Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Interfacial Barriers to Gas Transport in Zeolites: Distinguishing Internal and External Resistances

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Functional form of the force field used to represent bonded interactions in PI:

$$
\begin{aligned}
U^{bonded} &= \sum_{b}\left[k_2(b-b_0)^2 + k_3(b-b_0)^3 + k_4(b-b_0)^4\right] \\
&+\sum_{a}\left[k_2(\theta-\theta_0)^2 + k_3(\theta-\theta_0)^3 + k_4(\theta-\theta_0)^4\right] \\
&+\sum_{\phi}\left(\begin{array}{l}\left\{k_1\left[1-\cos(\phi-\phi_1^0)\right]\right\}+\left\{k_2\left[1-\cos(2\phi-\phi_2^0)\right]\right\} \\ +\left\{k_3\left[1-\cos(3\phi-\phi_3^0)\right]\right\}\end{array}\right) \\
&+\sum_{b}\sum_{b'}k(b-b_0)(b'-b'_0)+\sum_{b,\theta}k(b-b_0)(\theta-\theta_0) \\
&+\sum_{b,\theta}k(\theta-\theta_0)(\theta'-\theta'_0)+\sum_{\theta,\theta,\psi}k(\theta-\theta_0)(\theta'-\theta'_0)\cos\phi \\
&+\sum_{b,\phi}(b-b_0)\left[k_1\cos\phi+k_2\cos 2\phi+k_3\cos 3\phi\right] \\
&+\sum_{\theta,\phi}(\theta-\theta_0)\left[k_1\cos\phi+k_2\cos 2\phi+k_3\cos 3\phi\right] \\
&+\sum_{\chi}k_2\chi^2
\end{aligned}
\qquad \text{(S1)}
$$

Table ST1. Functional form of the force field used to represent the non-bonded interactions in this study (hybrid potential).

Interaction	**functional form**
Polymer -Polymer	$U_{ij}^{non-bond} = \sum_{i,j}\varepsilon_{ij}\left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^9 - 3\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right]$
Polymer-Zeolite	$U_{ij}^{non-bond} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right]$
Polymer-Gas	$U_{ij}^{non-bond} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right]$
Zeolite-Zeolite	none
Zeolite-Gas & Gas-Gas	$U_{ij}^{non-bond} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{q_i q_j}{r_{ij}}$

Table ST2. Lennard–Jones (12-6) parameters, partial charges for the EPM2 CO_2, and united-atom H_2

Molecule	Atom	$\epsilon_{gas-gas}$ (K^{-1})	$\sigma_{gas-gas}$ (nm)	$\epsilon_{gas-zeo}$ (K^{-1})	$\sigma_{gas-zeolite}$ (nm)	q(e)	Ref
Hydrogen (H_2)	H_2_UA	34.02	0.296	51.233	0.262	0	[1, 2]
Carbon dioxide (CO_2)	C_CO_2	28.129	0.2757	27	0.290	C_CO_2= 0.6512 O_CO_2=-0.3256 Si_{zeo} = +2 O_{zeo} =-1	[3, 4]
	O_CO_2	80.51	0.3033	79	0.305		

Table ST3. Kinetic diameters of gas molecules.

Molecule	Kinetic Diameter (Å)	Ref
CO_2	3.3	[5]
CH_4	3.8	[5]
H_2	2.9	[5]

Table ST4. Characterization of zeolite pore structure

Zeolite	Limiting window size	Limiting cage Size
SAS	4.22	8.99
MFI	4.46	-
PON	4.3	4.93

Table ST5. Length dependency of corrected diffusion coefficient (D_o) of methane in zeolites

SAS		MFI		PON	
L (nm)	D_o (x 10^9 m^2/sec)	L (nm)	D_o (x 10^9 m^2/sec)	L (nm)	D_o (x 10^9 m^2/sec)
3.15	2.0 (±0.1)	4.224	3.1 (±0.25)	2.97	1.1 (±0.1)
4.2	2.4 (±0.1)	6.207	3.8 (±0.25)	4.75	1.7 (±0.1)
6.25	3.1 (±0.1)	8.202	5.0 (±0.5)	6.53	2.0 (±0.1)
8.3	3.8 (±0.2)	10.19	6.8 (±0.5)	10.09	3.6 (±0.2)
10.4	4.5 (±0.2)	14.19	10.2 (±0.5)	13.66	4.8 (±0.2)
14.6	5.5 (±0.3)				

