membranes

Supplementary Materials: Enhanced Performance of Carbon Molecular Sieve Membranes Incorporating Zeolite Nanocrystals for Air Separation

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SUMMARY

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Table S1. Fitting parameters for O_2 and N_2 adsorptions for ETS-10, PS-MFI and SAPO-34 at 25 °C.

Sample	*gas*	q_{sat}	*b*	R^2 value
ETS-10	O_2	2.272	0.08588	1
	N_2	2.272	0.2268	0.9961
PS-MFI	O_2	3.774	0.04305	1
	N_2	3.774	0.04603	0.9999
SAPO-34	O_2	5.470	0.03192	0.9967
	N_2	5.470	0.03722	0.9966

Table S2. Fitting parameters for O_2 and N_2 adsorptions for ETS-10, PS-MFI and SAPO-34 at 35 °C.

Sample	*gas*	q_{sat}	*b*	R^2 value
ETS-10	O_2	2.241	0.07729	1
	N_2	2.241	0.1936	0.9991
PS-MFI	O_2	3.845	0.03399	0.9995
	N_2	3.845	0.03631	0.9999
SAPO-34	O_2	5.333	0.02703	0.9979
	N_2	5.333	0.03108	0.9978

Table S3. Porosity properties of CMSM and mixed-matrix CMSMs.

Membrane	Average micropore size (nm)	Micropore volume (cc)	Micropore surface area (m^2/g)
Matrimid® 5218	0.897	0.191	519
30 wt% ETS-10	0.547	0.209	556
30 wt% PS-MFI	0.673	0.241	643
30 wt% SAPO-34	0.701	0.260	692

Table S4. Solubility and diffusivity of O_2 and N_2 of CMSM and mixed-matrix CMSMs at 35 °C under the feed pressure of 1 bar (0.21 bar for O_2 and 0.79 bar for N_2).

Membrane	Density (g/cm^3)	O_2 solubility (mol/m^3-bar)	N_2 solubility (mol/m^3-bar)	O_2 diffusivity (m^2/s)	N_2 diffusivity (m^2/s)
Matrimid® 5218	1.288	143	86	2.65×10^{-13}	8.00×10^{-14}
30 wt% ETS-10	1.491	152	88	7.07×10^{-12}	3.11×10^{-12}
30 wt% PS-MFI	1.439	200	156	1.76×10^{-11}	5.08×10^{-12}
30 wt% SAPO-34	1.478	137	117	9.76×10^{-12}	2.88×10^{-12}

Table S5. Performance of pure CMSMs that have been reported in the literature for O_2/N_2 separation.

Membrane	Density (g/cm^3)	O_2 solubility (mol/m^3-bar)	N_2 solubility (mol/m^3-bar)	O_2 diffusivity (m^2/s)	N_2 diffusivity (m^2/s)
BTPA-ODA	550 °C, Argon	25 °C, pure gas	500	10.4	[1]
Kapton	550 °C, vacuum	25 °C, pure gas	45	4.4	[2]
Kapton-1	600 °C, vacuum	35 °C, pure gas	383	4.7	[3]
Matrimid	550 °C, Argon	35 °C, mixed gas (21/79)	5	5.5	This work
Matrimid-1	475 °C, vacuum	25 °C, pure gas	4	4.5	[2]
Matrimid-2	550 °C, vacuum	35 °C, 10 atm, pure gas	280	4.8	[4]
Br-Matrimid-2	550 °C, vacuum	35 °C, 10 atm, pure gas	850	5.1	[4]
ODPA-ODA	650 °C	50 °C, pure gas	70.3	6.0	[5]
ODPA-ODA-1	650 °C	50 °C, mixed gas (21:79)	33.2	5.1	[5]
P84	600 °C, Nitrogen	Pure gas	72	9.3	[6]
PEI	550 °C, vacuum	25 °C, pure gas	19	2.1	[7]
PEI-1	500 °C, vacuum	26 °C, pure gas	12	3.9	[8]
Polypyrrole	500 °C, Nitrogen	35 °C, pure gas	815	8.2	[9]
Poly(amino imide)	150 °C, Nitrogen	35 °C, pure gas	1	6.1	[9]
PPO-2	650 °C, vacuum	25 °C, pure gas	55	11.4	[10]
TMSPPO80	650 °C, vacuum	25 °C, pure gas	125	10	[10]

Note: BTDA: Benzophenone tetracarboxylic dianhydride; ODA = 4,4′-oxydianiline; PPO = poly(p-phenylene oxide); TMS = chlorotrimethylsilane

Table S6. Performance of mixed-matrix CMSMs that have been reported in the literature for O_2/N_2 separation.

