# Physical Adsorption Analysis of Intact Supported Zeolite Membranes (Supplementary Information)

Karl D. Hammond[*] Geoffrey A. Tompsett[*] Scott M. Auerbach[*,†,‡]
W. Curtis Conner, Jr.[*,‡]

February 27, 2007

[*]Department of Chemical Engineering / 159 Goessmann Laboratory / University of Massachusetts Amherst / Amherst, MA 01003

[†]Department of Chemistry / 701 Lederle Graduate Research Tower / University of Massachusetts Amherst / Amherst, MA 01003

[‡]Authors to whom correspondence should be addressed.
Electronic addresses: auerbach@chem.umass.edu (SMA), wconner@ecs.umass.edu (WCC)

Table 1. Summary of literature on porous membrane adsorption.

| System | Preparation | Meso/macropore size (nm) | Hysteresis | BET area ($m^2/g$), Pore volume ($cm^3/g$) | Ref. |
|---|---|---|---|---|---|
| **Zeolitic monoliths** | | | | | |
| MFI ZSM-5 | Polystyrene spheres arrayed as templates for macropores, tetraethylorthosilicate, and tetrapropylammonium hydroxide | ~250 ± 30 | none | 421 (half micro-, half macropore) | 1 |
| Si-MFI | Amorphous silica converted to ZSM-5 packed nanocrystalline bodies by: | | | | 2 |
| | 1. Direct hydrothermal treatment (HT) | 3–8 | | 471, 0.142 | |
| | 2. Impregnation of charge-reversed amorphous silica grains | 2–20 (max. at 10) | | —, 0.104 | |
| | 3. Electrostatic adsorption of ZSM-5 seeds on the amorphous grains followed by HT | (no loop) | | 480, 0.136 | |
| Si-MFI | 1. Self-assembly of monodisperse polystyrene spheres and silicalite crystals by slow evaporation of solvent | 10–45 | H1 | 407, 0.49 (meso) | 3 |
| | 2. Self-assembly followed by hydrothermal treatment of composite | 2–8; small loop due to pinholes | | 428, 0.51 (macro) | |
| Si-MFI | Self-assembled membrane: dried nanocrystal film on mica substrate | 35 interparticle pore size, 0.58 pore volume | H1 | 480, 0.18 | 4 |
| Si-MFI | Self-standing membrane: dried nanocrystal film on a mica substrate compressed to 100 MPa between two mica substrates | 22 interparticle pore size, 0.34 pore vol | H1 | 446, 0.18 | 4 |
| Si-MFI | Self-standing membrane with microwave treatment: compressed silicalite powder 4 × 10 min using a domestic microwave | 2.5 interparticle pore size, 0.08 pore volume | H1 | 397, 0.17 | 4 |
| Si-MFI | Spongy silicalite membrane prep from electrostatic coating in an ultrasonic bath on a cellulose acetate substrate | 200–300 nm with 100–200 nm wall thickness of microtube using 80 nm silicalite colloid | H1 | 240 (132 ext.), 0.12 | 5 |
| Si-MFI | Silicalite membrane with further treatment with a mixed vapor amine and steam on a cellulose acetate substrate | | H1 | 260 (60 ext.), 0.11 | 5 |
| Si-MFI | HT growth in a clear solution for 12 h at 100°C | | H1 | 300 (187 ext.), 0.14 | 5 |
| Si-MFI | Tubular alumina support. HT of silica in hydroxide solution in presence of support. | Support layer pores between 0.005 and 11 μm. | None | | 6 |
| **Mesoporous silica films** | | | | | |
| Silica | Spin-coated SAW substrate | 2–10 ($N_2$ and $CO_2$) | IV, H2 | 20.2 $m^2/m^2$, 2.95 $m^3/m^2$ | 7 |
| Silica | Mesoporous thin film | Kr at 77 K | H1 | 0.21 $nm^2$ | 8 |
| Silica | Porous film on silicon wafer cut into pieces | Kr at 77 K, < 1 μm pores | | | 9 |
| Silica | Mesoporous thin films from triblock copolymer templates | 3.4–9 (depends on template) | IV, H1 | 840, 1.13 | 10 |
| Silica | Mesoporous silica thin films | Nitrogen at 77 K | IV, H1 | | 11 |
| | SDA P123 | 8.4 | | 660, 1.1 | |

