Electronic Supplementary Information (ESI)

Nanoscale MOF/Organosilica Membrane on Tubular Ceramic Substrate for Highly Selective Gas Separation

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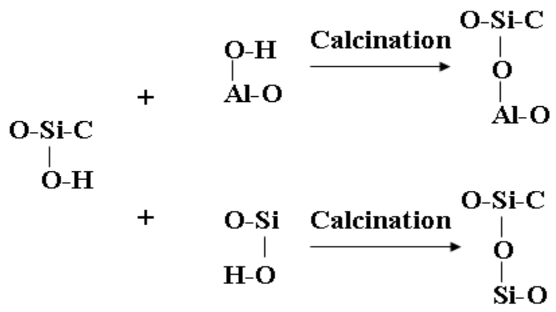


Figure S1 Schematic diagram of strong interactions between organosilica (O-Si-C) and ceramic (Al-O) or organosilica (O-Si-C) and silica (O-Si) (In order to obtain a thin and compact MOF/organosilica membrane, the substrate with large pore size and rough surface was modified by industrial colloidal silica before the fabrication of membranes. The strong interaction between organosilica, silica and ceramic substrate can be ensured during the calcination process because their -OH groups can be partly removed (Figure S1) at the high temperature).

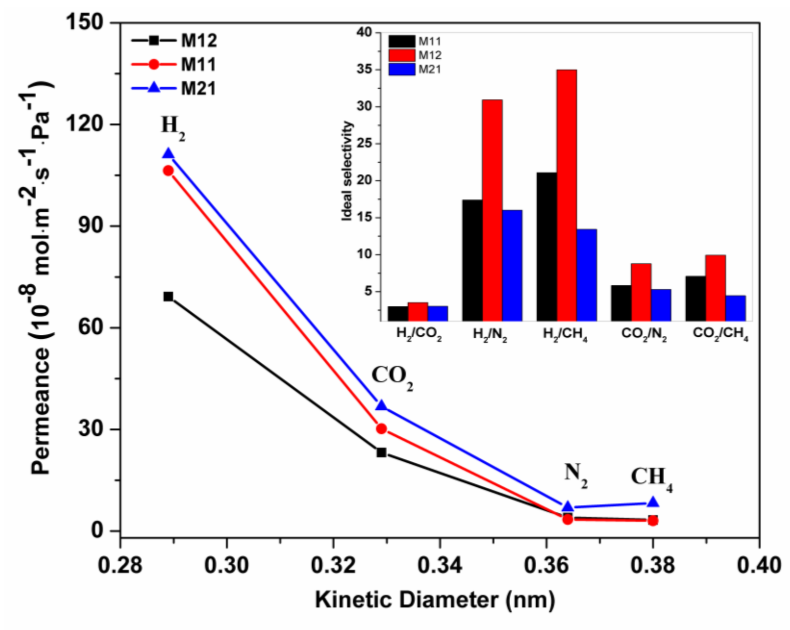
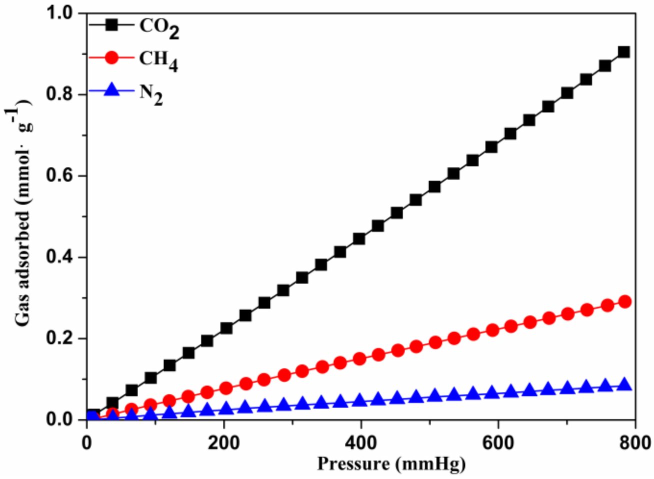
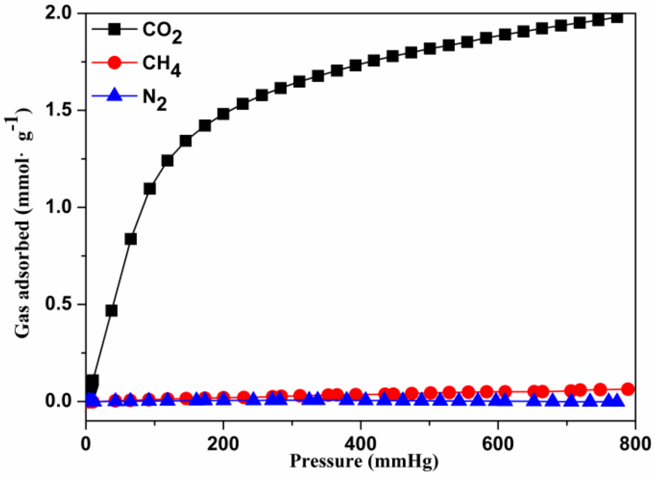


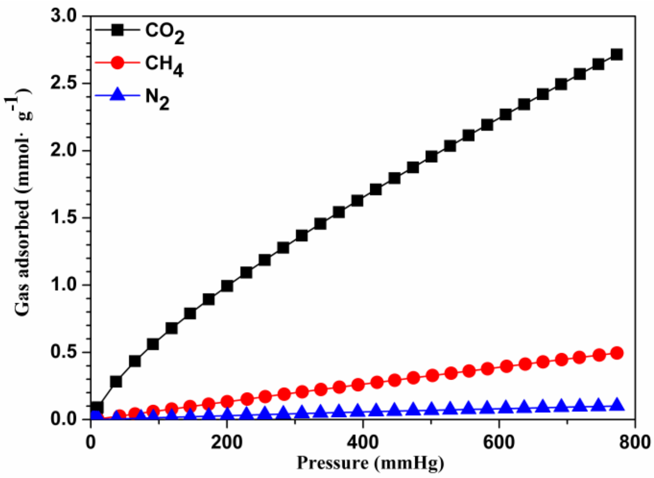
Figure S2 Single gas permeance of H_2, N_2, CO_2 and CH_4 through the as-prepared ZIF-8/organosilica membranes (The inset displays the ideal separation factors for the corresponding gas pair. Here three ZIF-8/organosilica solutions with different weight ratios (Wr = 1:2, 1:1, 2:1) of ZIF-8 to organosilica were prepared to fabricate ZIF-8/organosilica nanocomposite membranes. The resulting membranes were denoted as M1/2 (Wr = 1:2), M1:1 (Wr = 1:1) and M2/1 (Wr = 2:1), respectively. Permeance was measured at ΔP = 0.2 MPa and T = 298 K).