CMSM	Loading (wt%)	Measurement condition	O_2 permeability (barrer)	O_2/N_2 selectivity	F_{index}	Ref.
ETS-10 (Matrimid)	30	35 °C, mixed gas (21/79)	141	3.9	1.40	This work
PS-MFI (Matrimid)	30	35 °C, mixed gas (21/79)	465	4.5	3.35	This work
SAPO-34 (Matrimid)	30	35 °C, mixed gas (21/79)	170	4.0	1.68	This work
zeolite 5A-100 nm (Matrimid)	10	35 °C, mixed gas (21/79)	77	4.0	0.83	[11]
zeolite 5A-100 nm (Matrimid)	20	35 °C, mixed gas (21/79)	168	3.7	1.17	[11]
zeolite 5A-1 μm (Matrimid)	10	35 °C, mixed gas (21/79)	98	3.9	1.35	[11]
zeolite 5A-1 μm (Matrimid)	20	35 °C, mixed gas (21/79)	121	3.9	1.14	[11]
zeolite 5A (Matrimid)	10	35 °C, mixed gas (21/79)	84	4.4	1.45	[12]
zeolite 5A (Matrimid)	20	35 °C, mixed gas (21/79)	142	4.2	1.73	[12]
H-zeolite 5A (Matrimid)	10	35 °C, mixed gas (21/79)	151	4.4	2.03	[12]
H-zeolite 5A (Matrimid)	20	35 °C, mixed gas (21/79)	185	4.0	1.64	[12]
ZSM-5 (ODPA-ODA)	0.5	50 °C, pure gas	13	4.2	-3.74	[5]
ZSM-5 (ODPA-ODA)	0.5	50 °C, mixed gas (21/79)	4.2	4.1	-5.00	[5]

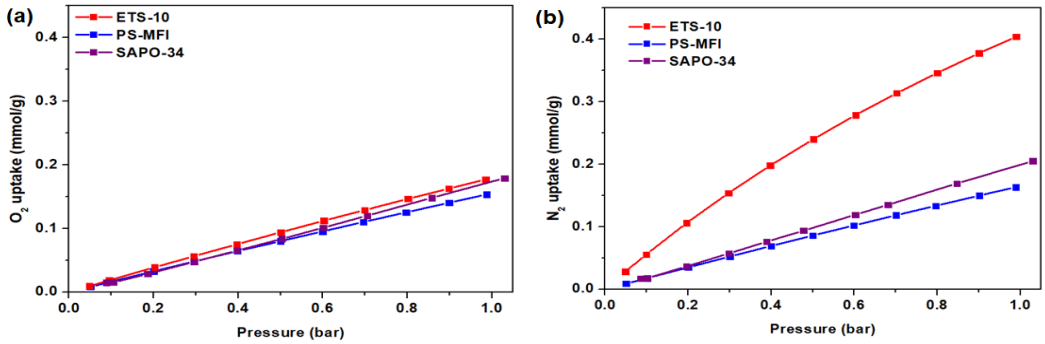

Figure S1. (a, b) O_2 and N_2 adsorption of ETS-10, PS-MFI and SAPO-34 fillers at 25 °C

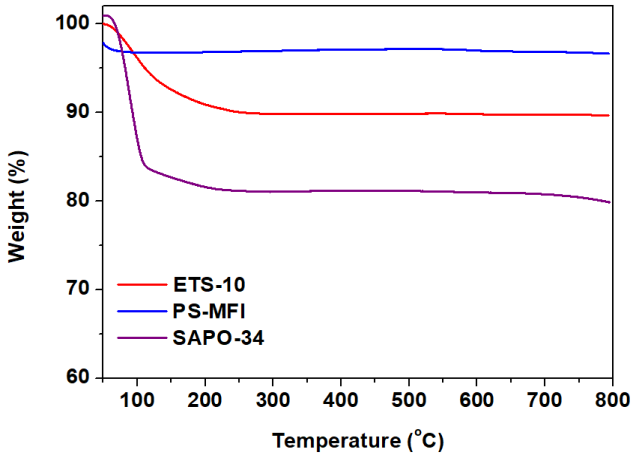

Figure S2. TGA analysis of ETS-10, PS-MFI and SAPO-34 fillers.

