, and also between oxygen atoms in Si-O-Si and Si-O-Al environments. Energy minimizations and molecular dynamics simulations performed to test the new forcefield give excellent agreement with experimental data on benzene heats of adsorption, benzene-Na distances and Na distributions for benzene in NaY (Si:Al = 2.4) and NaX (Si:Al = 1.2). Molecular dynamics simulations were performed over a range of temperatures (600-1500 K) and loadings (infinite dilution-4 benzenes per supercage) to evaluate simultaneously the self- and cooperative- (alternatively Maxwell-Stefan) diffusivities.

The simulated diffusivities agree well with pulsed field-gradient NMR and quasi-elastic neutron scattering data. This is the first such agreement that has been obtained between simulation and experiment for rare-event diffusion in cation-containing zeolites. Such systems are the rule in technological applications. Virtually all previous such comparisons have been made for simple alkanes (methane-butane) in cation-free (siliceous) zeolites. Our results are thus a major step forward to using simulation to model technologically important zeolites.

We then used the loading- and temperature-dependent Maxwell-Stefan diffusivities to predict single-

component fluxes for benzene in NaX membranes at steady state as a function of typical experimental parameters such as temperature, benzene feed side and permeate side partial pressures⁵. We explored whether support resistances need to be included in our transport model. We compared our model predictions with experimental permeation data, and found that our MD-simulated diffusivities overestimate experimental fluxes by two to three orders of magnitude when ignoring support resistance. On the other hand, when including support resistances, our predictions come within an order of magnitude of experimental data. The remaining discrepancy, which is analogous to those between microscopic and macroscopic probes of diffusion in zeolites, may arise from defects within zeolite membranes. This research highlights the importance of being able to characterize defect patterns that exist in real zeolite membranes.



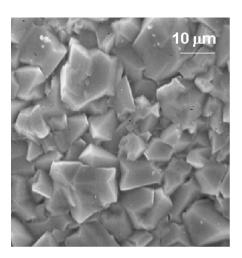


Fig 5a&b. Unit Cell Structure and SEM of Na-X Zeolite Membranes.

4. High-Resolution Adsorption on Supported Borosilicate MFI Structures

Karl D. Hammond, Mei Hong, Geoffrey A. Tompsett, Scott M. Auerbach, John L. Falconer, and W. Curtis Conner, Jr.

Abstract

In this article (planned for submission to *J. Membrane Science*), we analyze the structure of tubular boron ZSM-5 membranes with Si:B ratios of 12.5. The support, which is a smaller fraction of the total mass for these membranes than those previously studied, contributes little if any to the adsorption isotherm. The isotherms are nearly identical between powder and membrane, with one exceptions: the low-pressure (micropore-filling) region. This region is *significantly* steeper for the membrane samples than it is in the powders. Combined with our previous results (*Langmuir* 23: 8371–8384), this may indicate that membranes have a less flexible zeolite framework than do powders. We also note that the hysteresis that is characteristic of MFI at 77 K (nitrogen adsorption) is absent from all membranes we have ever seen analyzed. It is also absent in some silicalite powders (Ref. ⁶ and Fig. 6), indicating that small-scale defects may be significant to the structure and properties of membranes.

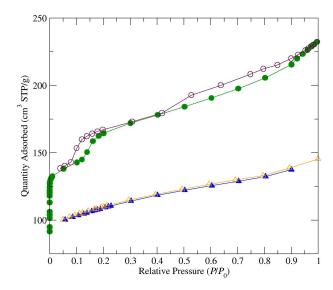


Figure 6. Isotherms of silicalite powders prepared commercially (top) and by conventional heating (bottom). Why the loop vanishes under some synthesis conditions is still unclear. The top isotherm has been translated by 50 cm³/g for clarity.

Motivation

Zeolite membranes made by *un*seeded growth are somewhat easier to synthesize than seeded growth membranes, though they lack the benefits orientation provides in terms of rate of diffusion. The membranes that motivated this study are grown in a tubular geometry, where the zeolite is grown layer-by-layer on a commercial alumina support. The supports have very large pores and very little surface area relative to their mass.

