Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Tailoring pore structure to improve permselectivity of organosilica membranes by tuning calcination parameters

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Sol synthesis:

First, 5 mL BTESE and 5 mL ethanol anhydrous were well mixed in a glove-box under a nitrogen atmosphere. Meanwhile, 5.24 mL HNO_3 solution (0.1 M) was mixed with 10 mL ethanol in a 50 mL beaker and the mixture was then dropwise added into the as-prepared BTESE/ethanol mixture under vigorous stirring (120 rpm) in an ice bath. Along with continuous stirring, the final mixture was refluxed in a water bath at 60 ℃ for 90 min. Prior to further use, the prepared sol solutions were stored at -16 ℃.

Table S1 Pore structure data of BTESE-derived organosilica powders calcined under different conditions.

Sample	Calcination parameter			S_{BET}	V_{total}	V_{micro}	V_{micro}/V_{total}
	T_c (℃)	r (°C/min)	t (min)	(m^2/g)	(cm^3/g)	(cm^3/g)	(%)
P1	300	0.5	180	362	0.185	0.151	81.6
P2	400	0.5	180	338	0.173	0.140	80.9
P3	450	0.5	180	296	0.156	0.115	73.7
P4	500	0.5	180	252	0.134	0.095	70.9
P5	550	0.5	180	200	0.109	0.073	67.0
P6	600	0.5	180	122	0.060	0.048	80.0
P7	600	2	180	153	0.078	0.048	61.5
P8	600	10	180	178	0.097	0.050	51.5
P9	600	10	5	222	0.114	0.073	75.3

Note: T_c, r, t, S_{BET}, V_{total}, V_{micro} and V_{micro}/V_{total} represent calcination temperature, heating rate, dwelling time, BET specific surface area, total pore volume, micropore volume and microporosity, respectively.

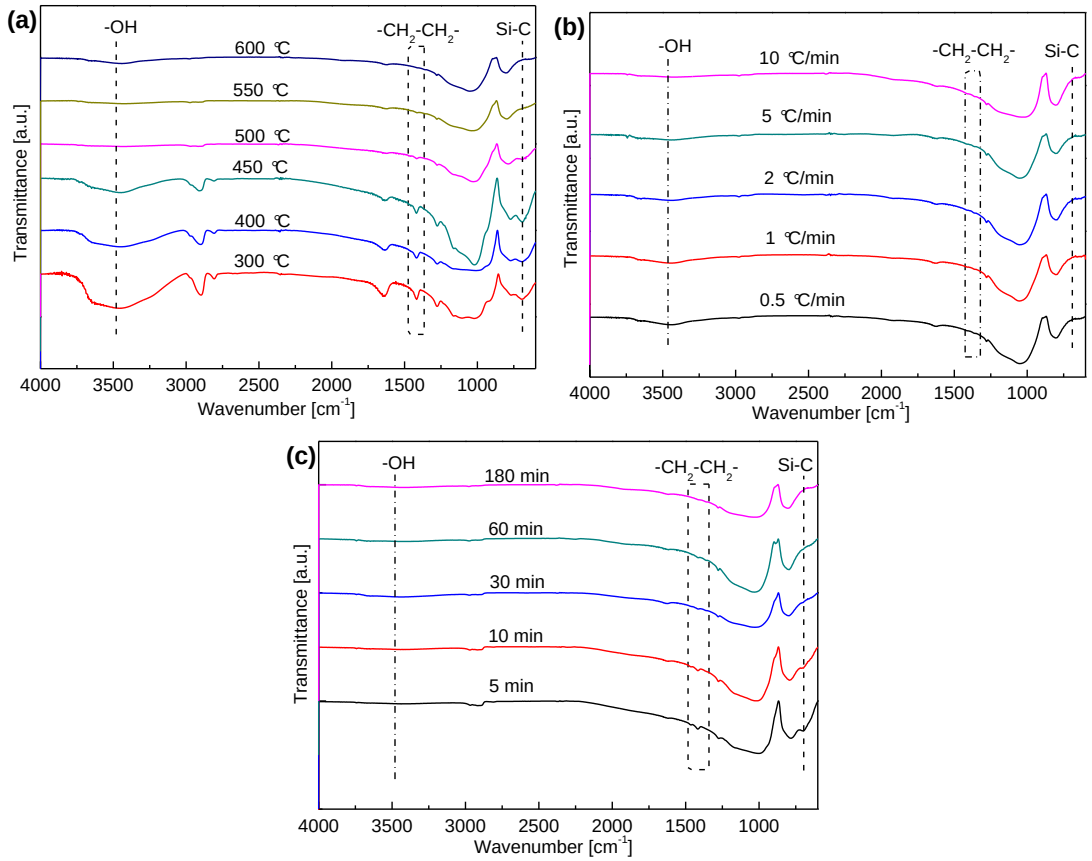

Fig. S1 FTIR spectra of organosilica powders calcined under different calcination conditions. (a) r=0.5 ℃/min, t=180 min; (b) T_c=600 ℃, t=180 min; (c) T_c=600 ℃, r=10 ℃/min.

