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

Electronic Supplementary Information

A Carbon-Silica-Zirconia Ceramic Membrane with CO_2 Flow-Switching Behavior Promising Versatile High-Temperature H_2/CO_2 Separation

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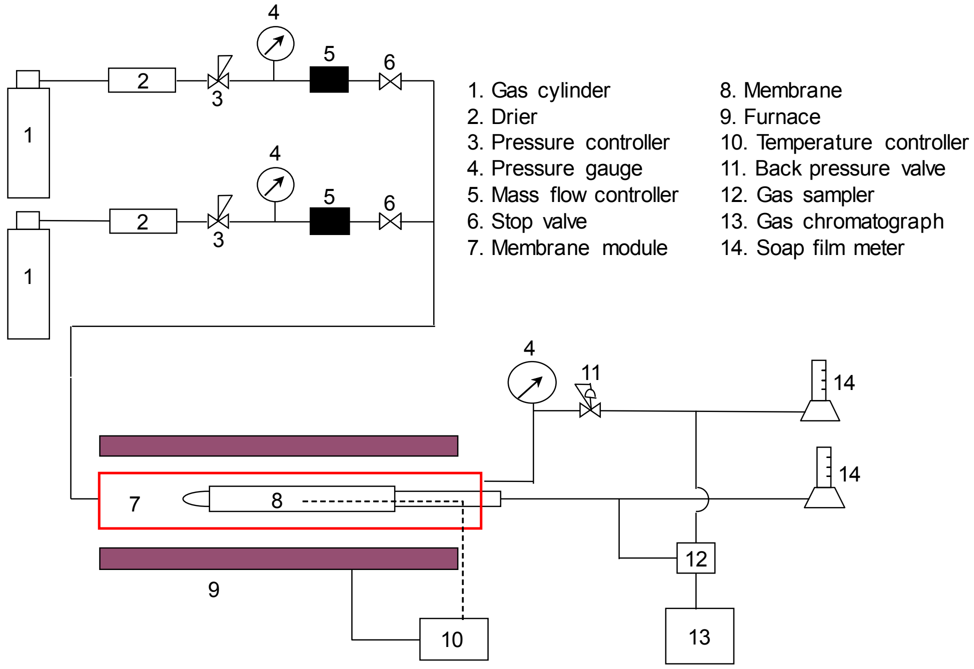

Fig. S1. Schematic flow diagram of the gas permeation testing setup (Test pressures: P_u = 200-500 kPa, P_d = 100 kPa)