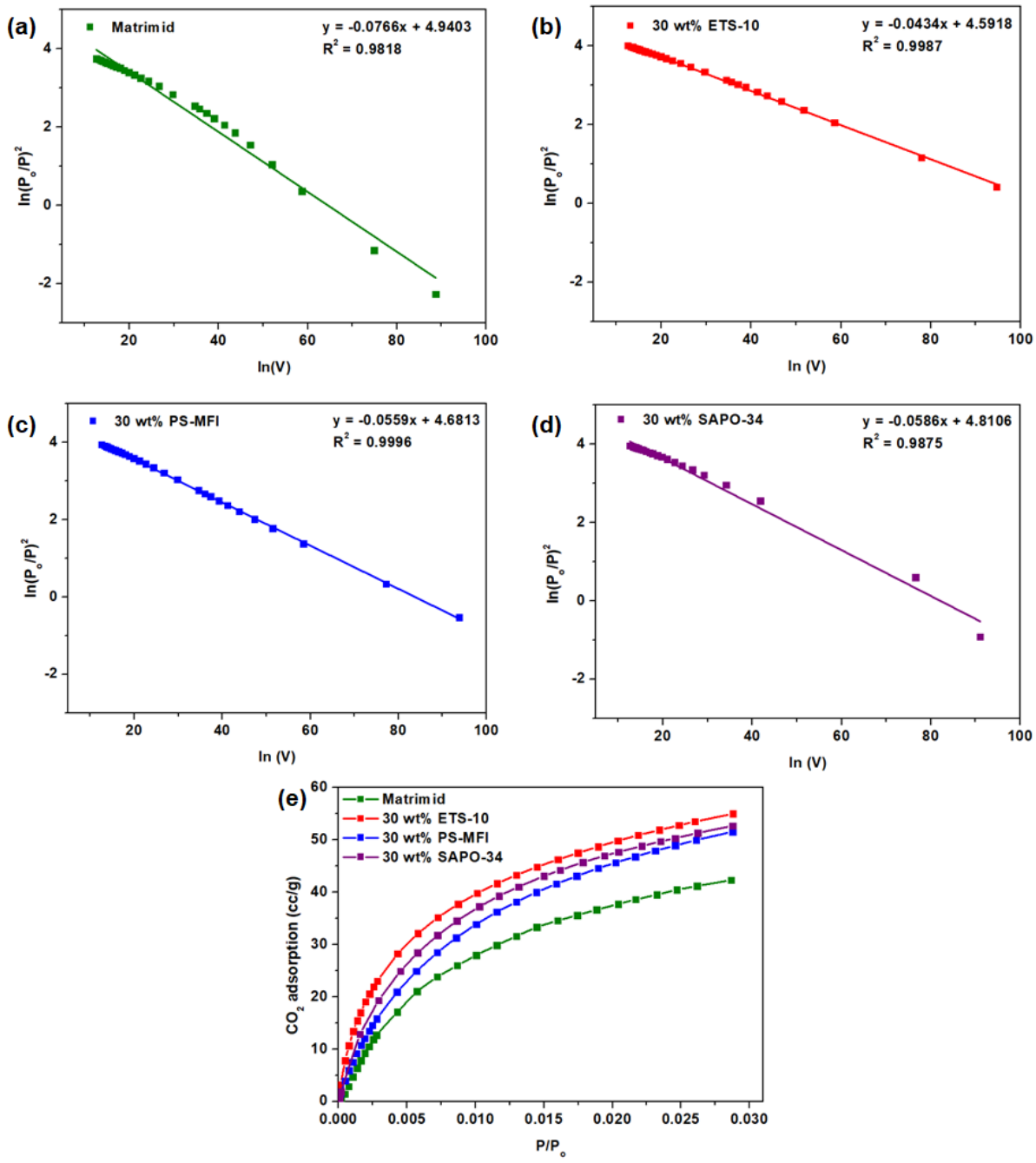

Figure S3 Dubinin-Radushkevich (DR) plot for CMSMs and mixed-matrix CMSMs: **(a)** Matrimid, **(b)** 30 wt% ETS-10, **(c)** 30 wt% PS-MFI, and **(d)** 30 wt% SAPO-34; **(e)** CO_2 adsorption of CMSMs and mixed-matrix CMSMs at 0 °C. The saturation pressure of CO_2 (denoted as P_o) is set at 26,141 torr

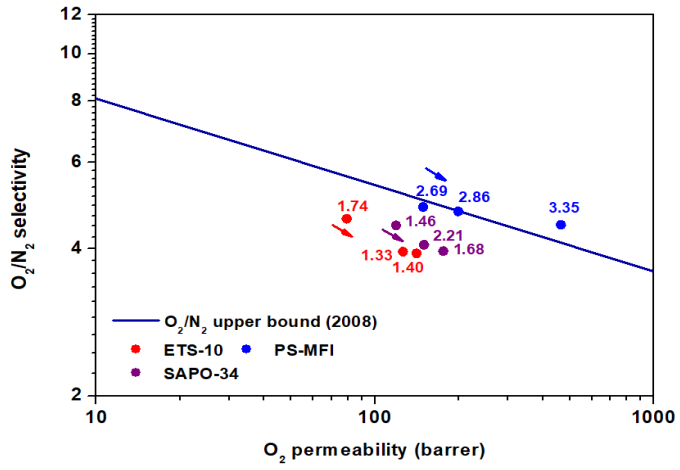

Figure S4 Performance of mixed-matrix CMSMs with F_{index} values indicated. The F_{index} values can be obtained from **Table 2**, based on calculations from equation (5)

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