The zeolite membranes grown by layered primary growth such as those used here have a relatively large amount of zeolite compared to the support. This means the support's contribution to the isotherm may by very different from that in previous studies. The size of the samples (about 1 cm in diameter and 5 cm long) makes them even more difficult to analyze than other membranes. Adding boron to the mix adds another parameter to the adsorption isotherms: silicalite and Al-ZSM-5 have been studied much more extensively than B-ZSM-5.

Results

The argon adsorption isotherm (Fig. 7) of these membranes continues the trend partially seen in other membrane samples (not shown): the isotherm is steeper in the low-pressure regions for membranes than it is for powders. The slopes of the powder isotherms are virtually identical for both silicalite and B-ZSM-5 powders. This increased "steepness" was seen to a lesser extent in secondary-growth membranes, but it is even more pronounced for these (primary-growth) membranes. This could indicate a difference in lattice flexibility due to the presence of other zeolite crystals: as more adsorbate fills the micropores, those pores would normally try to expand. The pores are prevented from expanding in membranes due to the presence of other crystals nearby that prevent this expansion. This would lead to a narrower range of pressures over which the micropores fill.

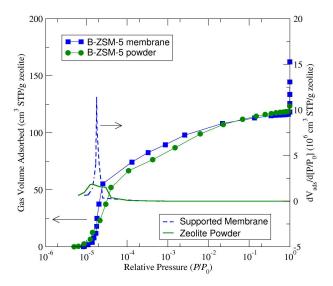


Figure 7. Isotherm (argon at 77 K) of B-ZSM-5 powder (circles) and membrane (squares), overlaid with the derivative of the isotherm. The membrane isotherm rises considerably more abruptly as the pressure increases.

The nitrogen isotherms of these membranes, like those of other membranes studied (Fig. 5 and Ref. 3), do not display the low-pressure hysteresis (Fig. 6) characteristic of silicalite and most Al-ZSM-5 powders. In these samples, this phenomenon may be linked to Si:X ratio (X = Al or B); we have found that this loop vanishes at ratios of Si:Al = $30:1.^{7-12}$ Since the Si:B ratio in these membranes is 12.5:1, we would not necessarily expect the loop to be present in these samples. We would, however, expect it to be present in the all-silica MFI powders we compared it to; under certain sets of conditions, this is not the case! The fact that this loop is absent in secondary growth membranes (Fig. 2) and self-standing silicalite structures³ means that it is not solely due to aluminum content. We are finalizing details that will confirm whether we can vary the synthesis time and change the shape and/or presence of the loop, but the fact that conventional synthesis of MFI powder in the absence of aluminum (Fig. 7) yields no hysteresis is interesting in itself.

Conclusions

We conclude that there is a difference between the way membrane micropores fill and powder micropores fill. We further conclude that synthesis time and other conditions may be responsible for the presence or absence of low-pressure nitrogen hysteresis in MFI. In accordance with previous studies, we think that the added rigidity imposed by the macroscopic structure of the membranes impedes the crystal morphology change from monoclinic to orthorhombic symmetry normally experienced by MFI crystals. We are in the process of testing this hypothesis, after which the paper will be submitted.

5. SYNTHESES OF MICRO-MESOPOROUS NETWORKS: SBA-15

Results from this are accepted for presentation at the AIChE Meeting in November 2007

In Preparation for submission to J. Porous Mater., August 2007.

Synthesis of SBA-15: Factors that influence the Microporosity

Eunyoung You, Geoffrey Tompsett and W. Curtis Conner

There have been growing demands for new types of mesoporous materials after discovering that M41S materials¹³⁻¹⁷ have poor thermal stress properties. A novel material, SBA-15, was first synthesized by the research group lead by Stucky^{18,19} at UC-Santa Barbara. SBA-15 earned much attention in the last decade owing to its excellent thermal stability, variable pore sizes, and tailored particle morphology. The pore topology consists of a two dimensional mesoporous network of uniform dimensions formed by microporous walls. Compared to zeolites which have pores in the micro-range (4~14 Å), SBA-15 material is a new type of mesoporous material with micropores, hence it is expected to lower the diffusion limitation that a microporous material typically experiences. Zeolites are crystalline while SBA-15's pore walls are essentially amorphous, however, pores of SBA-15 material are regularly spaced due to the templates liquid crystal micelle arrangement.²⁰