Table ST6. Kinetic and perm-selectivities of the gases

Gas	D_o (x10^{-9} m^2/sec)	S (cc(STP)/cc. atm)	Kinetic selectivity (H_2/CH_4)	Perm-Selectivity (H_2/CH_4)
CH_4	7.0 (±0.5)	13.10822	9 (±0.2)	0.38 (±0.05)
H_2	63 (±3)	0.548537		

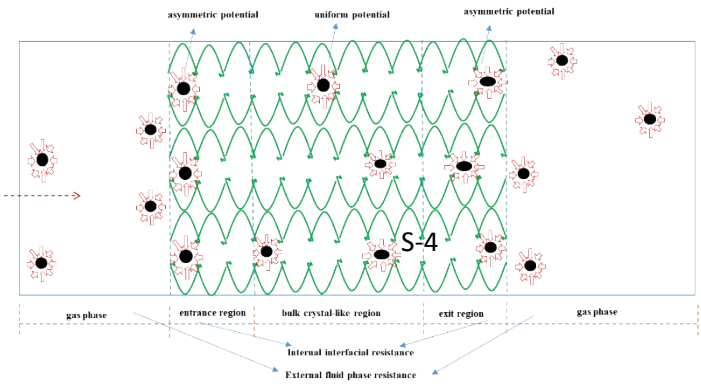

Figure S1. Schematic illustration of inside the zeolite and the mean force experienced by the gas molecules at different locations in the pore.

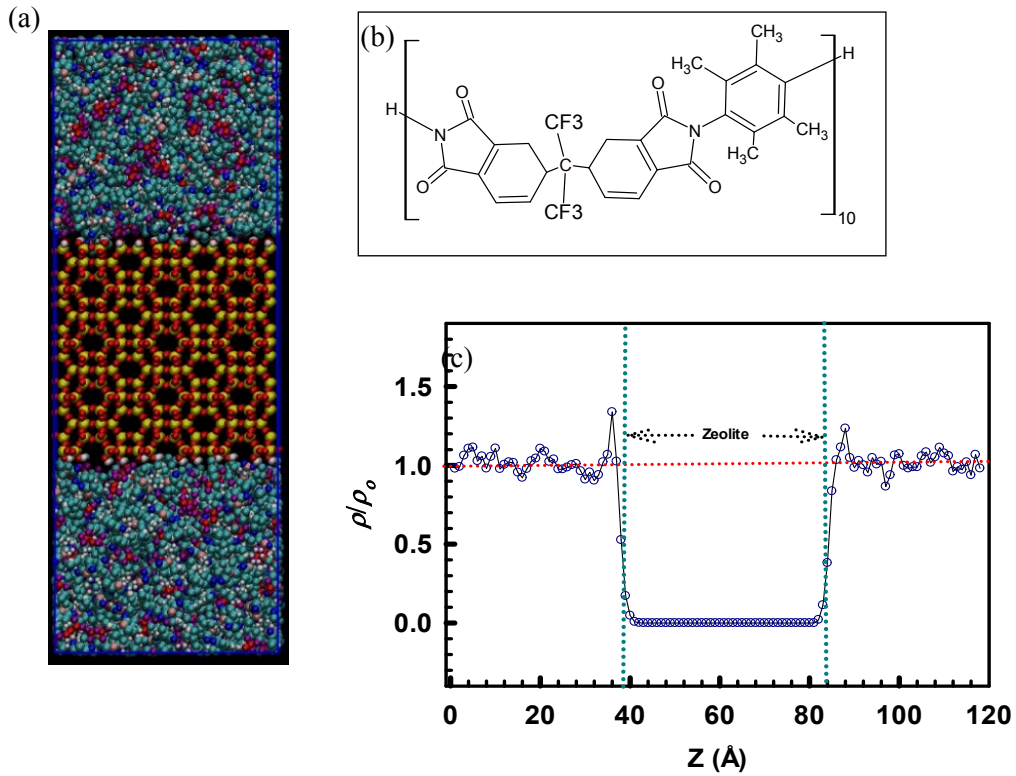

Figure S2: Structure of the (a) PI-SAS hybrid system, (b) 6FDA-Durene polyimide polymer chain and (c) Density profile of PI in the PI-SAS composite system at T=300K.