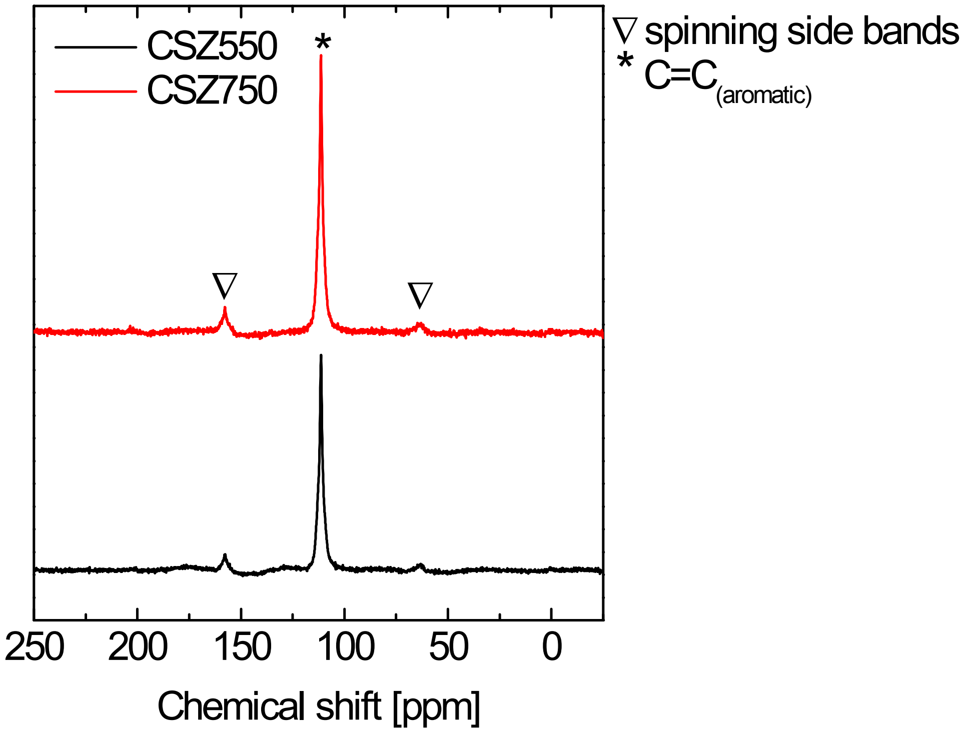

Figure S2. DD-MAS-^{13}C-NMR spectra of C-SiO_2-ZrO_2 prepared at 550 and 750 ^{o}C under N_2

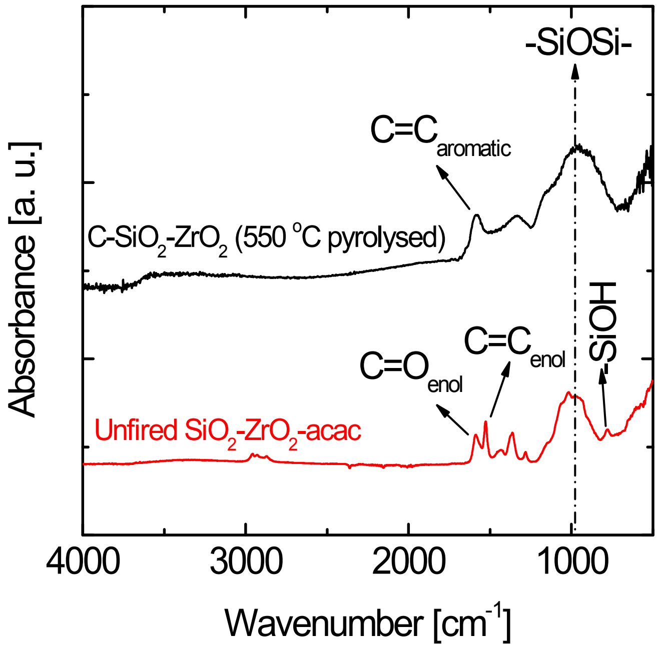

Figure S3. FT-IR spectra of SiO_2-ZrO_2-acac powder before and after pyrolysis at 550 ^{o}C under N_2

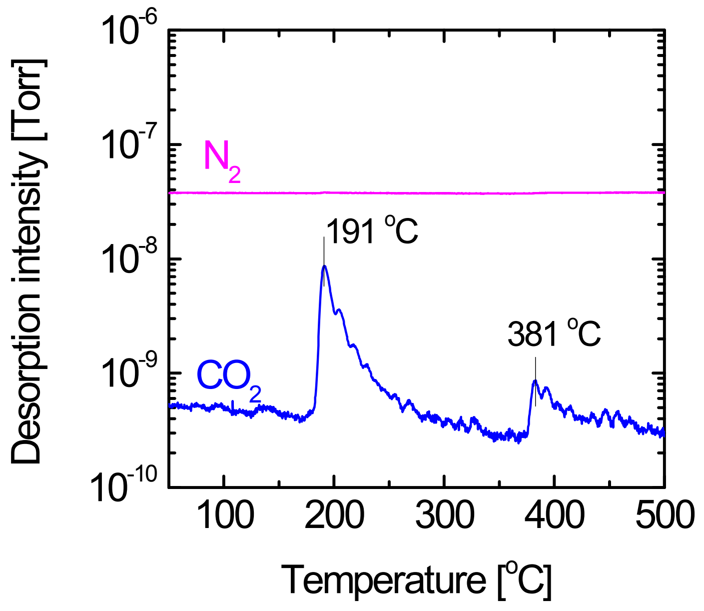

Figure S4. N_2/CO_2 mixture temperature programmed desorption in C-SiO_2-ZrO_2 powder prepared at 550 °C under N_2

