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Hierarchically porous binder-free silicalite-1 discs: a novel support for all-zeolite membranes

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S1- Rietveld analysis and cell parameters of silicalite-1 and alumina

The powder patterns were refined using the Rietveld method, with FullProf 2000 [1]. A pseudo-Voigt peak shape function was assumed, and the refined parameters consisted of the scale factors, zero point error, five background parameters with three Debye-like coefficients for the zeolites, unit cell parameters, peak profile parameters (U, V, W, X, Y, GauSiz), two asymmetry parameters and the overall thermal parameter. After the initial refinement the calculated silicon lines were compared with expected lines considering the calculated value of the unit cell at that temperature. A shift was usually observed, likely due to the shift in sample position resulting from the physical expansion of the sample holder and samples itself, and 2θ-axes of all patterns were corrected with a second-degree polynomial function that would shift the silicon lines to the calculated positions. A new refinement was then made with exactly the same refined parameters as before.

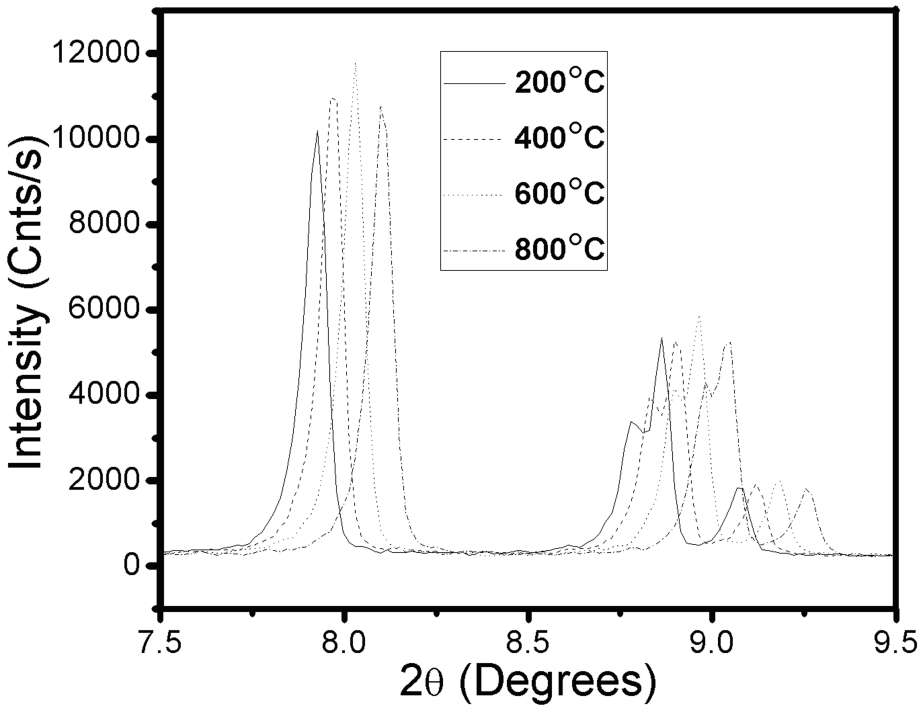


Figure S1: Shift of 2θ (Degrees) of silicalite-1 peaks with increase in temperature.

