

Unusual Adsorption Site Behavior in PCN-14 Metal–Organic Framework Predicted from Monte Carlo Simulation

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S Supporting Information

ABSTRACT: The adsorption equilibrium of methane in PCN-14 was simulated by the Monte Carlo technique in the grand canonical ensemble. A new force field was proposed for the methane/PCN-14 system, and the temperature dependence of the molecular siting was investigated. A detailed study of the statistics of the center of mass and potential energy showed a surprising site behavior with no energy barriers between weak and strong sites, allowing open metal sites to guide methane molecules to other neighboring sites. Moreover, this study showed that a model assuming weakly adsorbing open metal clusters in PCN-14, densely populated only at low temperatures (below 150 K), can explain published experimental data. These results also explain previously observed discrepancies between neutron diffraction experiments and Monte Carlo simulations.

A recent major advance in adsorbed natural gas technology has been the development of metal–organic frameworks (MOFs) with high methane uptake. Ma et al.¹ have synthesized a MOF material named PCN-14 that exhibits an impressive excess methane adsorption capacity of 220 cm³(STP)/cm³ at room temperature and 35 bar, which greatly exceeds the U.S. Department of Energy (DOE) target of 180 cm³(STP)/cm³. The PCN-14 sample was obtained by reacting dinuclear Cu₂(CO₂)₄ “paddlewheel” clusters with the organic linker 5,5′-(9,10-anthracenediyl)diisophthalate (adip). The Cu₂(CO₂)₄ clusters result in open metal coordination sites that are believed to intensify the adsorption of molecules. Besides this, the PCN-14 structure exhibits a topological diversity of adsorption sites, which can also help improve the increase in adsorption loading.

The interactions of methane with both metal clusters and organic linkers in PCN-14 need to be elucidated to direct experimental efforts toward new MOFs with enhanced CH₄ affinity. Moreover, force-field developments are necessary for the successful prediction of thermodynamics (in multicomponent mixtures, for example) and transport properties.

Wu et al.² recently applied several different techniques, including density functional theory (DFT), Monte Carlo simulations, and experiments (particularly powder neutron diffraction experiments using deuterated methane), in seeking to accurately describe the PCN-14 adsorption sites. The experimental data were treated and interpreted using grand canonical Monte Carlo (GCMC) simulations and DFT calculations. Adsorption sites were defined, and at the same time, the intricate topology of PCN-14 was described. One of the discrepancies found in this

study was related to the open metal coordination sites. Experimentally (powder neutron diffraction), methane presented high adsorption at the open metal coordination sites, which was also confirmed by the DFT calculations. However, the Monte Carlo simulations performed by those authors showed that the open Cu site does not act as an adsorption site. Since the force field used in that study was not previously fitted to the PCN-14 isotherm, the authors attributed this discrepancy (in the GCMC results) to the inadequacy of the force field used in the simulations.

In this study, we used the Monte Carlo methodology in the grand canonical ensemble to fit methane experimental adsorption isotherms at 150 and 290 K. With a new adjusted force field, we found that open metal coordination sites are populated at 150 K but not at 290 K. Indeed, we have identified an atypical “cooperation” behavior among PCN-14 adsorption sites.

We initially applied generic force fields (UFF³ and Dreiding⁴) to fit the isotherms at 150 and 290 K presented by Ma et al.¹ Our simulated isotherms showed that unlike those of other MOFs, the simulated isotherm of PCN-14 cannot be fitted to the experimental data using only the scaling factors of generic force fields.^{5,6} In the experimental results presented by Ma et al.,¹ we observed that the heat of adsorption decreases slowly at low methane loadings and that after a given loading (ca. 1.5 mmol/g) it gradually increases. On the basis of this information, we replaced the united-atom model of methane usually employed in the MOFs frameworks^{5,7,8} for the potential B model of Reid and Sparks.⁹ This new united-atom model has a larger value of the ϵ parameter, thus generating a higher fluid–fluid interaction, as suggested by the experimental results.

Additional adjustments were made in the parameters of the MOF structure [see the Supporting Information (SI)]. The experimental isotherms of methane in PCN-14 and the simulated ones obtained using the force field developed in this study are presented in Figure 1, which shows that the shape of experimental isotherms is nicely reproduced by the simulated isotherms.

