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

Supplementary Information

Inhibition of Non-permeating Component on Gas Permeability of Nanoporous Graphene Membrane

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1 Interaction potential

1.1 Lennard-Jones potential

The interactions for C and H atoms were modeled by the AREABO potential, of which the parameters can be found in the Ref. 1.[1] For the N_2 and its related interactions, the standard 12-6 Lennard-Jones (L-J) potential model was adopted, as follows:

$$E = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \quad r < r_c \tag{S1}$$

where r_c is the cutoff radius, ε is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero. Potential parameters between crossing atoms were obtained using the Lorentz-Berthelot mixing rule. The L-J potential parameters related to the nitrogen atom are listed in Table S1.

Table S1 Lennard-Jones potential parameters.[2, 3]

	ε (eV)	σ (Å)
N-N	3.126×10^{-3}	3.297
N-H	2.156×10^{-3}	2.974
C-N	2.746×10^{-3}	3.349

1.2 Harmonic bond potential

The internal bond interaction of the N_2 molecules was modeled by the *harmonic* bond potential,

$$E = K(r - r_0)^2 \tag{S2}$$

where K is the bond coefficient and r_0 is the equilibrium bond distance. For molecular nitrogen, r_0 = 1.112 Å and K = 1.426 eV·Å^{-2}.[4]

2 Calculation of Permeance

By analyzing the molecular motions, we can obtain the number of permeated molecules *versus* time in all cases, as shown in Fig. S1-S2. As seen from the figures, the H_2 and N_2 molecules permeate rapidly through the nanopore while the CH_4 molecules hardly pass through it.

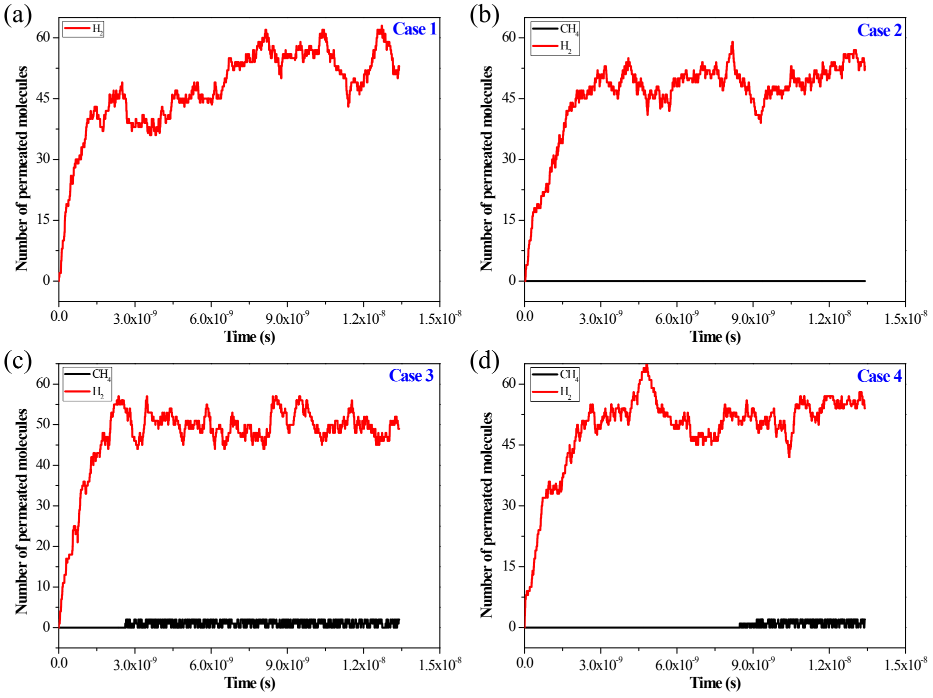

Fig. S1. Number of permeated CH_4 and H_2 molecules *versus* time in Case 1-4.