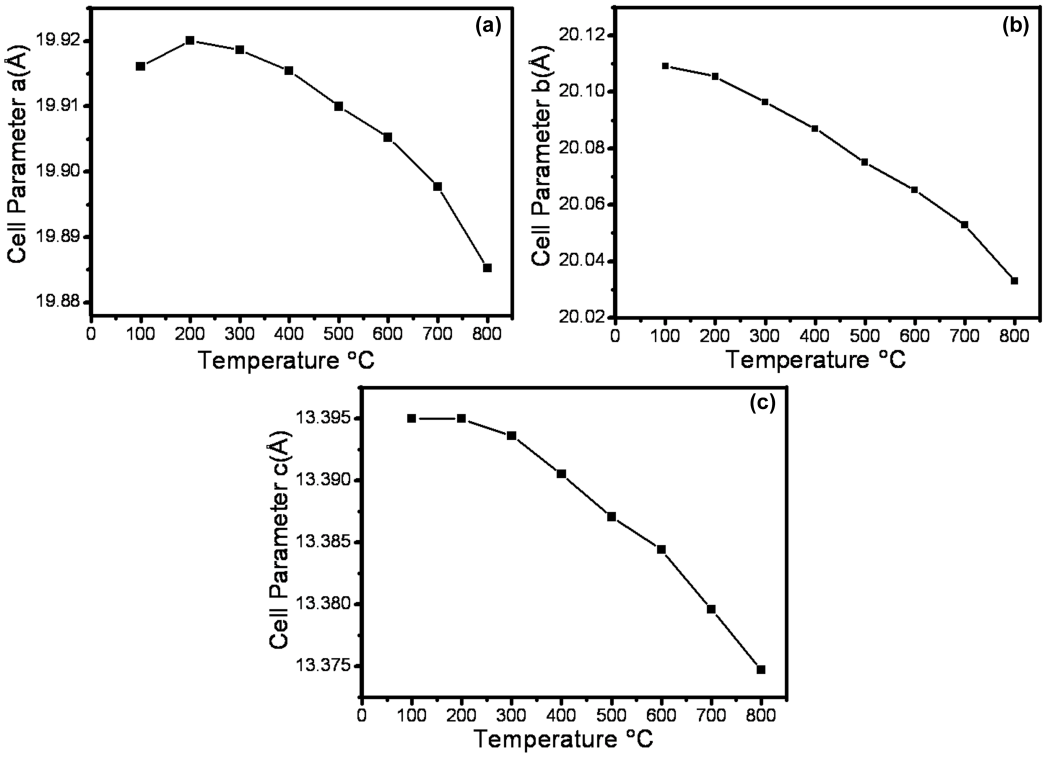


Figure S2: Change in Unit cell parameters (a,b,c) of as-received MFI silicalite-1 powder.

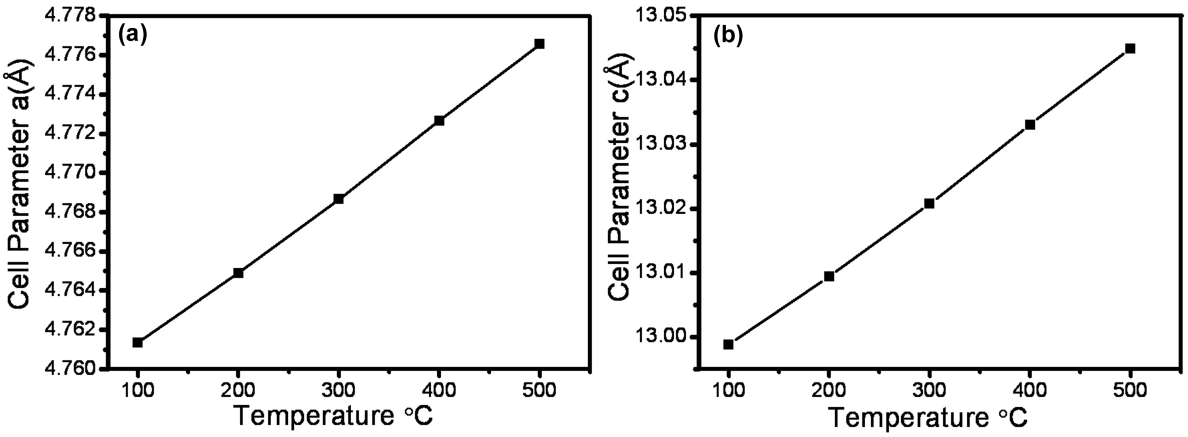


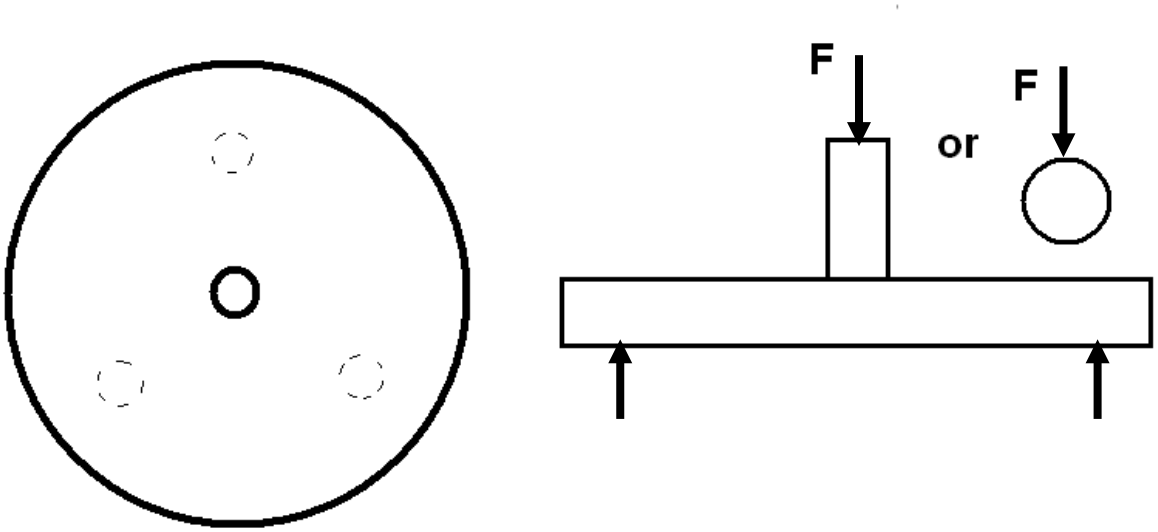
Figure S3: Change in Unit cell parameters (a,c) of alumina powder.