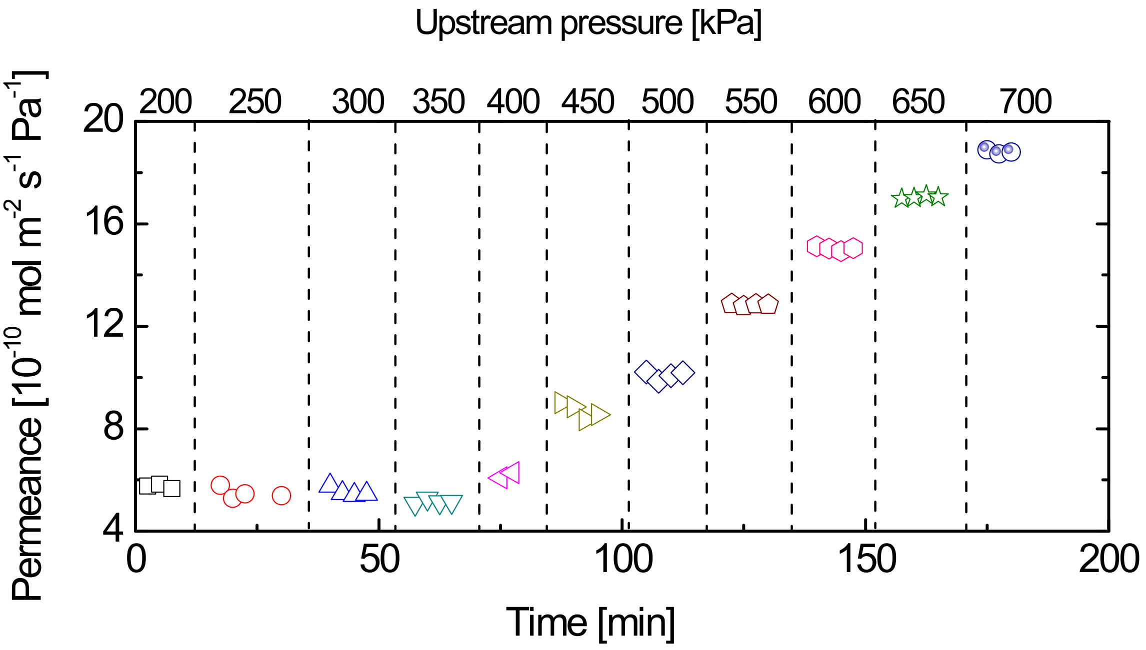

Figure S5. Detailed time course of single CO_2 permeance at pressures ranging from 200 to 700 kPa

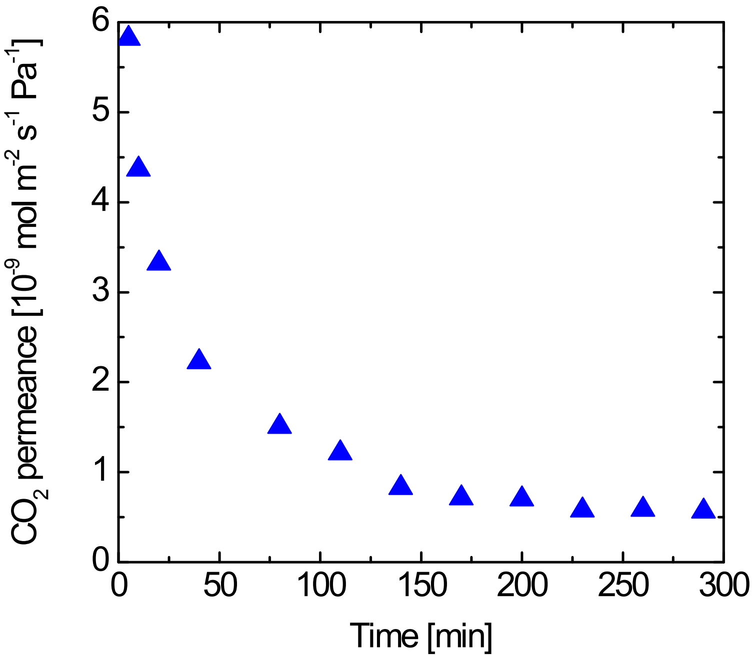

Figure S6. Initial transient CO_2 permeance at 200 kPa and 300 ^oC before steady state