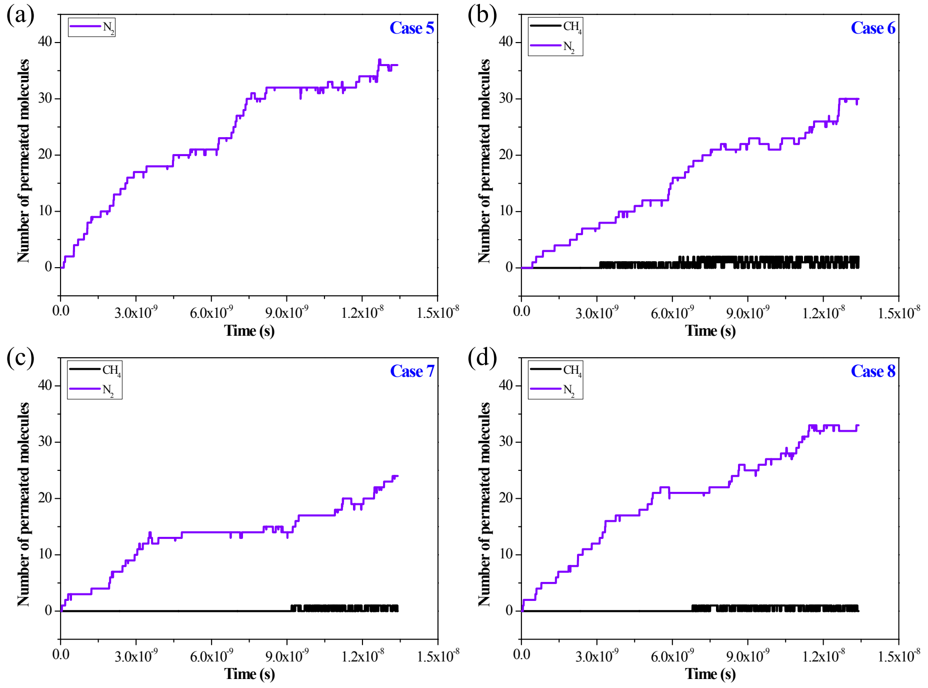

Fig. S2. Number of permeated CH_4 and N_2 molecules *versus* time in Case 5-8.

According to the Eq. (3) of the time-dependent of permeated molecular number (N), we can fit the curves of Fig. S1-S2 and obtain the permeances. For example, Fig. S3 shows the variation of N of the N_2 molecules *versus* time and the fitting curve by Eq. (3) in Case 5. Based on the fitted parameter B, we can obtain the permeances of molecules in all cases. Table S2 lists the values of permeances and their fitting standard errors.

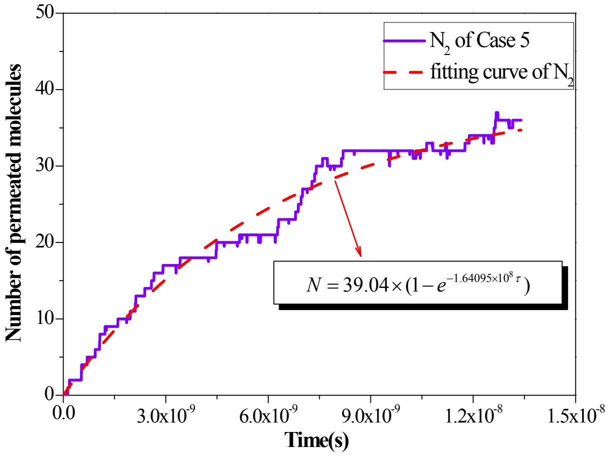

Fig. S3. Fitting curve of the permeated number of the N_2 molecules *versus* time in Case 5.

Table S2. Permeances and fitting standard errors of the H_2, N_2 and CH_4 molecules in all cases.

Molecule	Case	Permeance ($mol\cdot s^{-1}\cdot m^{-2}\cdot Pa^{-1}$)	Standard error ($mol\cdot s^{-1}\cdot m^{-2}\cdot Pa^{-1}$)
H_2	Case 1	2.09×10^{-3}	$\pm1.496\times10^{-5}$
H_2	Case 2	1.50×10^{-3}	$\pm1.898\times10^{-5}$
H_2	Case 3	1.83×10^{-3}	$\pm1.900\times10^{-5}$
H_2	Case 4	1.71×10^{-3}	$\pm1.897\times10^{-5}$
N_2	Case 5	2.08×10^{-4}	$\pm4.420\times10^{-7}$
N_2	Case 6	1.04×10^{-4}	$\pm2.217\times10^{-7}$
N_2	Case 7	7.39×10^{-5}	$\pm2.364\times10^{-7}$
N_2	Case 8	1.37×10^{-4}	$\pm2.365\times10^{-7}$
CH_4	Case 2	4.85×10^{-6}	$\pm2.287\times10^{-8}$
CH_4	Case 3	5.67×10^{-6}	$\pm2.754\times10^{-8}$

CH_4	Case 4	5.35×10^{-6}	$\pm3.121\times10^{-8}$

Continued

CH_4	Case 6	6.25×10^{-6}	$\pm2.329\times10^{-8}$
CH_4	Case 7	5.78×10^{-6}	$\pm2.802\times10^{-8}$
CH_4	Case 8	5.23×10^{-6}	$\pm2.311\times10^{-8}$

3 Selectivity

3.1 Simulated selectivity

The selectivity of this nanopore for two kinds of gas molecules can be obtained by $F_{A/B} = S_A/S_B$. In our simulations, only one or two CH_4 molecules can permeate through the nanopore, no crossing events even occur in Case 2. In order to calculate the selectivity, the permeated number of the CH_4 molecules is assumed to be 1 in Case 2. The selectivities of all cases are shown in Fig. S4.