ZIF-8 Powder



MIL-53-NH2 Powder



CAU-1-NH2 Powder

Figure S3 N_2, CH_4 and CO_2 adsorption properties of the as-prepared of ZIF-8, MIL-53-NH_2 and CAU-1-NH_2 powders.

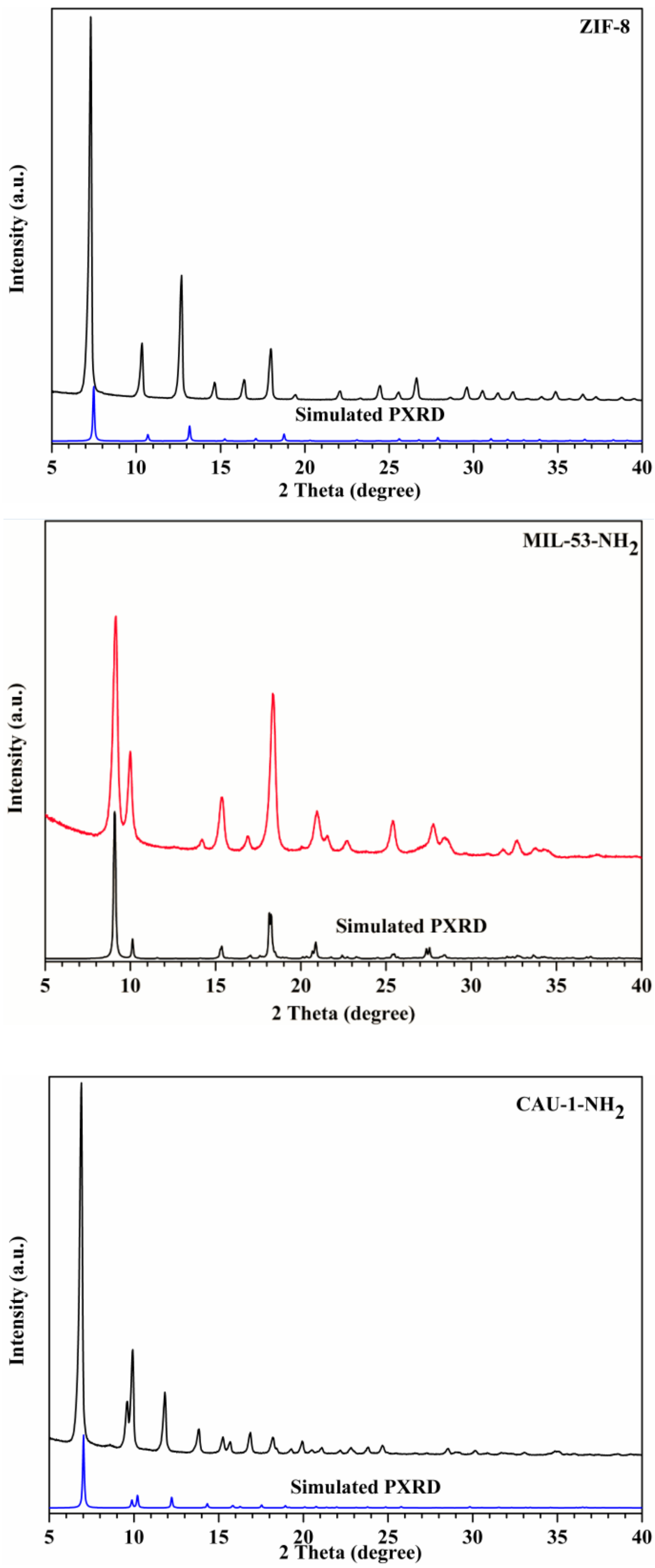


Figure S4 Powder XRD and simulated patterns of the as-prepared ZIF-8, MIL-53-NH_2 and CAU-1-NH_2.

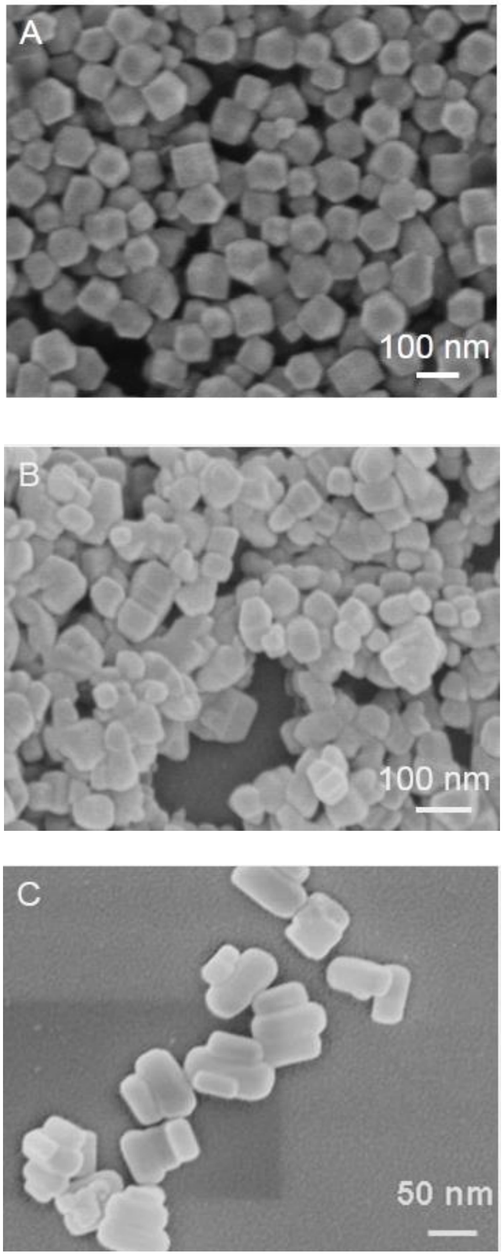


Figure S5 SEM images of the as-prepared ZIF-8 (A), MIL-53-NH_2 (B) and CAU-1-NH_2 (C) Powders.