With this fitted force field, we then proceeded to the analysis of adsorption sites. The PCN-14 unit cell (shown in Figure 2a) can be described in terms of a partial structure formed by three Cu₂(CO₂)₄ clusters linked to three adip ligands. This structure resembles a basketball basket, where the metal clusters form the basket rim and the organic linkers form the basket net. The basket is located in the small cages at the top and bottom of the squashed cuboctahedral cage defined by Ma et al.¹

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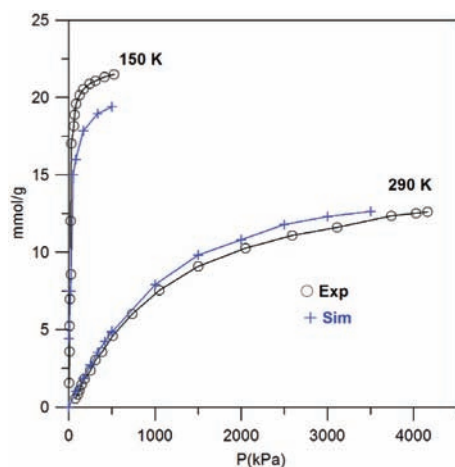


Figure 1. Simulated and experimental isotherms of methane in PCN-14 at 290 and 150 K. The experimental data were taken from Ma et al.¹ The lines are only to guide the eyes.

The rim formed by the three metal clusters resembles the zeolite oxygen windows. The two strongest adsorption sites are centrally located inside the basket rim, one just below the basket rim and the other on top of the rim (see Figure 2b). Along the z crystallographic axis of the unit cell of PCN-14, the baskets are arranged as if they are facing one another (Figure 2c). One low-energy adsorption site, IV, is located in the space between the rims, and the other low-energy site, V, can be found between each pair of baskets. Site IV is formed by a wide ring ($18 \text{ \AA} \times 18 \text{ \AA}$ center-to-center) of six adip molecules that can be seen in the crystallographic direction $[211]$. Site V consists of a smaller ring ($16 \text{ \AA} \times 14 \text{ \AA}$ center-to-center) of six metal clusters in the same crystallographic direction.

To investigate the temperature dependence of the siting of the methane molecules, we performed calculations of methane center-of-mass statistics and energy distribution in the grand canonical ensemble at 150 and 290 K for two frameworks: Cu-BTC¹⁰ and PCN-14 (see the SI). For Cu-BTC, we used the force field previously proposed by Yang and Zhong.⁷ The Cu-BTC framework was included in this study because it also contains the same dinuclear $\text{Cu}_2(\text{CO}_2)_4$ clusters and a basket partial structure similar to that in PCN-14. Indeed, Cu-BTC was also tested in the experimental neutron diffraction study.² For Cu-BTC and PCN-14 at 290 K, we did not identify methane molecules adsorbed in the open Cu sites in any simulated structure over the pressure range studied (1–3500 kPa). For 150 K, however, at 167 and 5 kPa in Cu-BTC and PCN-14, respectively, we clearly observed the open Cu sites to be populated (Figure 3).

In the unit cells of Cu-BTC and PCN-14 at 150 K, all of the adsorption sites were easily identified. At this temperature, Cu-BTC showed an interesting energy distribution (Figure 4) with four successive peaks, each corresponding to the energy of an adsorption site (I, II, open Cu, and large cage). The energy distribution of PCN-14 shows only two well-defined groups of adsorption sites with average energies separated by ~ 2 kcal/mol. The previous neutron diffraction study² also identified two different groups of adsorption sites for PCN-14 separated by the same amount of energy. Experimental studies of the mobility of methane in NaA¹¹ and NaY¹² zeolites, based on neutron scattering techniques, have shown that the ability of methane molecules to move is reduced considerably at 150 K. For NaY