The synthesis process to obtain solid powder SBA-15 involves dissolving of template (Pluronic 123) polymer in acidic solution, adding a silica source, which is typically either tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS), or sodium silicate. The mixed solution is aged at a temperature slightly above room temperature for 20 to 24 hours and heated up to 80 to 100°C either in a conventional oven or in a microwave oven for an appropriate amount of time. Precipitated solids are centrifuged, washed and dried. Finally, the organic polymer is removed by calcination (e.g. 550 °C for 24 hours). Figure 8 shows the schematic of the synthesis procedure.

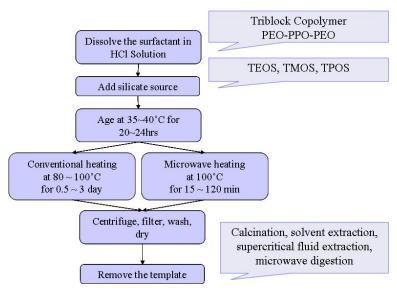


Figure 8. Simplified procedure for the synthesis of SBA-15.

A study of ramp time, hold time, and maximum power input influence on the synthesis of SBA-15 materials using microwave heating was performed. The surface areas and pore dimensions form adsorption analysis are summarized in Table 1.

The ramp rate has a strong influence on the a-parameter and the microporosity of the samples: the greater the heating rate, the larger the a-parameter, and the slower the rate, the higher the microporosity.

Hold time effects the BET surface area linearly in the sense that reacting at higher temperatures for prolonged periods of time gives a higher surface area.

Maximum power input had minor or insignificant effects on the structural properties of synthesized SBA-15 materials. Rather, it was a key factor in the ramp rate to the set temperature. Higher power is required for faster ramp rates, particularly with large amounts of precursor solution in the reaction vessel.

Table 1. Textural properties of microwave synthesized SBA-15 samples obtained from XRD and adsorption isotherms.

Sample ID	a (Å)	$\mathbf{D}_{\mathrm{BJH}}(\mathring{\mathbf{A}})$ ad/de	t (Å) ad/de ^b	SA _{BET} (m ² /g)	C _{BET}	d _{HK} (Å)	d _{SF} (Å)	V (cc/g)
MW-rhp	107.3	78.7/ 61.9	28.6/ 45.4	744.6	86.6	5.0	7.5	0.103
MW-RHp	106.8	78.8/ 61.8	28.0/45.0	668.9	75.9	5.0	7.9	0.086
MW-RhP	105.4	78.0/60.4	27.4/ 45.0	714.2	93.3	4.9	5.0	0.105
MW-rHP	107.5	84.1/64.0	23.4/ 43.5	700.2	56.1	5.1	8.0	0.070
MW-Rhp	103.5	78.1/60.3	25.4/43.3	658.8	68.9	5.0	8.0	0.078
MW-rHp	104.6	78.8/ 61.9	25.9/ 42.8	776.1	59.1	4.9	5.0	0.084
MW-rhP	105.3	78.1/60.3	27.2/45.0	705.3	69.3	5.1	7.6	0.087
MW-RHP	106.9	78.2/ 64.2	28.8/42.7	879.8	74.6	5.0	7.9	0.116

 $^{^{}a}$ D_{BJH} calculated based on adsorption isotherm (ad) and desorption isotherm (de). b Wall thickness t obtained from a-parameter by subtracting calculated D_{BJH} which was based on adsorption isotherm (ad) and desorption isotherm (de).

r is short ramp time, 2 min, and R is longer ramp time, 10 min. Similarly, hold time is denoted, h or H and maximum power as, p or P. Thus, for instance, MW-rHp was prepared in microwave oven with short ramp time, 2 min, long hold time, 120 min, and small power input, 300 W.

