Electronic Supplementary Information

Adsorption Behaviour of CH_4 on Microporous Carbons: Effect of Surface Heterogeneity

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Validation of computational methodology

Density functional theory (DFT)

In the current work, the equilibrium interlayer distance of perfect graphite is optimized to be 3.40 Å, consistent with the experimental value of 3.35 Å[1] and the DFT result of 3.34 Å[2] within an error of 0.2%.

Bader charge analysis

As shown in Table S1, for the Bader charge analysis in the current work, the atomic partial charges of H and O atoms in hydroxyl group are 0.359 ~ 0.552 e and -0.737 ~ -0.914 e, respectively. These results agree well with the DFT results of Wilcox *et al*[3] (0.575 e and -0.996 e corresponding to H and O atoms, respectively).

Grand canonical Monte Carlo (GCMC)

The adsorption isotherms of CH_4 in perfect graphite pore (pore width = 20.4 Å) at 313 K is chosen to compared with the results of D. D. Do *et al*.[4] Although two different force field types are used, there is a minor difference in adsorption isotherms for one-site model.

The good agreement between our result and the experimental and previous theoretical observations demonstrates the reliability of our model and levels of theory (including DFT, Bader charge analysis and GCMC).

Table S1 Bader charge analysis results of us and Wilcox *et al* for hydroxyl surface.

result	surface C			functional group	
from	direct-connected	peripheral	others	O	H
us	+0.161 ~ +0.163	+0.054 ~ +0.109	-0.016 ~ +0.020	-0.737 ~ -0.914	+0.359 ~ +0.552
Wilco	+0.355	-0.006 ~ +0.009	-0.006 ~ +0.033	-0.996	+0.575

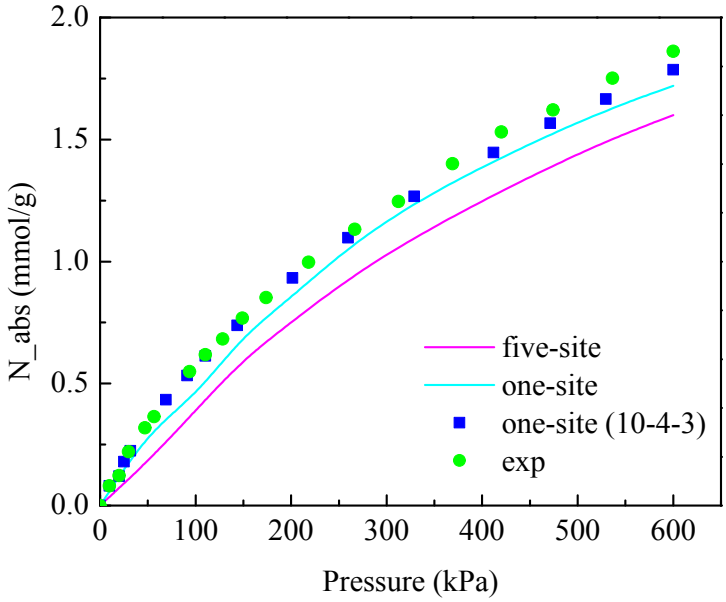

Fig. S2 Adsorption isotherms results of us and D. D. Do *et al* (one-site (10-4-3) and exp).