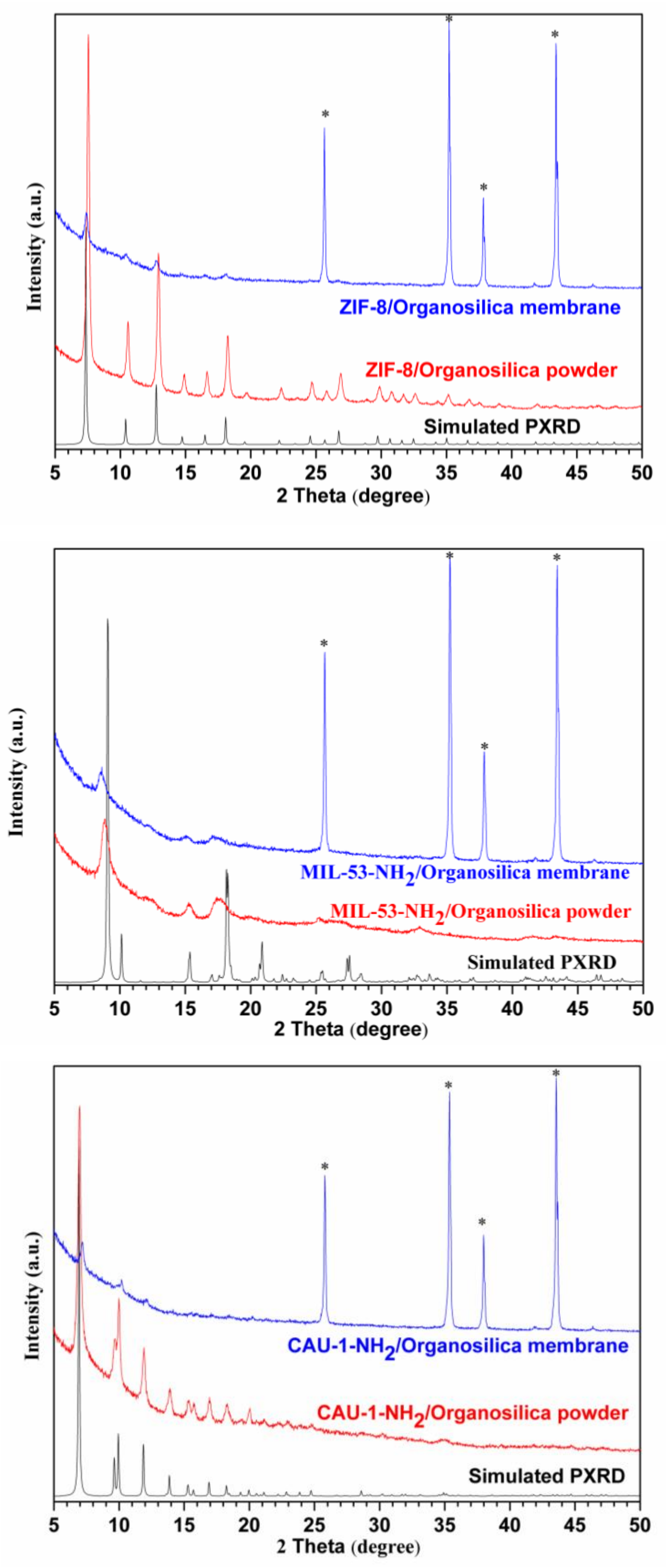


Figure S6 XRD patterns of the as-prepared MOF/organosilica membranes and powders. (*): Peak from alumina substrate.

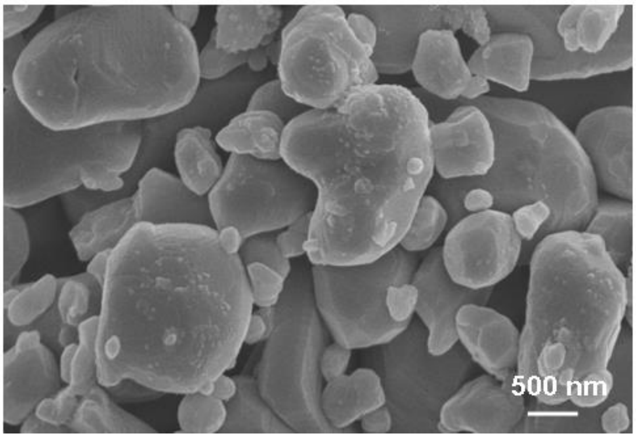


Figure S7 SEM surface image of the ceramic hollow fiber substrate.