S2- Biaxial flexural strength test

Biaxial flexural strength test with a piston on 3 balls geometry was conducted (Scheme 1). In the test one surface of the PCP consolidated disc was supported on three balls equidistant from its centre located in a ring with diameter 12 mm. The opposite surface of the disc was loaded with a piston with flat end of diameter 1.5 mm at the centre of the disc normal to the orientation of the plane. The loading rate was 0.5 mm/min. The fracture force was measured and the maximum principal tensile stress (σ_{max}) on the disc side opposite the piston loading was used to calculate the strength. Biaxial strength was calculated using the following equation [2]

$$\sigma_r = \sigma_f = \frac{3(1+\nu)P}{4\pi t^2}\left[1 + 2\ln\frac{a}{b} + \frac{(1-\nu)}{(1+\nu)}\left(1 - \frac{b^2}{2a^2}\right)\frac{a^2}{R^2}\right]$$

where a is radius of the support ring, b is the radius of piston, R is the radius of the disc, P is applied load at failure, t is the thickness of the disc and ν is the Poisson's ratio of the tested material. The Poisson's ratio 0.2 for silicalite-1 [3] was used to calculate the biaxial strength of the PCP consolidated silicalite-1 discs.



Scheme-1: Piston on 3 balls biaxial flexural strength test.

S3- Silicalite-1 powder and XRD of PCP-consolidated silialite-1 discs

As received silicalite-1 powder has an average particle size of 5µm (Figure 1a). The silicalite-1 particles show well defined faceted morphology and exhibit MFI crystal structure (Figure 1b). N_2 adsorption desorption isotherm (Figure 1c) shows that the powder is microporous with a BET surface area 390 m^2/g and pore volume 0.23 cm^3/g (Table I).