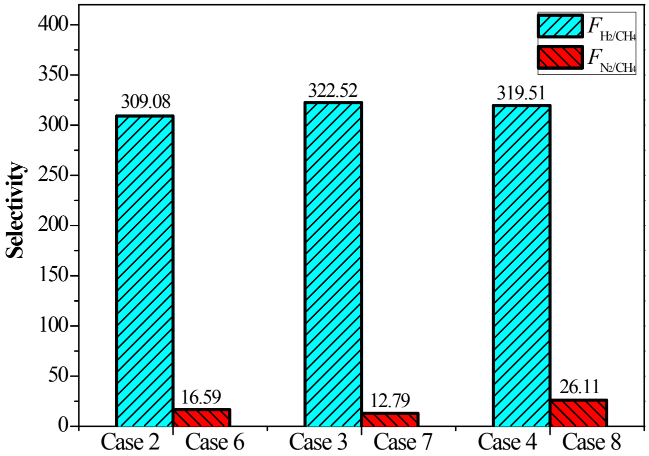

Fig. S4. Selectivities of H_2 over CH_4 and N_2 over CH_4 in Case 2-4 and Case 6-8.

3.2 Estimation of selectivity using interaction energy

The selectivity (F) of the NPG membranes can be estimated from interaction energy by using the Arrhenius equation for diffusion.

$$F_{H_2/CH_4} = \frac{D_{H_2}}{D_{CH_4}} = \frac{A_{H_2}}{A_{CH_4}} \frac{e^{-E_{H_2}/RT}}{e^{-E_{CH_4}/RT}} \tag{S3}$$

$$F_{\mathrm{N_2/CH_4}} = \frac{D_{\mathrm{N_2}}}{D_{\mathrm{CH_4}}} = \frac{A_{\mathrm{N_2}}}{A_{\mathrm{CH_4}}} \frac{e^{-E_{\mathrm{N_2}}/RT}}{e^{-E_{\mathrm{CH_4}}/RT}} \tag{S4}$$

where F is the selectivity, D is the diffusion rate, A is the prefactor and E is the diffusion barrier. Diffusion barrier is the difference between the highest and the lowest value of the interaction energy profile, as shown in Figure 8. In this paper, the room temperature $T =$ 300 K and we assumed that the prefactors of the two kinds of gases are in the same magnitude. Thus, $A_{\mathrm{H_2}} / A_{\mathrm{CH_4}} \approx 1$ and $A_{\mathrm{N_2}} / A_{\mathrm{CH_4}} \approx 1$ according to the work by Jiang et al.[5]

3.3 Comparison of the relative barrier heights

In our calculations of the interaction energy using the density functional theory, the geometry of the nanopore was fully frozen. To be more confident on the calculation, we compare the diffusion barriers in our study and those for the Pore A and Pore B in the study by Hauser and Schwerdtfeger,[6] as shown in Fig. S5. It can be seen that the diffusion barriers of the CH_4, N_2 and H_2 molecules in our study are generally lower than those for Pore A while higher than those for Pore B.

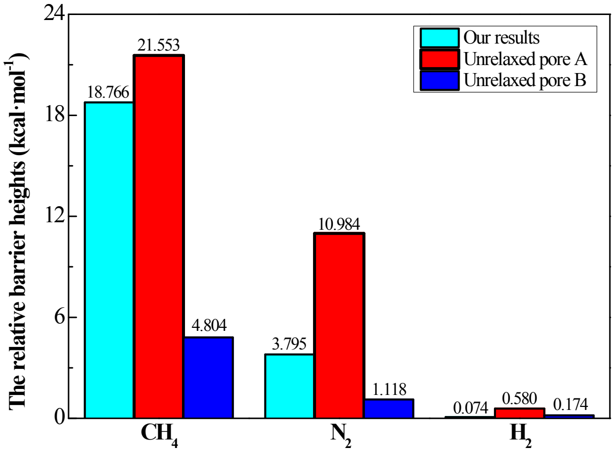

Fig. S5. The comparison between our results and those of the previous study.[6]

The size of the nanopore we used is larger than that of the pore A, which makes it easier for gas molecules to permeate. Thus, the relative barrier heights in our study are lower than that of the pore A. Moreover, pore modifications have a significant influence on the gas permeability and selectivity. For the pore B modified by N atoms and H atoms, the stronger attractive van der Waals interactions between N atoms and molecules make the gas molecules permeate easier. Therefore, the relative barrier heights of pore B are lower than those in our study. This comparison demonstrates that our calculation of the diffusion barriers is reliable.

References

1 S. J. Stuart, A. B. Tutein and J. A. Harrison, *J. Chem. Phys*, 2000, **112**, 6472-6486.

2 C. Sun, M. S. Boutilier, H. Au, P. Poesio, B. Bai, R. Karnik and N. G. Hadjiconstantinou, *Langmuir*, 2014, **30**, 675-682.

3 K. Chae and A. Violi, *J. Chem. Phys*, 2011, **134**, 044537.

4 J. Huheey and K. Cottrell, *The Strengths of Chemical Bonds*, Butterworths, London, 1958.

5 D.-e. Jiang, V. R. Cooper and S. Dai, *Nano. Lett*, 2009, **9**, 4019-4024.

6 A. W. Hauser and P. Schwerdtfeger, *Phys. Chem. Chem. Phys*, 2012, **14**, 13292-13298.