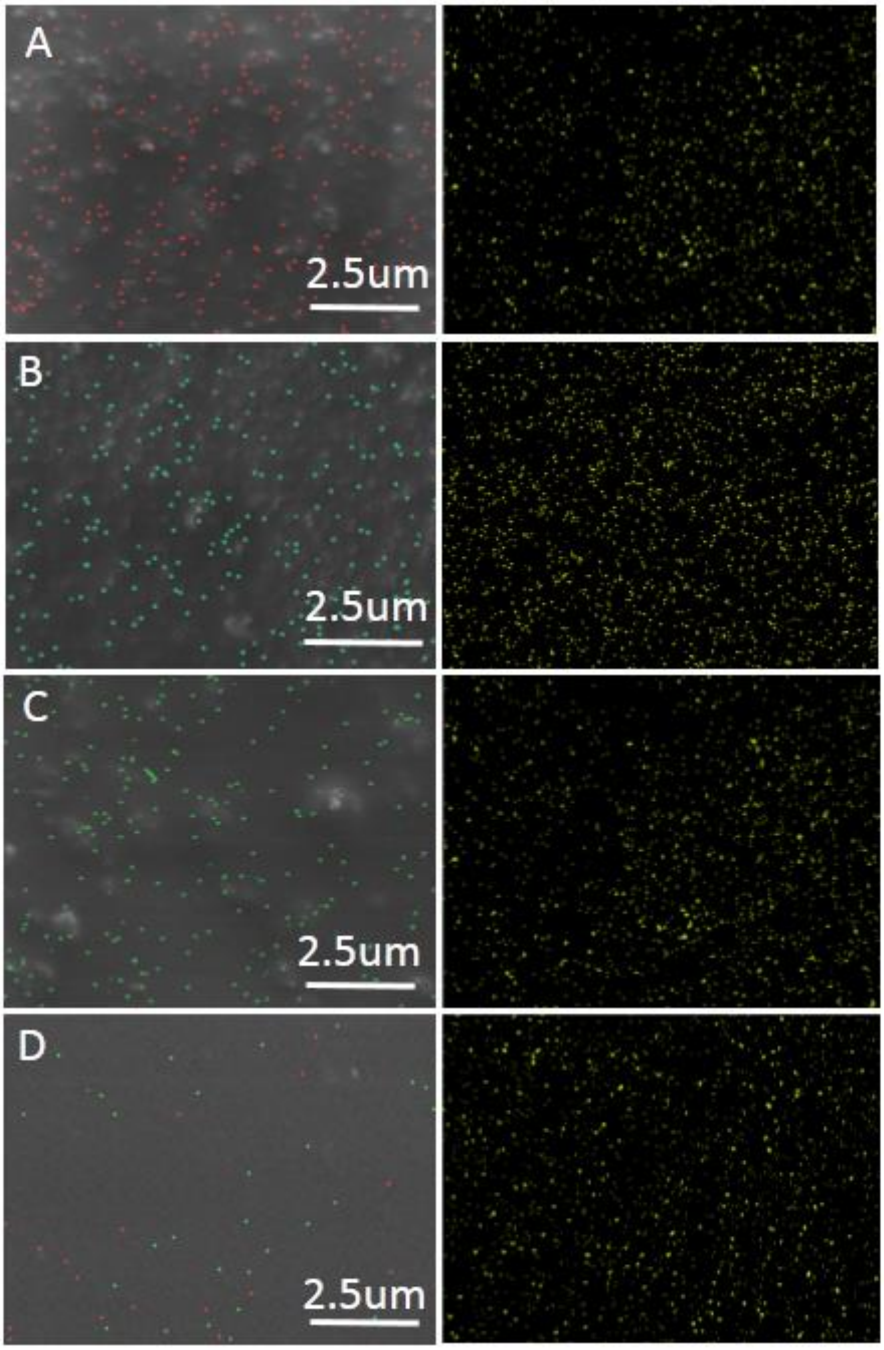


Figure S8 EDS mapping of the surface of ZIF-8/organosilica (A), MIL-53-NH_2/ organosilica (B), CAU-1-NH2/organosilica (C) and pure organosilica membranes (D). Color code: red = Zn; green = N; yellow = C (The signals of Zn (red) and N (green) from MOFs can be clearly observed from the surface mapping by energy-dispersive X-ray spectroscopy (EDS). In onctrast, the pure silica membrane has some discrete signals, which might be ascribed to the noise. It can be seen that the dispersedion of MOF signals is generally consistent with that of loaded MOFs, indicating that MOF nanocrystals were well incorporated and evenly dispersed into organosilica networks. It should be noted that some deviation of the EDS signals can be observed due to the influence of noise and scene shift).

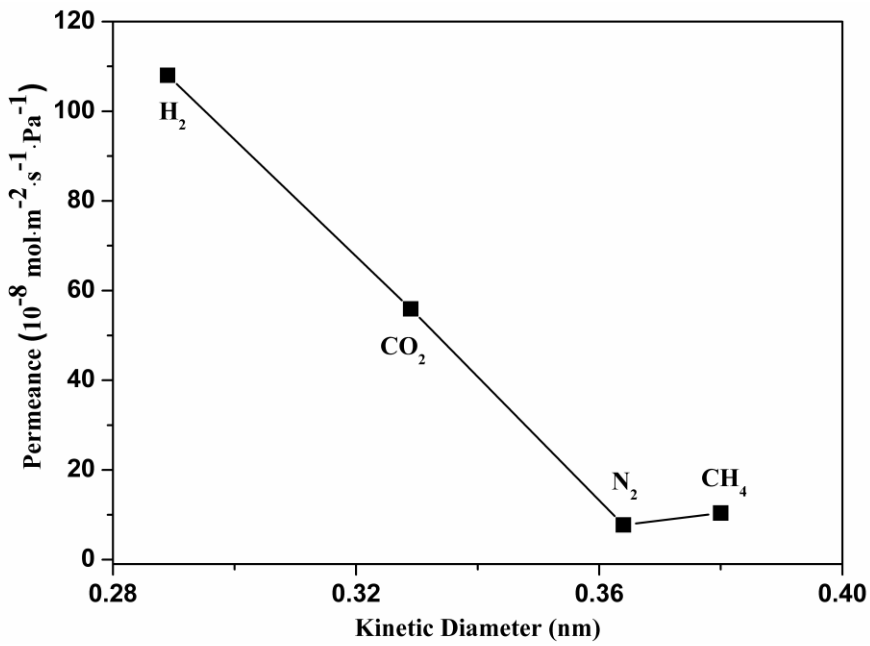


Figure S9 Gas permeation properties of the BTESE-derived organosilica membrane at 298 K.