Bader charge analysis

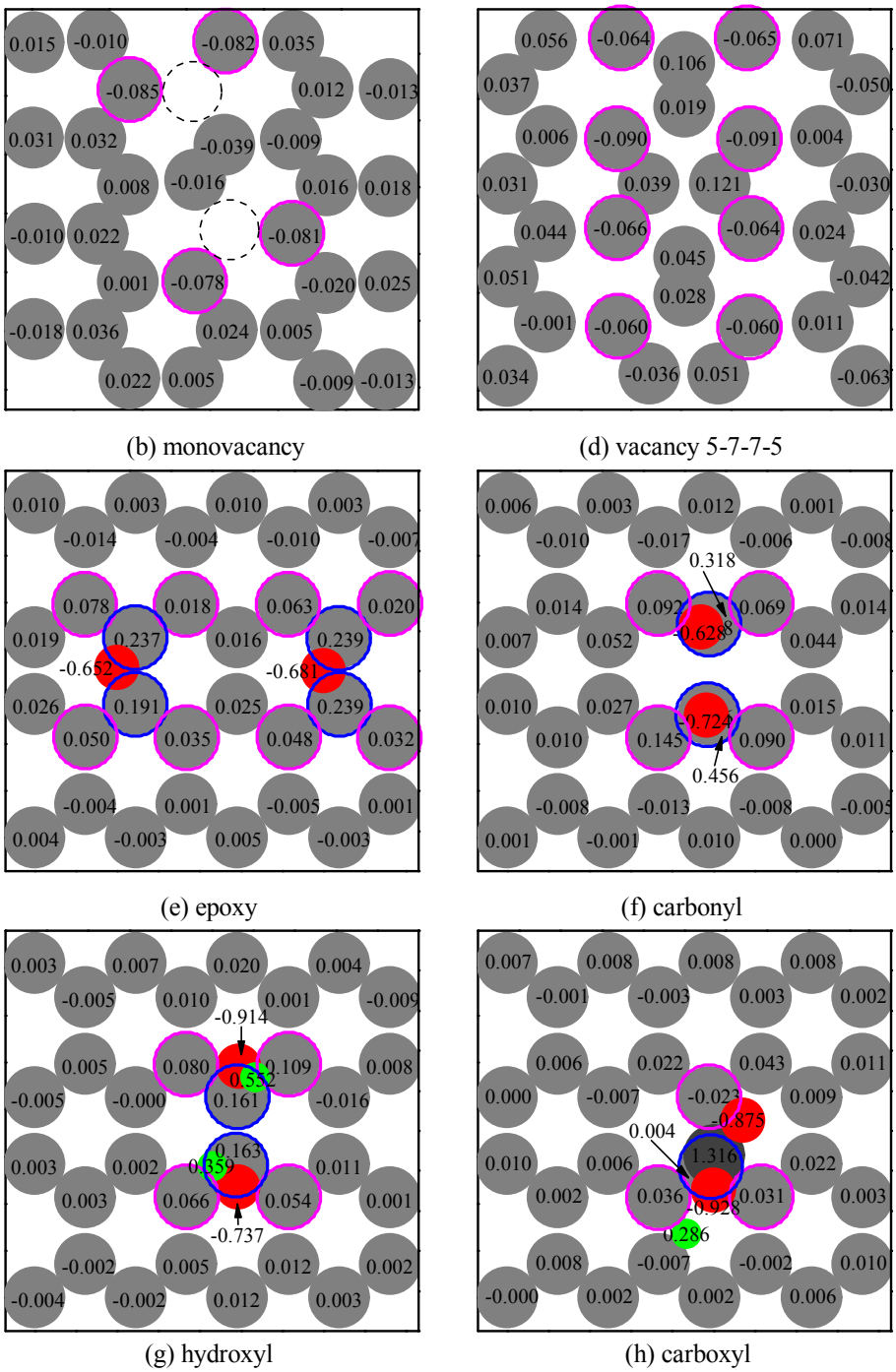

Fig. S3 Bader charge analysis results for defective and functionalized graphite surface. Color code: gray, C (graphite); dark grey, C (functional group); red, O (functional group); green, H (functional group). Graphic symbol: dotted circle, the missed C atoms of defective graphite surface; blue circle, the C atoms directly connected to the functionalized groups; magenta circle, the peripheral C atoms (the neighboring C atoms).

Computational methodology of the average density

For the primary and secondary peaks, the average density makes us understand the correlation between adsorption density and amount. The average density is calculated by the curvilinear integral and average of a certain peak. The equation used is as follows:

$$Average\ density = \frac{\int_{R(A)}^{R(B)} \rho(r)dr}{R(B)\text{-}R(A)} \quad (1)$$

where $\rho(r)$ is the CH_4 density distribution, and $R(B)$ and/or $R(A)$ denote the end and/or start distance of adsorption peak, and $R(B) - R(A)$ is the distance between sites *A* and *B* (*i.e.*, the width of adsorption peaks).