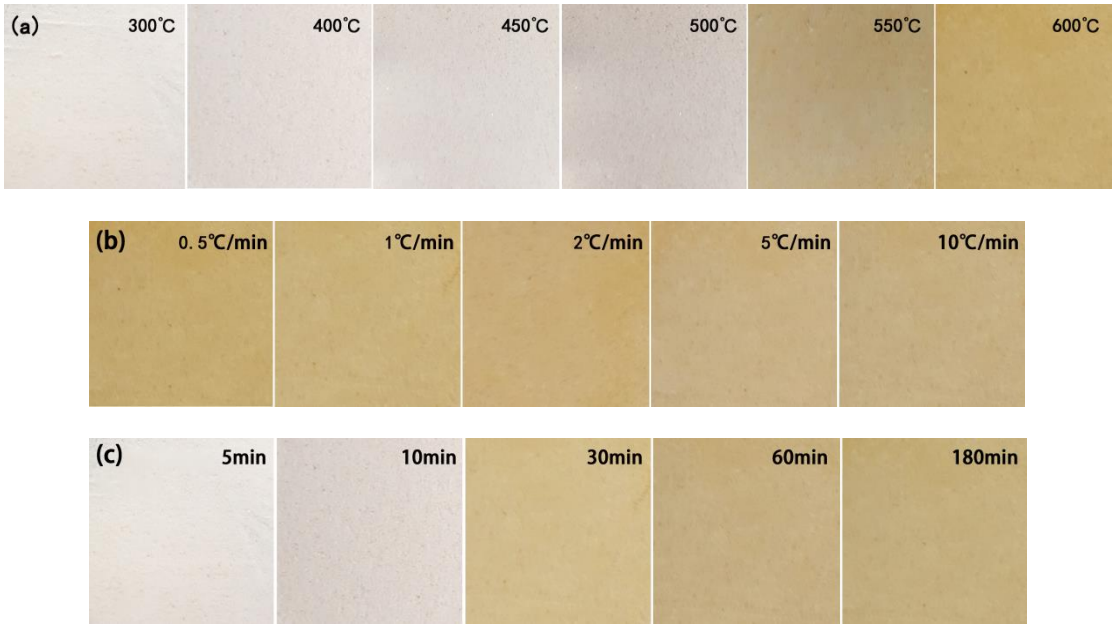

Fig. S2 Optical photos of organosilica powders calcined under different conditions. (a) r=0.5 ℃/min, t=180 min and T_c=300 ℃, 400 ℃, 450 ℃, 500 ℃, 550 ℃, 600 ℃; (b) T_c=600 ℃, t=180 min and r=0.5 ℃/min, 1 ℃/min, 2 ℃/min, 5 ℃/min, 10 ℃/min; (c)

T_c=600 ℃, r=10 ℃/min and t=5 min, 10 min, 30 min, 60 min, 180 min. The powders were uniformly spread on a petri dish, and the pictures of these powders were subsequently captured.

Table S2 XPS deconvolution details of Si2p peaks of organosilica powders

Sample	[a] BE (eV)	[b] FWHM (eV)	Assignment	Percentage (%)
P2	103.7	1.7	$SiO_{4/2}$	41.1
	102.9	1.2	$XSiO_{3/2}$	49.1
	102	1	$X_2SiO_{2/2}$	9.8
P6	103.7	1.7	$SiO_{4/2}$	100
P8	103.7	1.7	$SiO_{4/2}$	82.3
	102	1.2	$XSiO_{3/2}$	17.7
P9	103.7	1.7	$SiO_{4/2}$	38.9
	102.9	1.2	$XSiO_{3/2}$	49.7
	102	1	$X_2SiO_{2/2}$	11.4

[a] BE=Binding energy.
[b] FWHM=Full width at half maximum.

NKP method:

The normalized Knudsen-based permeance (NKP) method was proposed to estimate the pore size of microporous membrane. [1] In the calculation, f_{NKP} is the ratio of the experimental data divided by the ideal Knudsen permeance based on the permeance of standard gas (He in this work). It was defined as follows:

$$f_{NKP} = \frac{P_i}{P_{He}}\sqrt{\frac{M_i}{M_{He}}}$$

where P_i is the permeance of gas i, P_{He} is the He permeance, M_i is the molecular weight of gas i, and M_{He} is the molecular weight of He.

The pore size of membrane was calculated by the following formula:

$$f_{NKP}^{1/3} = \frac{d_p - d_{k,i}}{d_p - d_{k,He}}$$

Where d_p is the estimated pore size of membrane, $d_{k,i}$ is the kinetic diameter of gas i, and $d_{k,He}$ is the kinetic diameter of He.

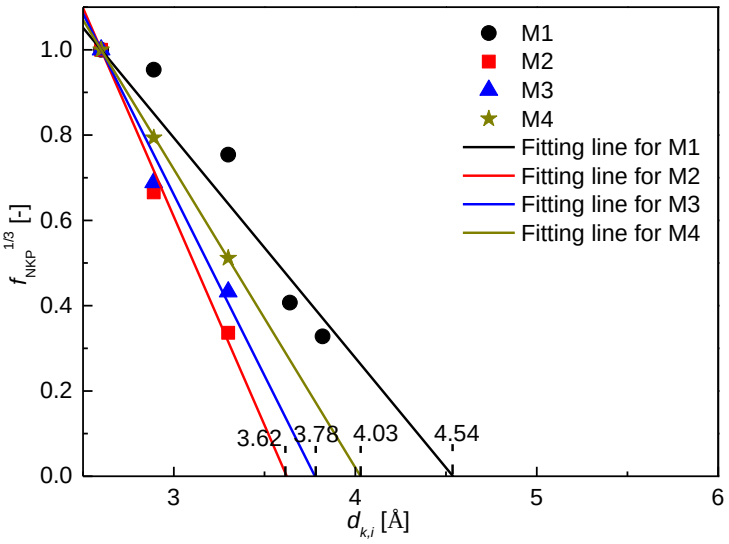

Fig. S3 Normalized Knudsen-based permeance (f_{NKP}) for M1, M2, M3 and M4 membranes as a function of gas kinetic diameter ($d_{k,i}$).

Reference

1. H. Nagasawa, T. Niimi, M. Kanezashi, T. Yoshioka and T. Tsuru, *AlChE J.*, 2014, **60**, 4199-4210.