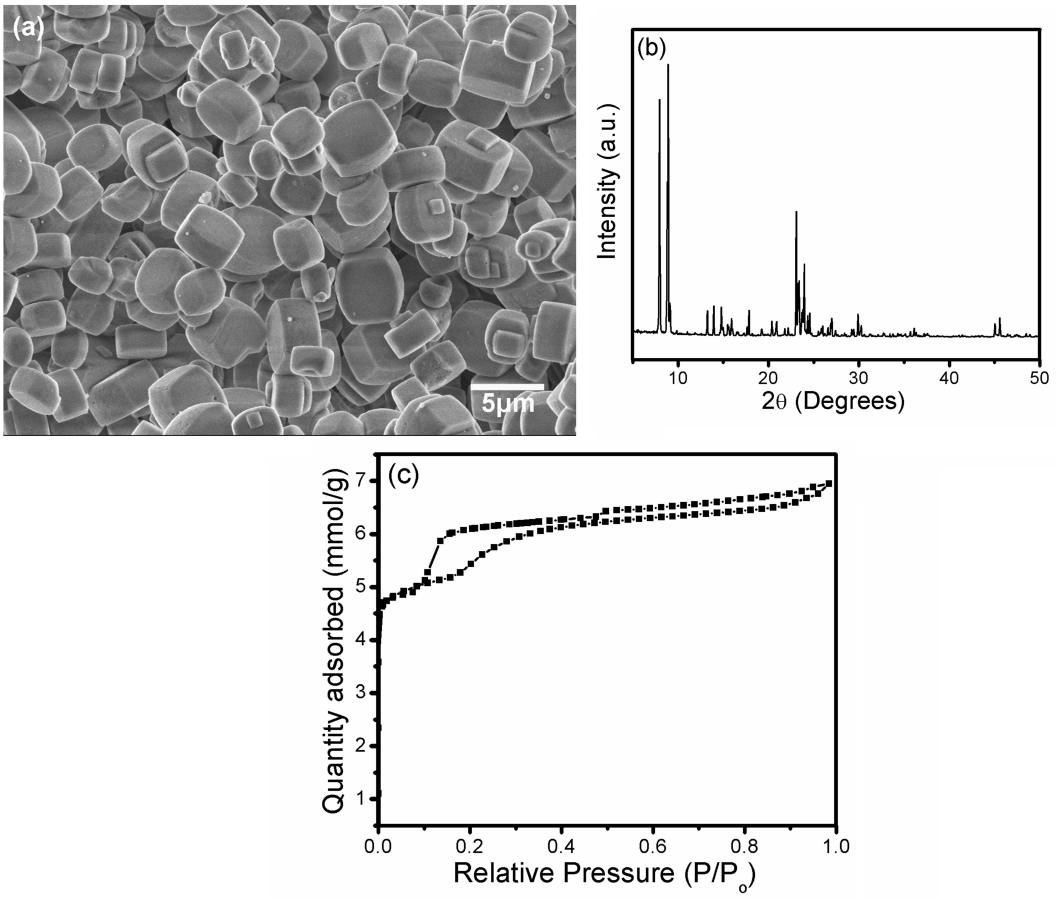


Figure S4: As-received silicalite-1 powder a) SEM micrograph; b) XRD pattern; c) N_2 adsorption-desorption isotherm.

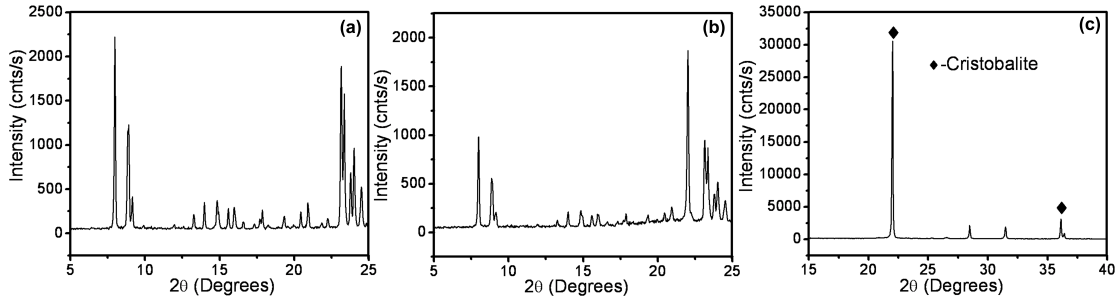


Figure S5: XRD of silicalite-1discs PCP-consolidated at a) 1300 °C; b) 1350 °C; c) 1400 °C.