We have successfully synthesized SBA-15 materials within 2~4 hours. The a-parameter values are nearly constant during the aging period and gradually increase with additional heating at higher temperature and long times. Microporosity is maximized with use of conventional heating with a slow temperature ramp. Microwave heating during the synthesis step produced larger mesopores and thinner walls. If the microwave heating ramp time is matched to the conventional (60 min), smaller mesopores and less microporosity is produced. Microwave heating favors more rapid silica condensation and retraction of the template from the pore walls, hence less microporoisty. An maxima of surface area and micropororosity was achieved using 2 hours aging at 40°C and 2 hours synthesis at 100°C using convention heating.

6. Empirical Model for the Characterization of Microporous Catalysts

Geoffrey A. Tompsett, Eunyoung You, Emma Trivella, Luaren Krogh, Elane Maglara and W.Curtis Conner Presentation at the North American Catalysis meeting, Houston, TX. 2007 Manuscript being submitted to Journal of Porous Materials

Introduction

The porous structure of catalyst materials such as zeolites, is typically characterized using adsorption techniques. The gas adsorption of microporous materials gives rise to a steep increase in volume over a short pressure range in the isotherm region below P/Po < 10⁻². This steep increase or "step" in the isotherm corresponds to the micropore pore filling. The size of the micropores is most often estimated using either the Horvarth- Kawazoe (HK, slit-like pores, usually for carbon based materials), Saito-Foley (SF, spherical and cylindrical models for oxide materials), the Dubinan-Radushkevich (DR) method or density functional theory (DFT). These models are based on the interaction of gas molecules and the walls of the microporous materials. Often there is a large discrepancy between the calculated pore size from the models (HK, SF, DR and DFT) and the actual pore size determined from crystallographic techniques as shown by Maglara²¹.

The "step" in the isotherm will shift in relative pressure depending on the pore size. An empirical model using the relative pressures at the "step" filling in the isotherm and the pore sizes from crystallography of a set of standard microporous materials, would give a correlation of size versus pressure directly from experimental data rather from theoretical models. Hence, a simplistic correlation may be able to be used instead of complicated models and give a more realistic pore size estimation of an unknown sample. An unknown sample is likely to consist of one of the new type of nanopoorus materials, including MCM and SBA type materials. For example, SBA-15 is known to contain both microporous and mesoporous pores depending on the synthesis conditions. New adsorption analysis techniques are required to give better estimation of the pore sizes from these new complex porous materials.

Table 2 Zeolite samples and dimensions for standard adsorption pressures.

Zeolite	Structure, space group	Ring size	Channel type	Pore shape	Pore dimensions from X-ray crystallography
ZSM-23 (MTT)	Orthorhombic, Pmmn	10 MR	1D	Ellipse	4.5 x 5.2 ²²
SSZ-20 (TON)	Monoclinic, Cmcm	10MR	1D	Ellipse	4.6×5.7^{22}
ZSM-12 (MTW)	Monoclinic, C2/m	12 MR	1D	Ellipse	5.6×6.0^{22}
SSZ-41 (VET)	Monoclinic, P-4	12 MR	1D	Circular	6.0 23
SSZ-55 (ATS)	Monoclinic, Cmc2 ₁	12MR	1D	Ellipse	6.52 x 7. ^{22 24}

Materials and Methods

The standard one dimensional zeolite samples used to calibrate the adsorption pressure of micropore af specific crystallographic sizes are listed in Table 2. Argon adsorption at 87 K of the zeolite samples was run using an Autosorb-1C (Quantachrome Instruments). A sample of about 0.035 g was weighed for each of the zeolites and placed in a spherical sample tube. Each of the samples was out-gassed at a temperature of 300°C, with a temperature ramp rate of 200°C/h. Surface area and micropore analysis was carried out using Autosorb ASWin ver 1.51 (Quantachrome) software. Micropore size to filling pressures from isotherms of the five

zeolites and literature values were combined to develop the empirical models, of ID and 3D micropores, using Microsoft ExcelTM spreadsheets.