*Continued on next page....*

| System | Preparation | Meso/macropore size (nm) | Hysteresis | BET area ($m^2/g$), Pore volume ($cm^3/g$) | Ref. |
|---|---|---|---|---|---|
| | SDA P103 | 7.7 | | 720, 1.12 | |
| | SDA P65 | 4.8 | | 930, 0.99 | |
| Silica | Dip-coated film on sodalime glass. Pluronic F127 template | Kr at 77 K | H1 | 42–91 $cm^2/cm^2$, $\sim 10^{-5}$ $cm^3/cm^2$ | 12 |
| Titania | Pluronic F127 template | | H2 | 113–140 $cm^2/cm^2$, 1.3–1.6×$10^{-5}$ $cm^3/cm^2$ | |
| Silica | Mesoporous silica film on silicon substrate, PEG, MW = 400 used as template. Argon plasma treatment of sol-gel precursor. | 2.2 | Poor isotherm shape (probably IV) | ~ 820 | 13 |

Table 2. Pore size distribution analyses. *Models:* Saito-Foley (SF),[16] Non-Linear Density Functional Theory (NLDFT).[17]

| | | | Peaks (Å) | | |
|---|---|---|---|---|---|
| **Adsorbent** | **Adsorbate** | **Model** | **Primary** | **Secondary** | **Tail** |
| planar *c*-oriented membranes | $N_2$/77 K | NLDFT | 8.9 (s)[a] | 31 | broad |
| planar *c*-oriented membranes | Ar/77 K | SF | 6.2 (s) | 16.3 (vb) | very broad |
| planar *c*-oriented membranes | Ar/77 K | NLDFT | 6.0 (s) | N/A | none |
| planar *h*0*h*-oriented membranes | Ar/77 K | NLDFT | 8.8 (s) | 31 | broad |
| planar *h*0*h*-oriented membranes | $N_2$/77 K | SF | 7.2, 9.7 | 11.8, 14.2, 18.3 (b), 23.3 (vb) | noisy |
| planar *h*0*h*-oriented membranes | Ar/77 K | SF | 7.1 (s) | 4.8 (s) | very broad |
| planar *h*0*h*-oriented membranes | Ar/77 K | NLDFT | 7.1 (s) | 18.1, 22.5 (b) | noisy |
| silicalite powder | $N_2$/77 K | SF | 5.3 (s), 10.2 (s) | 7.1, 8.6, 12.2 (b), 16.4 (vb) | none |
| silicalite powder | $N_2$/77 K | NLDFT | 8.8 (s) | 29.4 (b) | none |
| silicalite powder | Ar/77 K | NLDFT | 5.6 (s) | N/A | none |
| silicalite powder | Ar/77 K | SF | 13.2 | 6.6, 9.1, 17 (b), 20.4 (vb), 26.4 (vb) | noisy |
| tubular primary growth membrane | Ar/77 K | NLDFT | 5.6 (s) | N/A | none |
| tubular primary growth membrane | $N_2$/77 K | NLDFT | 8.8 | N/A | none |

[a]Symbol legend: (b) = broad peak; (vb) = very broad peak; (s) = sharp peak; nothing = moderately sharp peak.

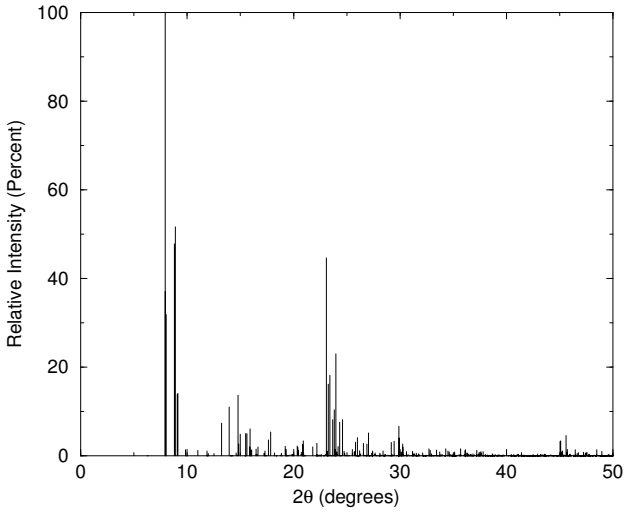


Figure 1. X-ray diffraction (XRD) pattern of silicalite powder. The crystals are randomly oriented, so each face has a significant contribution to the scattering pattern. Taken from Reference 14.