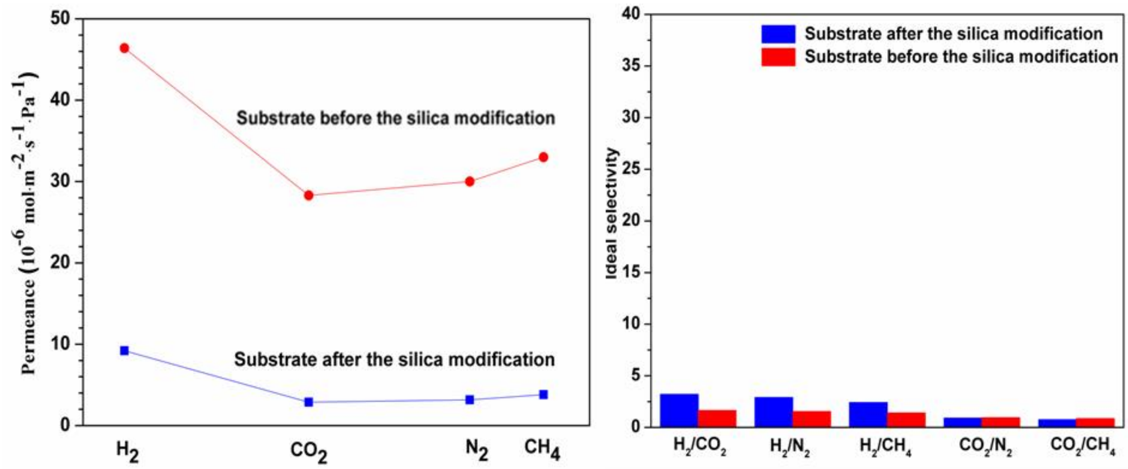


Figure S10 The gas permeation properties of the tubular cceramic substrate and colloidal silica modified substrate at 298 K.

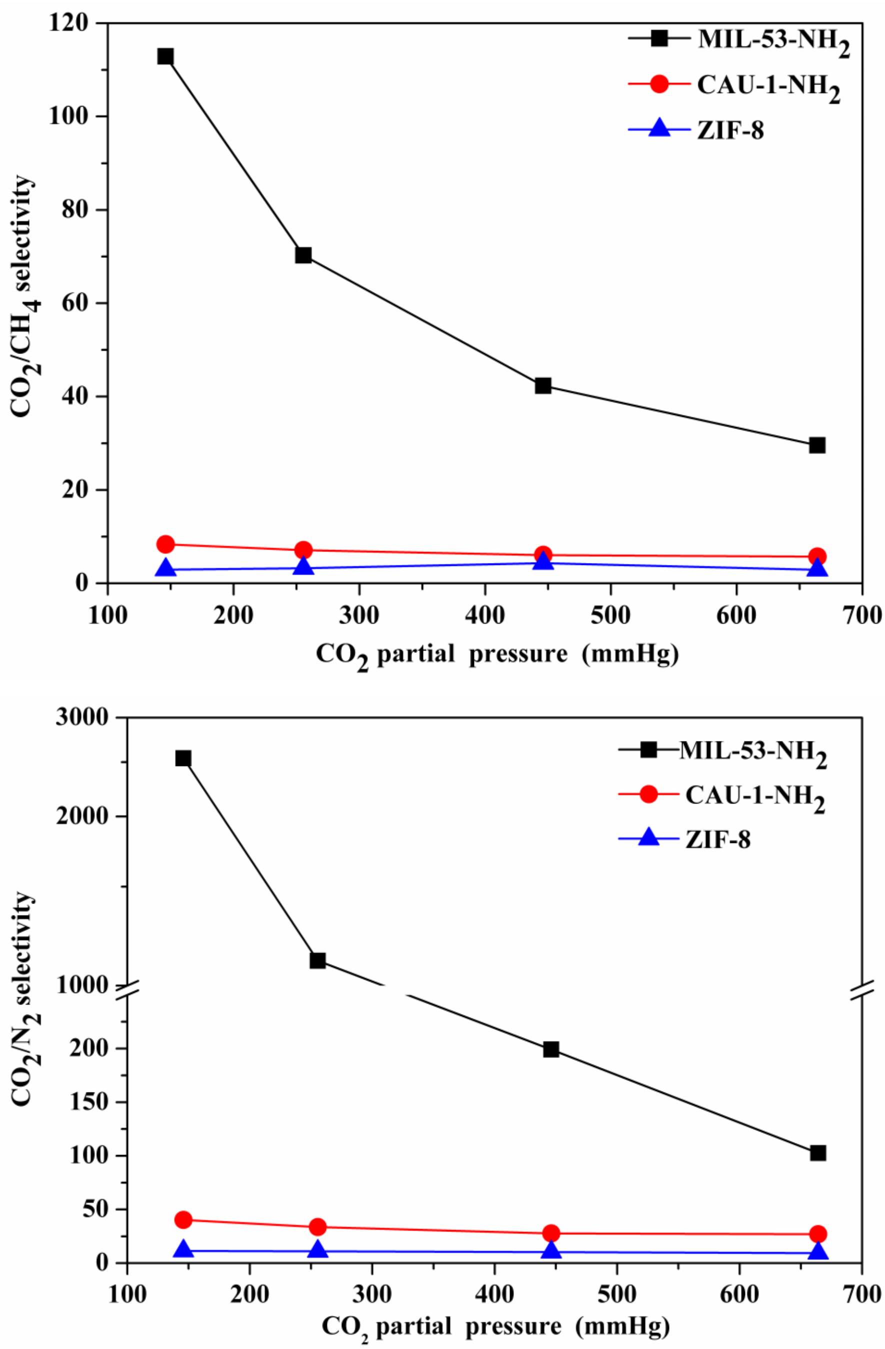


Figure S11 The calculated adsorption selectivities of CO_2/CH_4 and CO_2/N_2 mixtures for ZIF-8, MIL-53-NH_2 and CAU-1-NH_2 powders at 298 K.