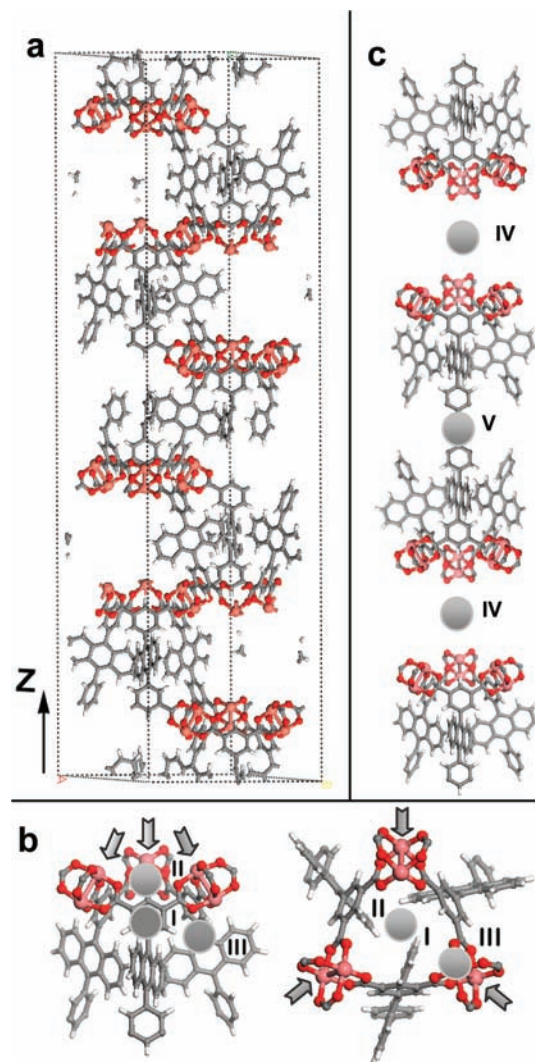


Figure 2. (a) Unit cell of PCN-14 with the basket partial structure highlighted. Red = oxygen, pink = copper, gray = carbon, and white = hydrogen. (b) Top and side view of the basket partial structure with adsorption sites I, II, and III (circles) and open Cu sites (arrows). (c) Baskets positioned along the z crystallographic axis with adsorption sites IV and V.

zeolite, for instance, no methane molecules diffuse from supercage to supercage at 100 K, while at 250 K, such motion is observed for 82% of the methane molecules.¹² Thus, at high temperatures, only the strongest adsorption sites of the PCN-14 framework have enough residence time to be revealed by the statistical probability distribution of adsorbed methane. This must be the reason that no adsorption at the open methane Cu sites at 290 K was found using Monte Carlo, and also why neutron diffraction experiments performed at low temperature identified methane around open Cu sites.

To examine further the methane siting in the open Cu site, we calculated the total solid–fluid interaction potential energy of the methane molecule in specific planes through the basket partial structure using our fitted force field. The plane that goes from the copper atoms of a $\text{Cu}_2(\text{CO}_2)_4$ cluster and crosses the center of the basket partial structure captures very well the relationship between the adsorption sites. A surprising result of the potential energy calculation is that there are no energy barriers to

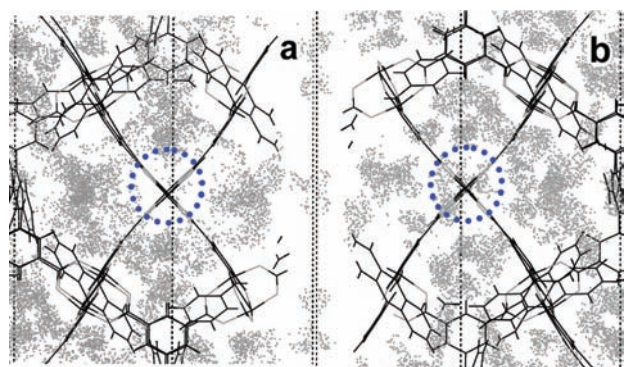


Figure 3. Probability distributions of the centers of mass of methane in PCN-14 at (a) 3500 kPa and 290 K and (b) 5 kPa and 150 K, viewed along the [211] crystallographic direction. The circles show the probability distributions of the centers of mass of methane molecules in the region where methane molecules are expected to be positioned to populate the open Cu site.

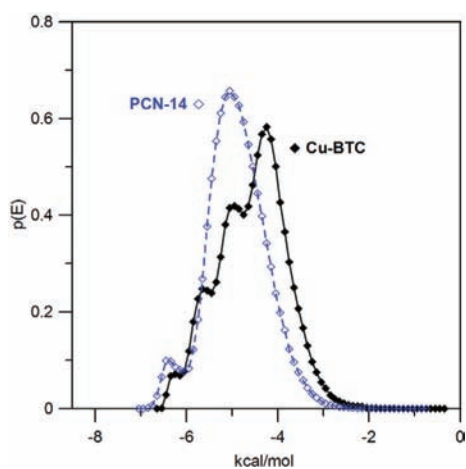


Figure 4. Energy distribution functions for methane in PCN-14 and Cu-BTC at 150 K.

jump in the basket partial structure when methane molecules go from the open Cu site (potential energy = 0.85 kcal/mol) to site II (potential energy = 3.9 kcal/mol) and then to site I (potential energy = 5.6 kcal/mol) or from the open Cu site to site III (potential energy = 3.5 kcal/mol) (Figure 5a). This gives rise to an unusual adsorption site behavior. The open Cu sites act as the first agents in the process of adsorption of methane molecules. Above the basket rim, they send molecules to site II or I. Below the basket rim, the open Cu sites send molecules to site III. To the best of our knowledge, this site interrelationship has not been previously evidenced in molecular sieves.