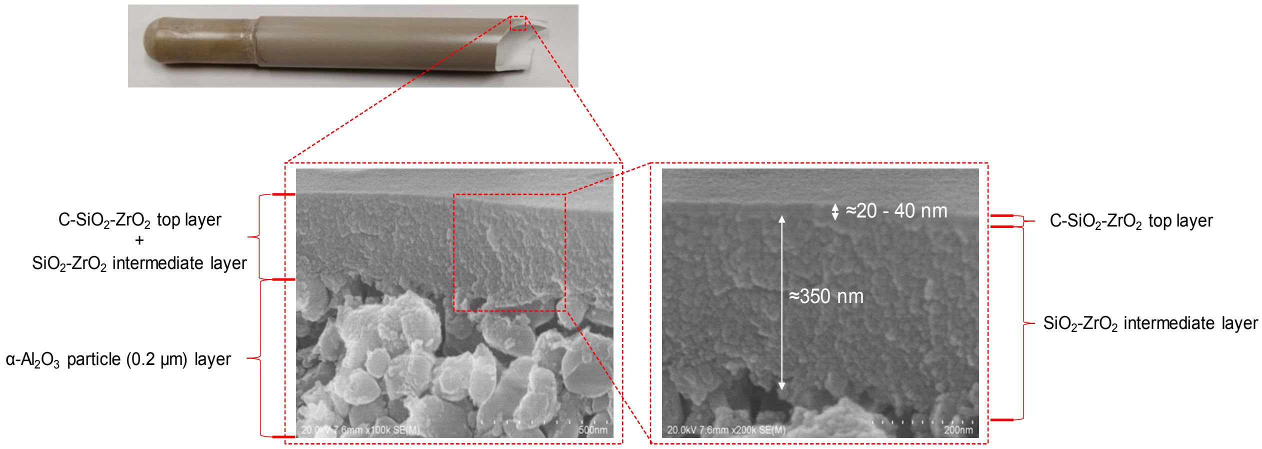

Fig. S7 FE-SEM images of the cross-section profile of a C-SiO_2-ZrO_2 membrane.

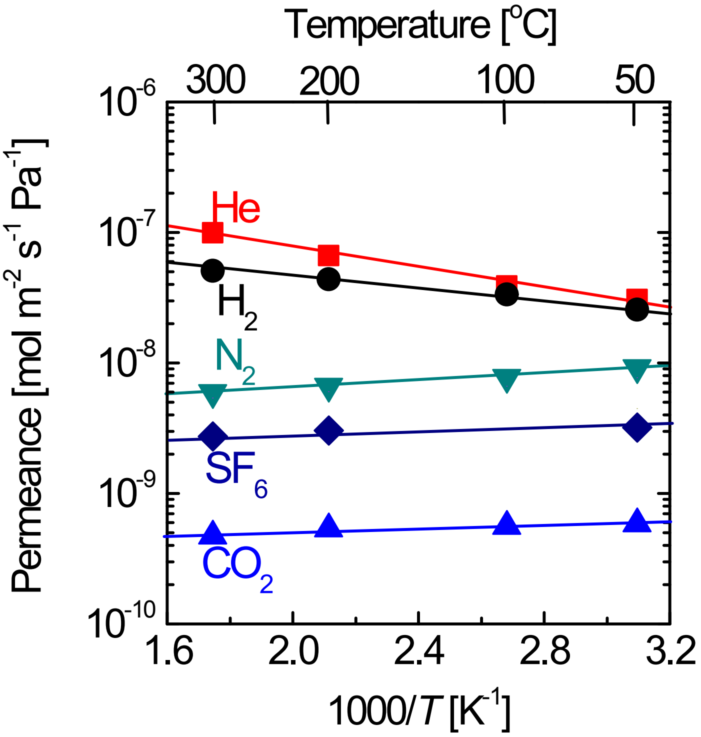

Figure S8. Temperature dependence of single-gas permeance and permeance ratios at temperatures ranging from 50 to 300 °C for a C-SiO_2-ZrO_2 membrane prepared at 550 °C