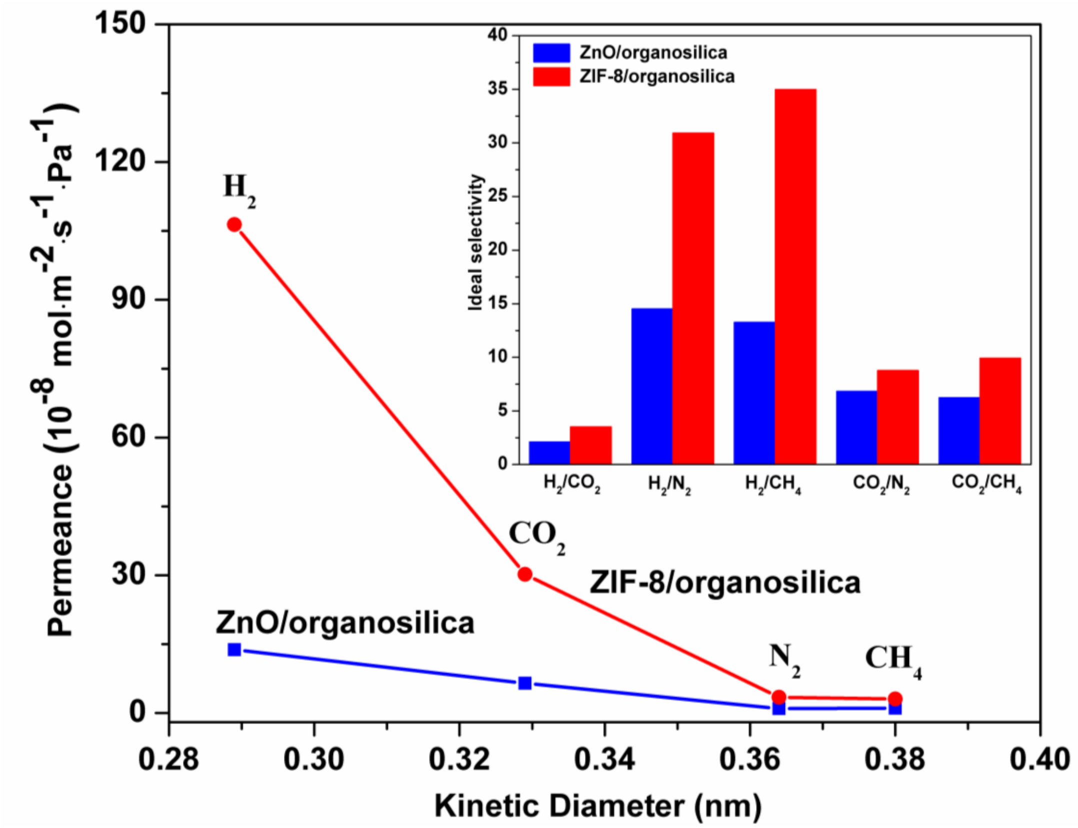


Figure S12 Single gas permeance of H_2, N_2, CO_2 and CH_4 through the as-prepared ZnO/organosilica and the as-prepared ZIF-8/organosilica membrane, the inset displays the ideal separation factors for the corresponding gas pair. Permeance was measured at ΔP = 0.2 MPa and T = 298 K (Here ZnO incorporated organosilica (Wr = 1:1) membrane was prepared by the same process. Results indicate that the H_2 permeance (1.38×10^{-7} mol▪m^{-2}▪s^{-1}▪Pa^{-1}) and selectivity are much lower than that of the ZIF-8/organosilica membrane. This is because the tested gas cannot selectively pass through the "inert" ZnO nano-particles).

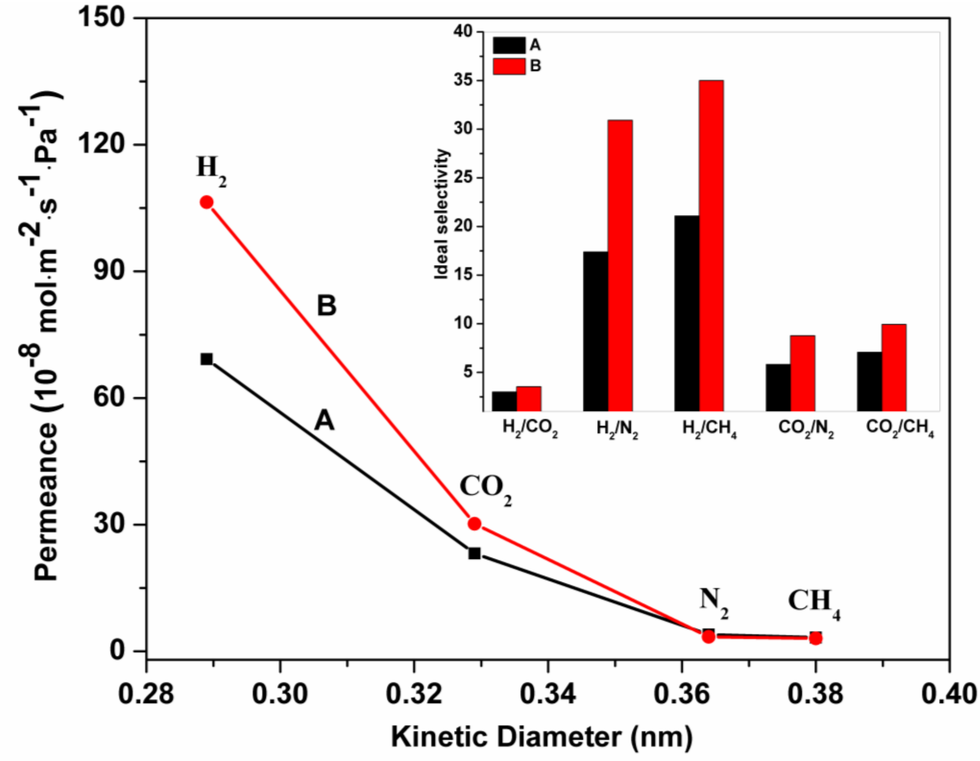


Figure S13 Single gas permeance of H_2, N_2, CO_2 and CH_4 through the ZIF-8/ organosilica (A) prepared with thicker organosilica network and the as-prepared ZIF-8/organosilica membrane (B), the inset displays the ideal separation factors for the corresponding gas pair. Permeance was measured at ΔP = 0.2 MPa and T = 298 K (The ZIF-8/organosilica membrane with thicker organosilica layer was prepared by the same process. The gas permeation results show that the molecular sieving performance and H_2 permeance decrease apparently because of the thicker organosilica layer).