Results and Discussion

Low-pressure isotherms of five 1D-channel type zeolites MTT, TON, MTW, ATS and VET, of varying pore size, were obtained using argon adsorbate at 87 K, between 10^{-7} and 0.2 P/Po. The isotherms were characterized using several standard analysis techniques, including BET surface area, Vt-plot, α -plot micropore volume. An empirical correlation between the crystallographic pore diameter and the relative pressure of the isotherm "step" was determined for 1D and 3D zeolite types combining also literature data. Figure 9 shows three different models fitted to experimental data for 1D type zeolites. It can be seen that all three types, in particular the Halsey give a very good fit. Using these models we were able to apply it to determine the micropore distribution of complex meso-microporous materials; SBA-15.

Significance

Many new microporous catalyst materials such as SBA-15 type meso-microporous systems are being developed and employed in the catalytic and separation industry. The accurate estimation of the pore size of these materials is critical in order to fully utilize the structural properties of these systems. This model allows the quick and accurate determination of micropores from isotherm data.

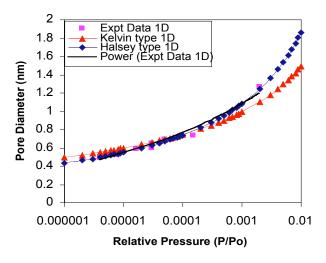


Figure 9. Correlation between pore diameter and relative pressure for 1D zeolites, with three types of mathematical equation fits, Kelvin, Halsey and power type.

Acknowledgements

The authors would like to thanks Stacey Zones, Chevron Texaco Energy and Research Center for the zeolite samples.

7. ISOLATING SORPTION IN MESOPORES FROM MICROPORES.

presented at North American Catalysis Society Meeting in Houston, June 2007 Paper in draft for submission to Langmuir, August , 2007

Characterization of Mixed Micro- Meso-porous Catalysts for Membrane Applications Karl Hammond, Eunyoung You, Geoffrey A. Tompsett, Ryan Pavlica, Audrey McLain, Bhrugesh J. Patel, W. Curtis Conner and Scott M. Auerbach

Introduction

New porous catalyst and separation materials such as SBA-15, PHTS and FDU type silicas have recently been developed. These materials possess a complex porous structure of both micro and mesopores. These materials require new careful techniques to separate the microporous and mesoporous components of the structure, in order to give valid estimations of the surface areas and pore distributions. We have developed a combination of three techniques to achieve this purpose. Namely, employing pre-adsorption to separate the mesoporous nature of the materials from the micropore component (<2 nm). Secondly the use of an accurate empirical model to estimate the micropore size distribution of a non-crystalline microporous solids, such as SBA-15. 25,26 (see section 6). Thirdly, incorporating a novel technique which has been developed to measure porous structure of intact membranes and supported catalyst materials. The technique involves a specially designed re-sealable cell in which the membrane can be placed followed by the measurement of high resolution adsorption (see Fig. 1 above). This technique has been successfully demonstrated on alumina supported silicalite membranes of differing geometries. 27,28.

Materials such as zeolites formed into a membrane or SBA-15 can comprise micropores as well as mesopores in their porous networks. Standard sorption experiments yield data that exhibit a combination of the processes by which each range of pores are filled. We have pointed out for a long time that in particular the surface area measurement by using the BET theory is invalid for samples containing micropores. Yet the wall thickness of mesoporous materials and the estimation of pore size distribution by adsorption analyses depend on a n estimate of the surface area, One approach to isolate the mesopores from the micropores is by preadsorption.

Materials and Methods

SBA-15 materials were prepared based on the work by Luan et al.²⁹ employing both conventional and microwave heating. Plugged hexagonal templated silicas (PHTS),were prepared in accordance with the procedure described by van der Voort et al.³⁰

Adsorption and desorption isotherms were measured at the boiling point of nitrogen (77 K) and argon (87 K) using an AUTOSORB-1C (Quantachrome Instruments; Boynton Beach, FL) gas adsorption system or our own high-resolution adsorption equipment as described in Refs. ³¹ and ³². Nitrogen and argon were used as adsorbates, and a constant level of the liquid N₂ or Ar bath was maintained during all measurements. Dead space measurements were conducted using helium; saturation pressures were determined by condensing/subliming the adsorbate in a separate vessel inside the cryogenic bath at intervals throughout the experiment or by condensing/subliming adsorbate in the sample container at the end of the experiment. All gases used in the experiments are ultra-high purity.