Effects of pore size and temperature on the CH_4 adsorption density

The pore size effect: In this work, several different pore sizes are assessed with the aim to study the pore size effect on the CH_4 adsorption. The density profiles along the pore radius (z-direction), based on the MD simulations, are shown in Fig. S4. We can find the density profiles in most cases show the strong peak close to the pore walls, the minor peak slightly far from the walls, and a platform region approaching the centre, that is, primary peak, secondary peak, and bulk region[5]. The adsorbed phase region is mainly composed of these two peaks. In order to directly compare the density of adsorption regions in pore space with different sizes, the detailed information is provided in Fig. S5. For H = 6.8 Å, most of the CH_4 molecules locate at the middle of the slit pore in the adsorbed phase, exhibiting the highest primary density among ten slit pores from 6.8 Å to 91.8 Å. The average density reaches up to 1.800 g/cm^3 due to the extra strong surface-surface interaction[6]. For H = 10.2 Å, only the primary peak is founded to centre at 1.587 Å, and the ensemble average density decreases to 0.798 g/cm^3. For H = 20.4 Å, usually defined as a micropore[7], double peaks appear in the density profile. This adsorbed phase extends from the pore wall to the centre, indicating that the whole pore space is just filled with the absorbed CH_4 and without bulk region exists. As for the pore size larger than 20.4 Å, all of the density profiles have the adsorbed phase layer width from 7.707 to 8.251 Å. Along with the increase of pore size, the maximum and the

average density become smaller and smaller. This is due to the fact that the CH_4-CH_4 interaction in the primary layer is stronger than that in bulk region. So, partial of the CH_4 molecules are pushed into the weak interaction bulk region.

The temperature effect: In this section, we consider the effect of temperature on the density of CH_4 in adsorbed phase. The condition involves the selected pore width of H = 20.4 Å, the average bulk density of 0.180 g/cm^3, and the temperature ranging from 298 to 403 K. Fig. S6 presents the calculated density profiles along the pore radius, and the maximum and average density in the primary and secondary regions are shown in Fig. S7. As the temperature increases from 298 to 403 K, the first maximum density and average density of primary peak show similar decrease trend. For the primary peak, the maximum density decreases sharply, from 1.125 g/cm^3 to 0.946 g/cm^3, and the average density of adsorption phase shows a decrease to a less extent, from 0.570 g/cm^3 to 0.519 g/cm^3; while the corresponding density for the secondary peak increases slightly from 0.305 g/cm^3 to 0.349 g/cm^3 and 0.246 g/cm^3 to 0.297 g/cm^3, benefited mainly from the corresponding decrease of the primary peak. This phenomenon is due to the increase of the temperature which promotes the activities of the adsorbed CH_4 molecules and thus facilitates the molecules diffusion from the high-density primary peak to the low-density secondary peak.

Therefore, H = 20.4 Å and 313 K are chosen as an optimal pore size and a representative temperature to study the effects from surface heterogeneity on CH_4 adsorption.

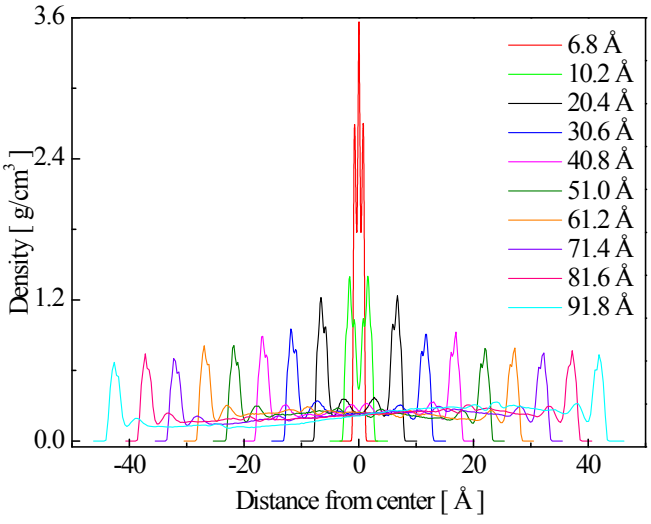

Fig. S4. Density profiles of CH_4 in perfect graphite slit pores with different pore widths (6.8-91.8 Å).