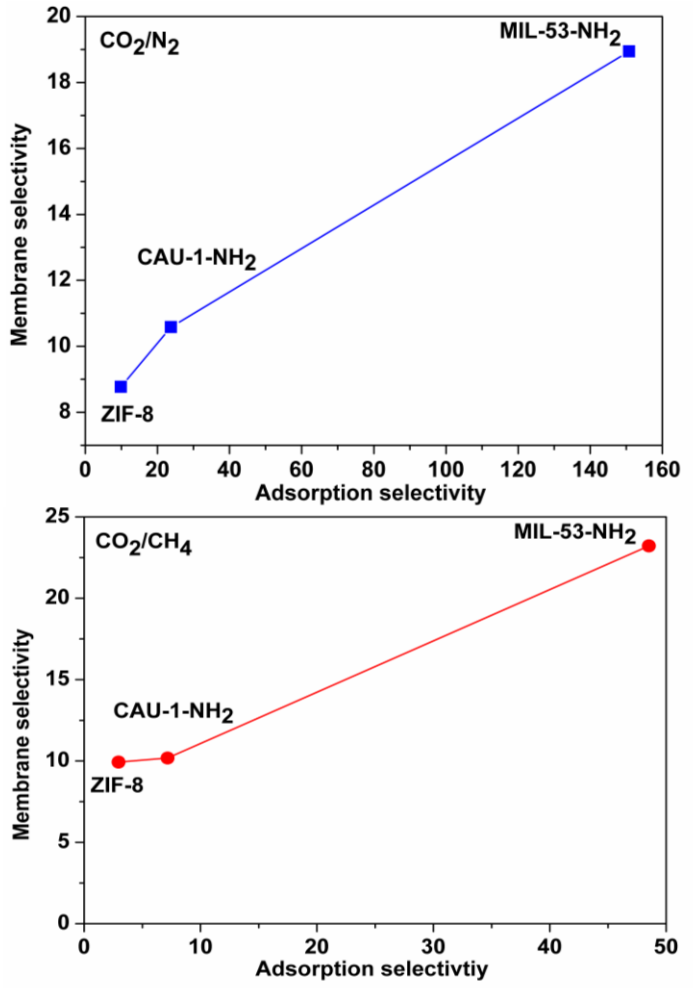


Figure S14 The ideal gas selectivities of MOF/Organosilica membranes as a function of ideal gas adsorption selectivities of MOFs.

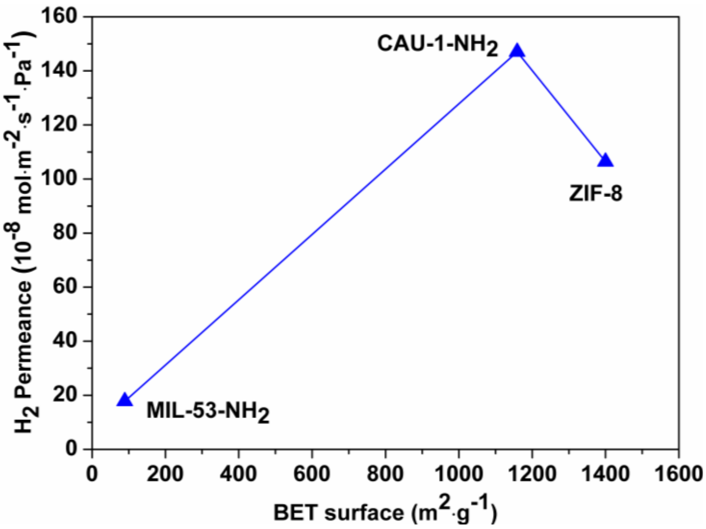


Figure S15 The H_2 permeance of MOF/Organosilica membranes as a function of BET surface areas of MOFs.

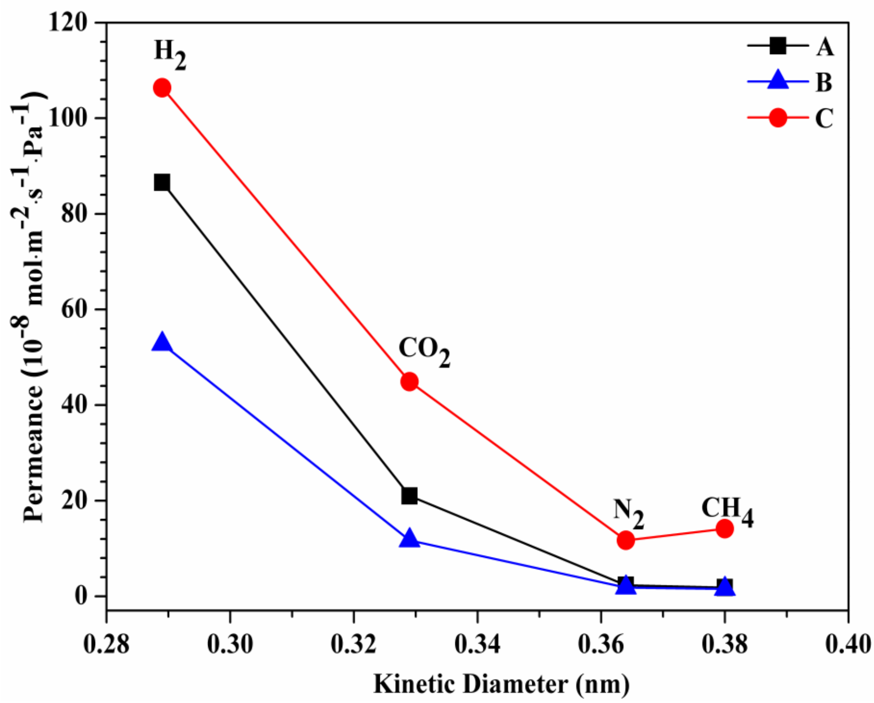


Figure S16 Single gas permeance of the as-prepared ZIF-8/organosilica (A), MIL-53-NH_2/organosilica (B) and CAU-1-NH_2/organosilica (C) membranes at 423 K.