In preadsorption one first fills the micropores with an adsorbent under conditions where there is little sorbed on the walls of the mesopores. This is readily accomplished as the micropores fill often several orders of magnitude lower in pressure than do the mesopores. At a relative pressure of $P/Po = 10^{-4}$ less than 1% of the mesoporous surface will be covered while 100% of the micropores will be filled. Then one can drop the temperature to liquid nitrogen or argon temperatures where the adsorbent is frozen while the mesopores can be subject to isolated sorption analyses. We settled on the use of n-nonane adsorption at room temperature as the preadsorbing gas. The sample was then pumped on for a period of time and then cooled to cryogenic temperatures.

Pre-adsorption was performed procedure provided by Sayari et al³³. for the sequential adsorption experiments with little alteration. Argon or nitrogen adsorption isotherms were obtained from the AUTOSORB[®]-1C instrument and n-nonane vapor adsorption was performed using the VAS³². Samples of 30~90 mg was placed in a glass adsorption sample cell (1/4" outside diameter stem) with stopcock (1/4" outside diameter stem), where sample cell and stopcock were connected by Ultra-Torr[®] union (1/4" tube outside diameter) with appropriate size Viton[®] o-rings. All the samples were outgassed at 300°C for 12~20 hours prior to the adsorption experiments. N-nonane (99%) was obtained from Acros and used as received.

Results and Discussion

Complex micro-meso-materials included SBA-15 and PHTS were investigated using a combination of techniques. Figure 10 shows the argon adsorption isotherms of an SBA-15 material, before and after preadsorption of nonane. It can sem the the micropours component can be masked leaving the mesoporous structural component the same under analysis by argon adsorption. The mesopore distribution can then be determined using standard BJH analysis. Micropore distributions were then determined using a empirical model developed at UMass.²⁵

These new catalysts materials in the form of supported membranes are under investigation using the intact cell setup described above.

Significance

Many new microporous catalyst materials such as SBA-15 type meso-microporous systems are being developed and employed in the catalytic and separation industry. The accurate estimation of the pore size distributions of these complex materials is critical in order to fully utilize the structural properties of these systems. This approach allows us to measure the mesopore sizes independently.

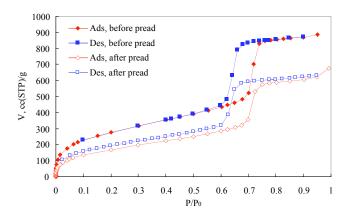


Figure 10 Argon adsorption at 87 K on SBA-15 sample before and after n-nonane pre-adsorption in normal scale.

8. STABILITY WITHIN THE HYSTERESIS LOOP: SCANNING BEHAVIOR

ABSTRACT of Published Manuscript

Cover article, Langmuir, 21 8214-8225 (2005)

Hysteresis and Scanning Behavior of Mesoporous Molecular Sieves

Geoffrey A. Tompsett, D. W. Griffin, L. Krogh and W. Curt. Conner,

Abstract

Sorption hysteresis is a widely studied phenomenon whose predicted behavior is well documented and researched. On the other hand, there is much less known about the region that lies between sorption isotherms, believed to be a meta-stable region. Scanning curves are a way of understanding the mechanism of hysteresis and a tool for hysteresis model validation. Scanning curves were produced for mesoporous materials; SBA-15 and MCM-41, for N₂ sorption at 77 K and Ar sorption at 87 K. A limited set of different scanning behaviors are identified. Like most hysteresis theories, it was found that a single model for scanning behavior can not be extended to all materials under the same or different experimental conditions. Two behaviors are consistent with recent theories and simulations; however, several are not. The implications as to the characterization of pore dimensions and structure are discussed.

Significance

The hysteresis loop in adsorption presents a complexity in measurement of mesoporous dimensions. Should one use adsorption or desorption to characterize the sizes? The nature of the hysteresis loop may also provide evidence for the nature of the porous network... is it tortuous? These dimensions and network characteristics will then dictate the transport rates and competition in multicomponent diffusion. As an example "single-file" diffusion is dictated in one-dimensional pores. Thus, it is necessary for us to understand the nature of sorption hysteresis to quantify the pore sizes and the network structure in order to understand and design pore structures for separations and catalysis.