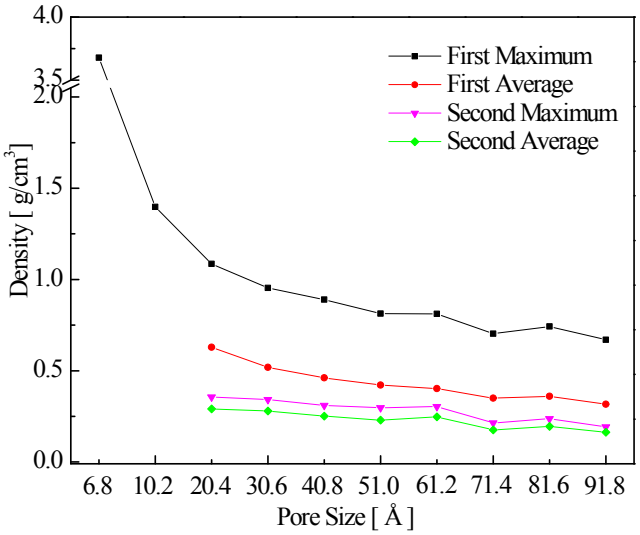

Fig. S5 Maximum and average densities of primary and secondary peaks in different pore widths (6.8-91.8 Å)

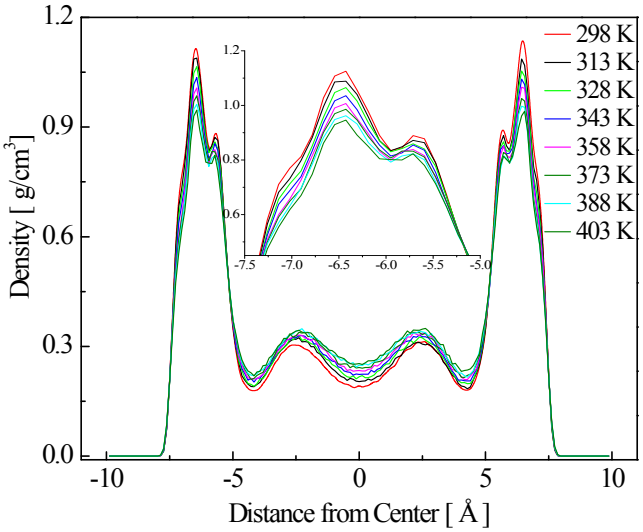

Fig. S6 Density profiles of CH_4 in perfect graphite slit pores at different temperature (298-403 K).

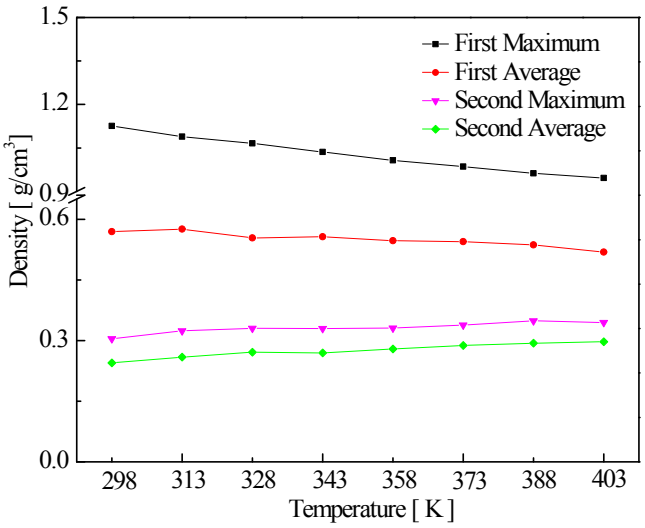

Fig. S7 Maximum and average density values of primary and secondary peaks in perfect graphite slit pores at different temperature (298-403 K).

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