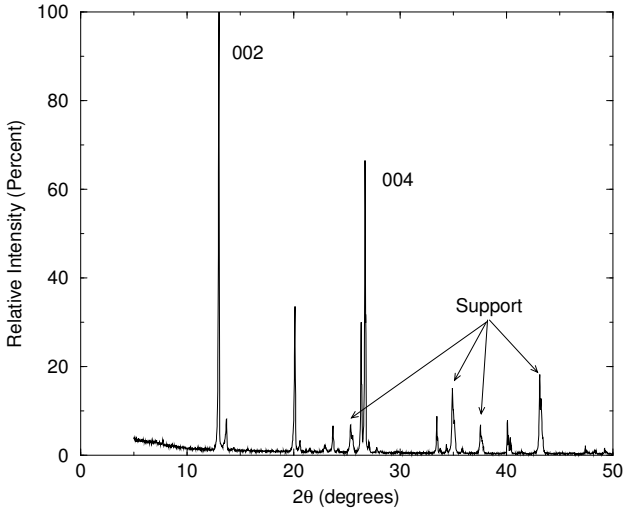


Figure 2. XRD pattern of a silicalite membrane oriented with the *c*-axis (00$\ell$ face) of the crystals pointing up.

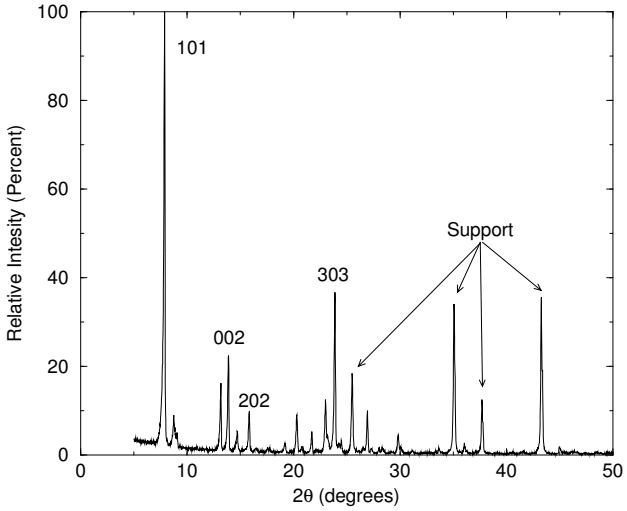


Figure 3. XRD pattern of a silicalite membrane oriented with the *h*0*h* faces up. For an excellent comparison of various MFI membrane XRD patterns, please see Lai *et al.*[15]

# References


1. Holland, B. T.; Abrams, L.; Stein, A. *J. Am. Chem. Soc.* **1999**, *121*, 4308–4309.
2. Mintova, S.; Hölzl, M.; Valtchev, V.; Mihailova, B.; Bouizi, Y.; Bein, T. *Chem. Mater.* **2004**, *16*, 5452–5459.
3. Valtchev, V. *J. Mater. Chem.* **2002**, *12*, 1914–1918.
4. Huang, L.; Wang, Z.; Wang, H.; Sun, J.; Li, Q.; Zhao, D.; Yan, Y. *Microporous Mesoporous Mater.* **2001**, *48*, 73–78.
5. Wang, Y.; Tang, Y.; Dong, A.; Wang, X.; Ren, N.; Shan, W.; Gao, Z. *Adv. Mater.* **2002**, *14*, 994–997.
6. Uzio, D.; Peureux, J.; Giroir-Fendler, A.; Dalmon, J. A.; Ramsay, J. D. F. In *Characterization of Porous Solids III*, *Stud. Surf. Sci. Catal.*, Vol. 87, 1994; pp 411–418.
7. Hietala, S. L.; Smith, D. M. *Langmuir* **1993**, *9*, 249–251.
8. Chao, K.-J.; Liu, P.-H.; Huang, K.-Y. *Comptes Rendus Chimie* **2005**, *8*, 727–739.
9. Yanazawa, H.; Hironori, M.; Itoh, H.; Nakai, K.; Suzuki, I. *J. Vac. Sci. Tech. B* **2002**, *20*, 1883–1835.
10. Zhao, D.; Yang, P.; Melosh, N.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1998**, *10*, 1380–1385.
11. Zhao, D.; Yang, P.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **1999**, *11*, 1174–1178.
12. Bartels, O.; Zukal, A. *J. Mater. Sci.* **2005**, *40*, 2603–2605.
13. Zhang, J.; Palaniappan, A.; Su, X. D.; Tay, F. E. H. *App. Surf. Sci.* **2005**, *245*, 304–309.
14. International Zeolite Association, *Database of Zeolite Structures*, http://www.iza-structure.org/databases, Available as of October 8, 2006.
15. Lai, Z.; Bonilla, G.; Diaz, I.; Nery, J. G.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M.; Vlachos, D. G. *Science* **2003**, *300*, 456–460.
16. Saito, A.; Foley, H. C. *AIChE J.* **1991**, *37*, 429–436.
17. Quantachrome Instruments, *AUTOSORB-1 AS1Win Version 1.50 Operating Manual*; Quantachrome Instruments: Boynton Beach, FL, 2004.