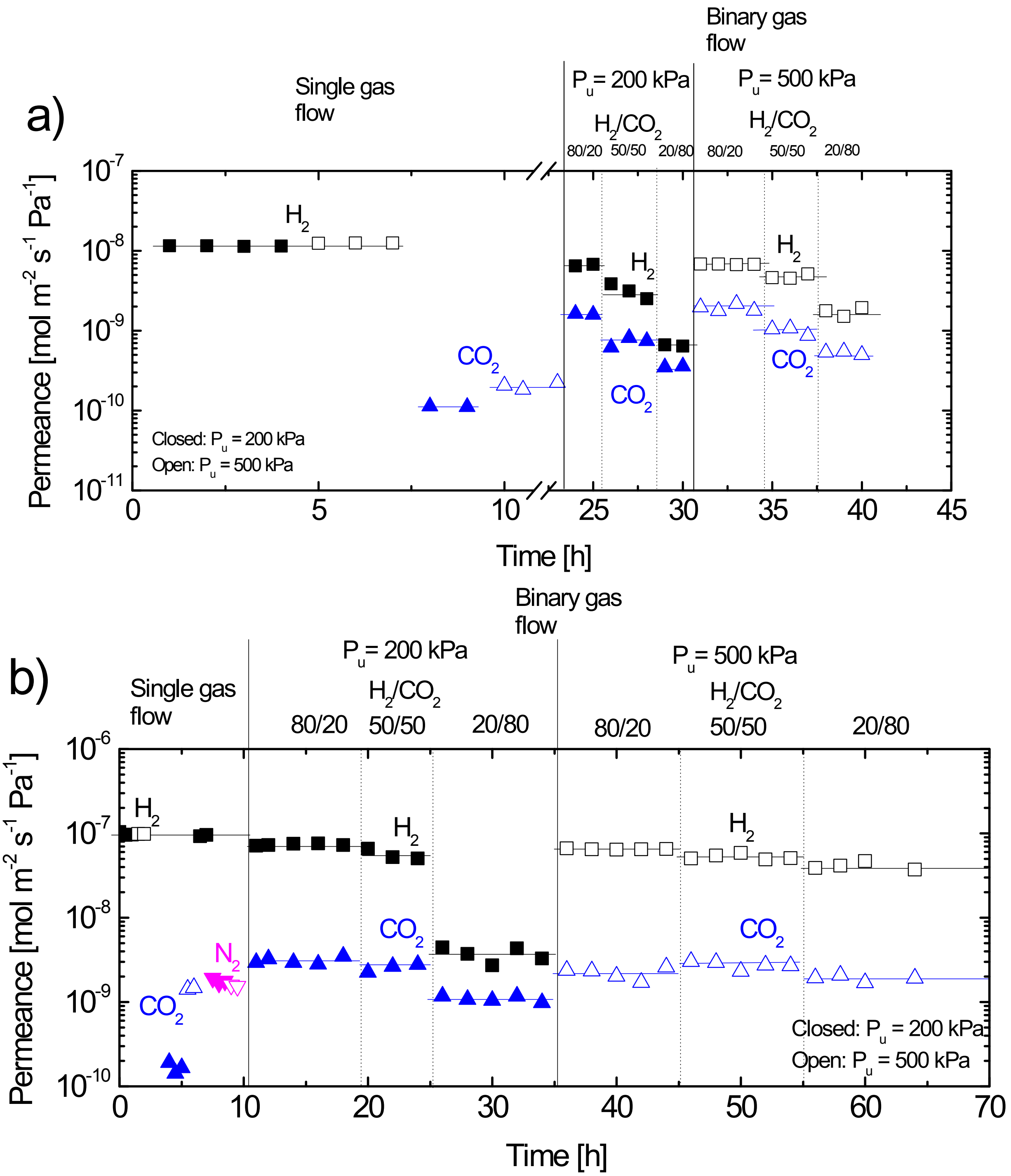

Figure S9. Detailed time courses for the permeance of single-gas and a binary-gas mixture at 50 (a) and 300 °C (b)

As presented by Kamaruddin and Koros [1], the mass flux of a species, A, that is the result of the bulk motion of a mixture of gases, A and B, can be written as follows:

$$n_A^{bulk} = (n_A + n_B)\omega_A \tag{S1}$$

Where n_A, n_B and ω_A are the total mass flux of components A and B and the concentration of component A, respectively. Equation S1 for the mass flux of CO_2 caused by the bulk motion of a mixture of CO_2 and H_2 could be written as follows:

$$n_{CO_2}^{bulk} = \left(n_{H_2} + n_{CO_2}\right)\omega_{CO_2} \tag{S2}$$

The fraction of the bulk-flow contribution that a component makes to the total mass flux in a gaseous mixture is defined as the ratio of the bulk mass flux of the component to the total mass flux. For the CO_2 component in a H_2/CO_2 mixture, equation S3 gives the fraction of the H_2-CO_2 bulk flux contributed by the CO_2 flow [1].