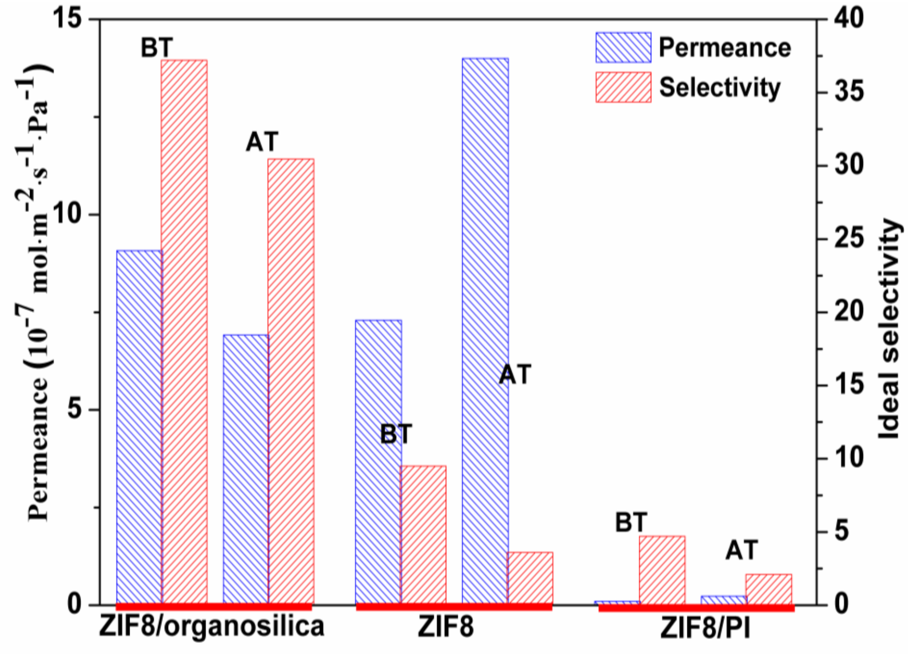


Figure S17 Single gas permeation properties of H_2 and CH_4 through as-prepared ZIF-8/organosilica, pure ZIF-8 and ZIF-8/PI membranes on the tubular ceramic substrate before treatment (BT) and after treatment (AT) under water (gas) for 8 h. Permeance was measured at ΔP = 0.2 MPa and T = 298 K (Here ZIF-8 membrane on the substrate was prepared by seeded method. ZIF-8/polyimide (PI) was prepared by dip-coating ZIF-8/PI (ZIF-8, 20 wt%) precursor onto the substrate and dry processes).

Table S1 Comparison of gas separation performance of ZIF-8/organosilica membrane with other reported H_2-selective MOF membranes at room temperature.

Membr.	Substrate	H_2 Permeance (10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1})	H_2/CH_4 Selectivity		Ref.
			Single gas	Gas Mixture	
ZIF-8	TiO_2 disc	6.0	12	11.2	1
	α-Al_2O_3 disc	10 (mix)	15.2	15	2
		14	12.1	12.9	3
		17	13.1	-	4
		23	~11.5	-	5
		36	4.5	-	6
		47	11.3	-	7
	Hollow fiber	154	13	13	8
		99	4.0	-	9
		42	13.41	12.31	10
		73	10.8	-	11
	α-Al_2O_3 tube	20.8	10.4	-	12
		15.9	12.6	11.4	13
		9.1	~9.1	-	14
	Nanotube (carbon)	80	9.8	-	15
	α-Al_2O_3	1.9	9.5	-	16
	γ-Al_2O_3 disc	14.7	12.1	12.5	17
ZIF-8/ organosilica	Hollow fiber	106.4	35	26.5	This work

Table S2 Gas separation performance of BTESE-derived organosilica membranes.

Membr.	Substrate	Tem.	H_2 Permeance (10^{-8} mol▪m^{-2}▪s^{-1}▪Pa^{-1})	H_2/CH_4 Ideal selectivity	Ref.
BTESE-derived organosilica	α-Al_2O_3 tube	50 °C	63.3	25	18
	γ-Al_2O_3 tube	200 °C	110	7.1	19
	Hollow fiber	25 °C	108	10.3	This work

Table S3 Comparison of gas separation performance of MIL-53-NH_2/organosilica membrane with other reported CO_2-selective MOF, polymer and zeolite membranes.

Membrane		CO_2 Permeance ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	CO_2/CH_4 Selectivity		Ref.
			Single gas	Gas Mixture	
MOF	ZIF-8	1.33×10^{-8}	2.77	2.96	1
	ZIF-8	3.9×10^{-8}	2.19	2.13	13
	HKUST-1	1.5×10^{-7}	1.73	0.88	20
	ZIF-78	1×10^{-8}	0.55	0.67	21
	ZIF-69	$23.6\pm1.5\times10^{-9}$	2.7	4.6	22
	MIL-53(Al)	1.3×10^{-7}	0.55	0.71	23
	$[Cu_2L_2P]_n$	1.5×10^{-8}	3.5-5	4-5	24
MOF/ Polymer	NH_2-MIL-53/PI	1.3×10^{-10}	-	40	25
	ZIF-8/PEES	8.14×10^{-10}	20.8	-	26
	UIO-66-NH_2/PSF	2.37×10^{-10}	24	-	27
	Ni_2(dobdc)/ 6FDA-DAM	1.14×10^{-8}	16	15	28
	MIL-53-NH_2/ 6FDA-DAM	7.37×10^{-9}	-	28	29
	ZIF-90/6FDA-DAM	4.02×10^{-9}	28	37	30
polymer	PBI	6.42×10^{-11}	31	-	31
	PES	3.16×10^{-8}	8.33	-	32
	PSF	6.65×10^{-9}	23.12	-	33
	6FDA-ODA-TeMPD	5.4×10^{-10}	15.4	14.2	34
zeolite	SSZ-13	17×10^{-8}	13	13.5	35
	ZSM-5	450×10^{-8}	6	-	36
	DDR	1.2×10^{-8}	-	98	37
MOF/ organosilica	MIL-53-NH_2/ organosilica	14.4×10^{-8}	23.2	18.2	This work

Supplementary References

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