Assuming that the parameters for the copper atoms in the $\text{Cu}_2(\text{CO}_2)_4$ cluster may be underestimated, we decided to test one of the highest well-depth values suggested for the copper atom by generic force fields, which proposes a well depth (ϵ) of 3.81 kcal/mol (CPFF force field¹³), as opposed to only $\epsilon = 0.006$ kcal/mol used in our force field. Applying this well depth to the same plane previously presented gave a very interesting result from the potential calculations. The open Cu site potential showed a poor improvement, while the potential of site II increased considerably (Figure 5b). This result would suggest that stronger Cu parameters do not give rise to stronger open Cu

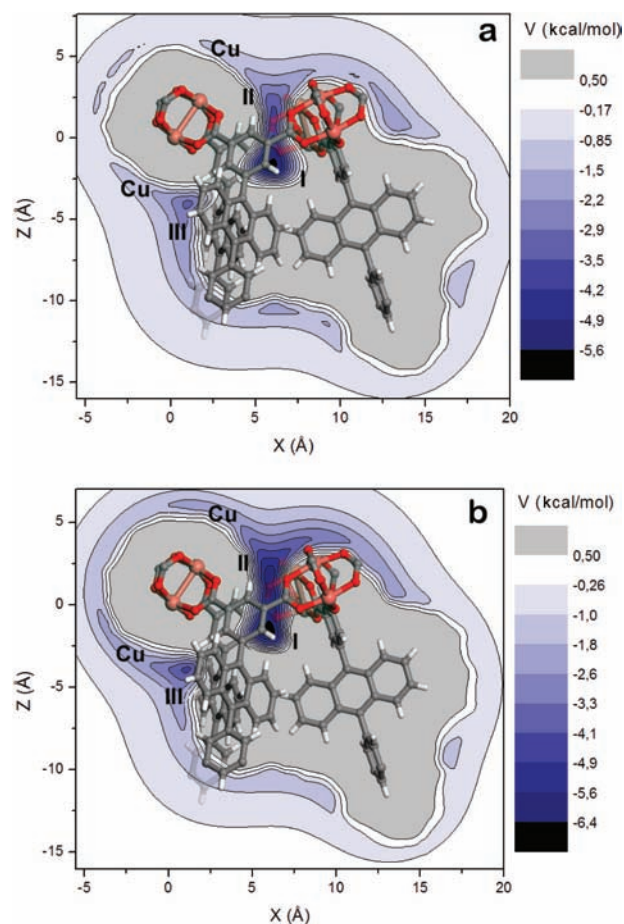


Figure 5. (a) Contour plot of the calculated potential energy of methane molecules in the xz plane that goes from the copper atoms of a $\text{Cu}_2(\text{CO}_2)_4$ cluster, crossing the center of the basket partial structure. $\epsilon_{\text{Cu}} = 0.006$ kcal/mol. (b) Contour plot of the potential energy for $\epsilon_{\text{Cu}} = 3.81$ kcal/mol. Red = oxygen, pink = copper, gray = carbon, and white = hydrogen.

sites. Because of the particular arrangement of copper atoms in the basket partial structure, increasing the well-depth parameter for the copper atoms benefits only adsorption site II.

On the basis of these results, we can assert that the open Cu sites in PCN-14 are weak methane binding sites. Karra and Walton⁸ also had a similar conclusion with respect to the open Cu site in the Cu-BTC structure. In their study of CO/CH_4 mixtures, CO molecules were found to adsorb near the metal sites, while methane molecules were uniformly dispersed throughout the unit cell.

In conclusion, this study has proposed a new force field for the methane/PCN-14 system that gives improved fitting between experimental and simulated isotherms. The methane siting investigation showed that methane populates the open Cu sites at low temperature (150 K) but not at high temperature (290 K). This result underlines the necessity of mobility studies at different temperatures in frameworks with multiple adsorption sites. Methane adsorption sites in the basket partial structure present an unusual behavior with no energy barriers between weak and strong sites, allowing open Cu sites to perform as first attractors that direct methane molecules to the other neighboring sites. Open Cu sites can be classified as weak methane adsorption sites in PCN-14 frameworks. Multiple adsorption

sites (six in all) and efficient linking between them can explain the high methane uptake in the PCN-14 framework.

■ ASSOCIATED CONTENT

S Supporting Information. Models and Lennard-Jones parameters, PCN-14 structural details, computational methods, and additional simulated results for methane adsorption. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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