$$\prod_{CO_2}^{bulk} = \frac{n_{CO_2}^{bulk}}{n_{CO_2}} = \frac{\left(n_{H_2} + n_{CO_2}\right)\omega_{CO_2}}{n_{CO_2}} = (1+r)\omega_{CO_2}^{avg} \tag{S3}$$

Where Π^{bulk} is the fraction of the bulk flux contribution, r is the permeance ratio of H_2 to CO_2 and ω^{avg} is the average CO_2 concentration across the membrane thickness. Applying the log mean difference of CO_2 concentration across the membrane thickness, equation S3 becomes

$$\prod_{CO_2}^{bulk} = (1+r)\frac{(\omega_{CO_2}^{f} - \omega_{CO_2}^{r})}{\ln\left(\frac{\omega_{CO_2}^{f} - \omega_{CO_2}^{p}}{\omega_{CO_2}^{r} - \omega_{CO_2}^{p}}\right)} \tag{S4}$$

For a single CO_2 flow, while adopting a single H_2 flow as the frame of reference with a linear CO_2 concentration gradient, equation S3 can be written as follows:

$$\prod_{CO_2}^{bulk} = \left(1 + {}^{1}/_{r}\right)\left(\frac{\omega_{CO_2}^{f} + \omega_{CO_2}^{p}}{2}\right) \tag{S5}$$

Where ω^f, ω^r and ω^p are the concentrations of CO_2 in the feed, retentate and permeate, respectively, and r becomes the ideal selectivity of H_2 over CO_2. Equations S4 and S5 can thus be plotted against the CO_2 feed-side pressure, as shown in Figure S8. Clearly, the bulk phase flow contribution of CO_2 is much higher in the binary mixture than in pure CO_2 flow and increases as the CO_2 feed pressure increases.

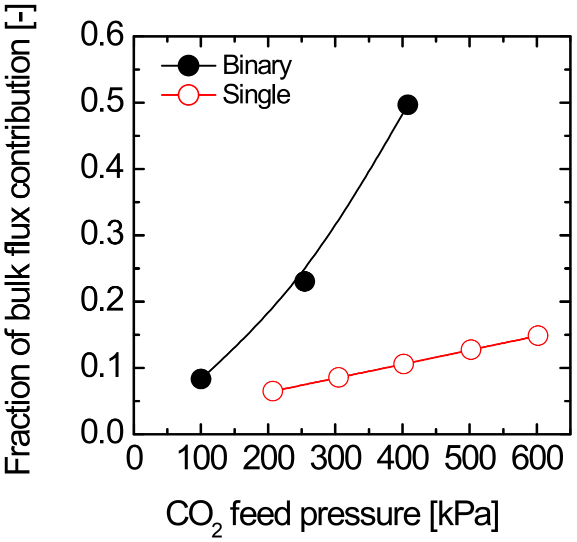

Figure S10. Calculated fraction of the CO_2 bulk flux contribution at 300 °C as a function of the CO_2 feed pressure in single and binary systems (at total P_u = 500 kPa)

Table S1. Comparison of H_2 permeance-H_2/CO_2 mixture selectivity trade-off of high-temperature H_2/CO_2 separation membranes

No.	Membrane type	Separation mechanism	H_2 permeance x 10^{-8} [mol $m^{-2}s^{-1}Pa^{-1}$]	H_2/CO_2 selectivity [-]	Reference
200-300 °C					
1	Zeolite (SAPO-34)	Size exclusion	7	23	[2]
2	ZIF-7	Size exclusion	4.5	13.6	[3]
3	Zeolite (B-ZSM-5)	Size exclusion	0.6	33	[4]
4	SiC	Size exclusion	0.89	49	[5]
5	Si	Size exclusion	50	6.8	[6]
6	Pd-organosilica	H_2 flow enhancement	5.8	33.5	[7]
>300 °C					
7	SiO_2-TiO_2	Size exclusion	24.2	13.6	[8]
8	MFI-type Zeolite	Size exclusion	39.6	141	[9]
9	Zeolite (B-ZSM-5)	Size exclusion	10	47	[4]
300 °C, 500 kPa					
	C-SiO_2-ZrO_2	Flow transition H_2 enhancement	7	20-30	This work

Supplementary references

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