S4- Gas permeation of silicalite-1 discs

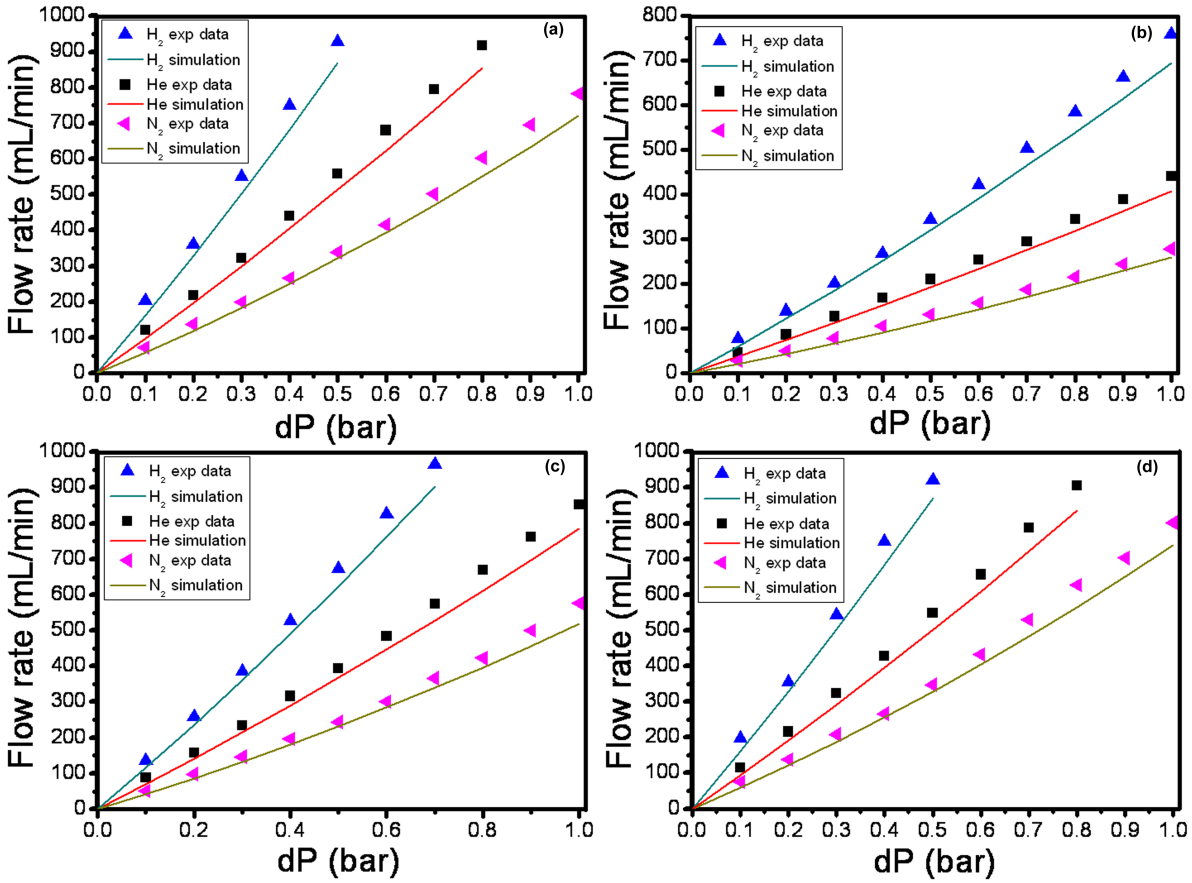


Figure S6: Single gas permeation of (a) specimen 2 (b) specimen 3 (c) specimen 4 (d)

Specimen 5.

Table S1: Transport parameters obtained from the model

No.	Specimen	K_0 (x 10^{-10} m)	B_0 (x 10^{-17} m^2)	δ_{sub} (mm)	K_{0c} (x 10^{-5})	B_{0c} (x 10^{-12} m)
1	Silicalite-1 Support	614.84 +/- 15.04	806.47 +/- 24.76	2.9	2.78	2.12
2	Silicalite-1 Support	594.35 +/- 17.28	768.13 +/- 26.35	2.0	3.84	2.97
3	Silicalite-1 Support	371.77 +/- 11.70	428.84 +/- 18.04	4.1	1.05	0.91
4	Silicalite-1 Support	564.44 +/- 17.18	823.92 +/- 26.18	2.0	4.12	2.82
5	Silicalite-1 Support	721.3 +/- 21.24	1062.4 +/- 32.38	2.6	4.09	2.77
6	Alumina Support[4]	8.16*	9.90*	0.03 (layer 1) 3.0 (layer 2)	3.30	2.72

*) Parameters of layer 1

**) $K_{0c} = K_0 / \delta_{sub}$; $B_{0c} = B_0 / \delta_{sub}$

S5- Coefficient of thermal expansion of alumina and silicalite-1 discs

Table S2: Coefficient of thermal expansion (CTE) of alumina and silicalite-1 discs; determined by dilaometery.

No.	*Temperature Range*	*CTE of Alumina Disc* (X 10^{-6}/°C)	*CTE of Silicalite-1 Disc* (X 10^{-6}/°C)
1	RT-200	5.94	3.35
2	200-400	8.35	-0.35
3	400-600	9.85	-0.76
4	600-800	10.10	-0.78
5	200-800	9.48	-0.64

References

1- J. Rodrı´guez-Carvajal, *Commission on Powder Diffraction (IUCr) Newsletter,* 2001, 26, 12.
2- ASTM F394-78(1996) Test Method for Biaxial Flexure Strength (Modulus of Rupture) of Ceramic Substrates. DOI: 10.1520/F0394-78R96
3- C. Sanchez-Valle, Z. A. D. Lethbridge, S. V. Sinogeikin, J. J. Williams, R. I. Walton, K. E. Evans, J. D. Bass, *Journal of Chemical Physics,* 2008, 128, 184503.
4- F. Jareman, J. Hedlund, *Microporous Mesoporous Materials,* 2005, 82, 201.