9. STABILITY WITHIN THE SORPTION HYSTERESIS LOOP: PERTURBATIONS

The Effects of Mechanical and Thermal Perturbations on States Within the Hysteresis of Sorption Isotherms of Mesoporous Materials

Kristofor R. Payer, Karl D. Hammond, Geoffrey A. Tompsett, Lauren Krogh, Michael N. Pratt, and W. Curtis Conner, Jr.

Submitted to Journal of Porous Materials, June 2007

Abstract

In this study (*Journal of Porous Materials*, submitted July 16, 2007), we studied the effects of thermal and mechanical shocks to an adsorbed phase. Specifically, we tested the effects on physical states corresponding to points *inside* the hysteresis loops of mesoporous materials. Scans were run to points inside the loop, where sound waves and/or temperature changes were applied to the sample. We found that vibrations in the 0–500 kHz range have no substantial effect on the adsorbed phase. We also found that thermal shocks tend to return the system back to either the adsorption or desorption branch, depending on whether the adsorbent was raised or lowered in temperature: for increases in temperature, the state shifts onto the adsorption branch, while for decreases in temperature it moves to the desorption branch.

Motivation

Mesoporous materials are characterized by hysteresis in the adsorption/desorption isotherms for nitrogen and argon at cryogenic temperatures. The nature and origins of hysteresis are still being debated, but the region *inside* the hysteresis is even less well-understood. Indeed, certain models of hysteresis³⁴ predict that some states inside the loop are unstable and should not be accessible by scanning. It was suggested to us (M. L. Rosinberg, personal communication) that even minor perturbations such as sound waves should destabilize points inside the hysteresis, causing the adsorbed state to return to either the adsorption or the desorption branch of the equilibrium isotherm.

Results

We found, on the whole, that mechanical vibration has no effect whatsoever on the state (quantity adsorbed versus relative pressure) of the sample. No changes were observed at 8, 250, and 500 kHz, and various frequencies in between on time scales of 30 minutes or longer. This indicates that either the sound waves are not penetrating into the sample (unlikely, since the adsorbent is in contact with the glass, which is in turn in contact with the speaker) or that they simply are not powerful enough to disturb the fluid. Either way, the idea that any perturbation of any size will cause the interior of the loop to be unstable is flawed.

Thermal shocks, in contrast to vibrations, all had pronounced effects on the scanned states. Three types were performed: (I) 77 K to 87 K, equilibrating, then back to 77 K; (II) 87 K to 77 K and back; and (III) removing the 77 K bath for 30 seconds and then replacing it. Shocks of types I and II always changed the state to lie on the adsorption or desorption isotherms for Type I or II, respectively (see Figs.11–12). Type III shocks moved the isotherms *toward* the adsorption branch, but not always onto it.

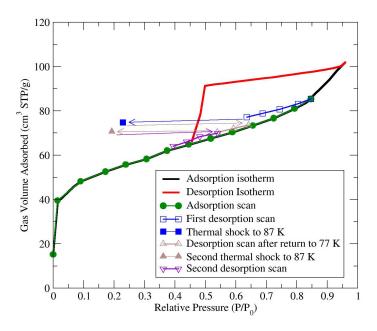


Figure 11. Adsorption isotherm and results of thermal shocks to a sample of mesoporous clay. The sample begins at 77 K, is heated to 87 K by replacing the bath, and is subsequently returned to 77 K.

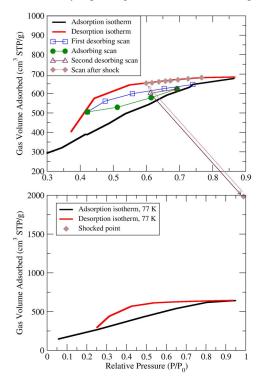


Figure 12. Shock to a state within the loop low temperature to high-temperature. The shock was administered after scanning down, up, and back down again in pressure.