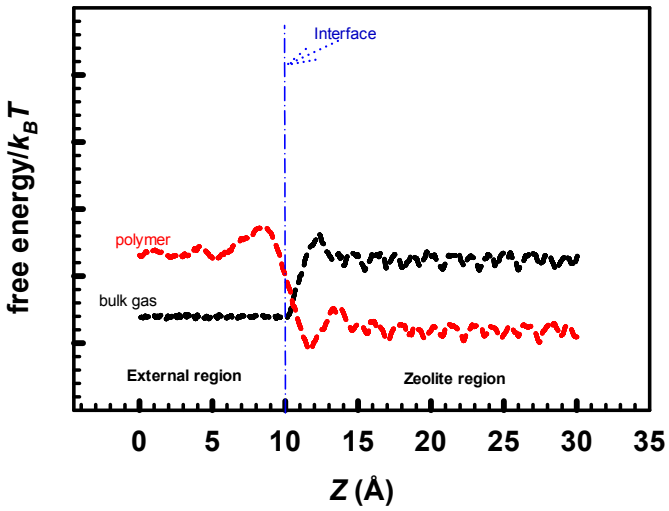

Figure S3: Free energy profiles of CH_4 gas in SAS zeolite at T= 300K in the presence of bulk gas and polymer at the loading of ~1 mol/u.c.

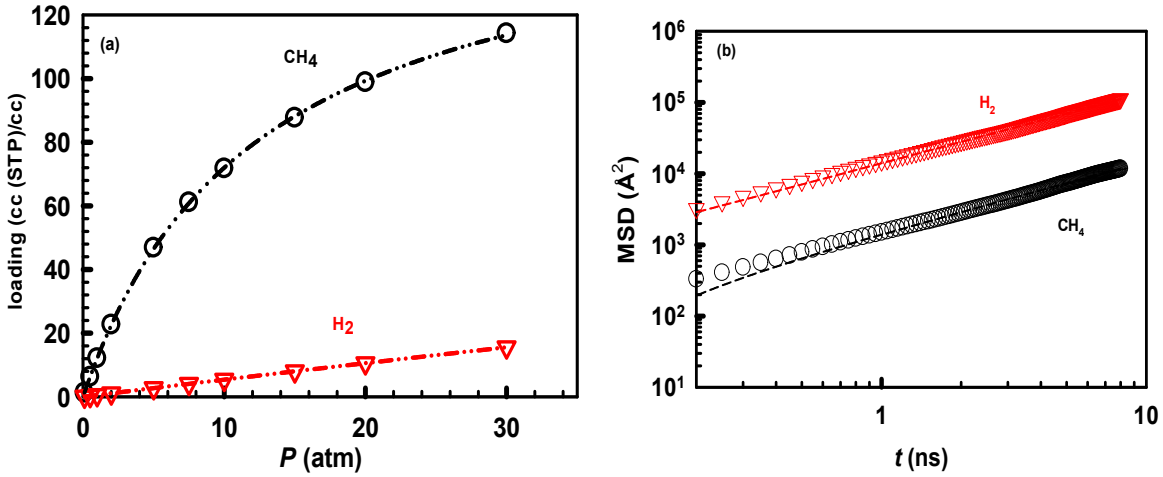

Figure S4: (a) Adsorption isotherms of CH_4 and H_2 in SAS zeolite at *T*= 300 K. The dashed lines indicate the fitted adsorption isotherms using the "Langmuir sorption" model eq (15), and (b) log-log plot of centre of mass mean square displacement (MSD) of CH_4 and H_2 *vs.* time (window size average) in SAS zeolite at a loading of 1 molecule per unit cell.

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