10. VARIABLE ANGLE ATR TO MEASURE COMPETITIVE DIFFUSION

Presented at the AIChE Meeting 2004

To be submitted to Journal of Applied Spectroscopy

Variable Angle ATR FTIR System – Spectroscopy of Silicalite Membranes

G. Tompsett, R. Laurence and W. Curt. Conner

Abstract

Variable angle attenuated reflectance, VA-ATR, employing Fourier transform infrared spectroscopy enable one to probe varying distances from an interface. We have developed such a system in conjunction with Harrick Scientific, (Ossining, N.Y.). A sample, such as a membrane, is placed in contact with a hemispherical, infrared-transparent ATR crystal. This in situ system enables one to expose one side of the membrane sample to a sorbing/diffusing gaseous species. The system optics enables one to vary the angle with which the probing light is incident at the crystal/sample interface. Thus, one can probe at varying distances with the sample by varying the angle of optical incidence. Quantification of transport within a membrane requires one to measure concentration as a function of distance as well as time. Infrared spectroscopy is able to detect and distinguish between hydrocarbon (and other) species adsorbed within a membrane. Therefore, diffusion of hydrocarbons (even competitive sorption of mixtures) through a membrane can be monitored in situ using VA-ATR as a function of distance and time. Competitive hydrocarbon diffusion through a silicalite membrane is demonstrated as an example.

OTHER DOE SUPPORTED PUBLICATIONS IN PREPARATION

Presented at the AIChE Meeting 2004

For submission to the A.I.Ch.E Journal

Competitive Diffusion of Hydrocarbons in ZSM-5 by Frequency Response

Michael D. Turner, Laurent Capron, Robert L. Laurence, and Wm. Curtis Conner

Abstract

While the individual uptake of individual species can be measured, it is more difficult to characterize the individual diffusivities of multiple species in the same experiment. The problem is even more complex for diffusion of certain species or in zeolites with complex pore networks where individual species can diffuse at different rates through different pores, e.g., diffusion of benzene in the straight channels of ZSM-5 is an order of magnitude faster than diffusion in the zig-zag channels. Frequency response pioneered by Yashuda and Rees is able to measure the individual characteristic diffusion times. We employed frequency response to measure the changes in diffusivities for a single species as we add other diffusing species. Thus, changes in the diffusion of one species (e.g., p-xylene) in the straight and zig-zag channels are monitored by frequency response as benzene or hexane is introduced into the gas phase. We find that benzene and hexane influence the diffusion of xylenes in the straight or zig-zag pores of ZSM-5 in different ways. The diffusion of a single species is found to increase,

to decrease or, essentially, to remain constant with the addition of a second diffusing gas. These changes are documented by frequency response analyses and the reasons for these differences are discussed. Current theories do not predict these behaviors.

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Articles being submitted summer 2007

- "Synthesis of SBA-15: Factors that influence the Microporosity"
 Eunyoung You, G. Tompsett and W. C. Conner
- 10. "Empirical Model for microporosity from High Resolution Sorption Geoffrey A. Tompsett, Eunyoung You, Emma Trivella, Luaren Krogh, Elane Maglara and W.Curtis Conner
- 11. "Characterization of Mixed Micro- Meso-porous Catalysts for Membrane Applications Karl Hammond, Eunyoung You, Geoffrey A. Tompsett, Ryan Pavlica, Audrey McLain, Bhrugesh J. Patel, W. Curtis Conner and Scott M. Auerbach
- 12."High-Resolution Adsorption on Supported Borosilicate MFI Structures
 Karl D. Hammond, Mei Hong, Geoffrey A. Tompsett, Scott M. Auerbach, John L. Falconer, and W. Curtis
 Conner, Jr. Paper drafted for submission to J. Membrane Science

Articles in Preparation

- "Variable Angle ATR System Spectroscopy of Silicalite Membranes"
 G. Tompsett, R. Laurence and W. Curt. Conner
 For Submission to Journal of Applied Spectroscopy
- 14. "Competitive Diffusion of Hydrocarbons in ZSM-5 by Frequency Response" Michael D. Turner, Laurent Capron, Robert L. Laurence, and Wm. Curtis Conner For submission to the A.I.Ch.E Journal