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GCMC simulations of dynamic structural change of Cu–organic crystals with N₂ adsorption

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N₂ adsorption on Cu–organic crystals [Cu(bpy)₂(BF₄)₂] (bpy = bipyridine) at 77 K begins suddenly at $P/P_0 = 0.1$. This unique adsorption is named gate adsorption. Gate adsorption is associated with the change of crystal structure from GCMC and dynamic GCMC simulations. An expansion of 10% opens internal pore spaces in the crystal, giving rise to gate adsorption. The complete filling of the internal spaces with N₂ molecules induces an expansion of 30%.

Keywords: Metal–organic framework; Gate adsorption; GCMC simulation; Structure change

1. Introduction

Metal–organic framework (MOF) materials have attracted great attention due to their potential application in gas separation, storage, catalysis, and magnetism, and due to the ease of designing materials with appropriate structure and functionality [1, 2]. Although several structure and adsorption studies have been conducted on MOF materials [1, 3], the adsorption mechanism on these materials is not well understood at a molecular level.

The Cu–organic crystal [Cu(bpy)₂(BF₄)₂]_n (bpy = bipyridine) has a two-dimensional square grid structure, consisting of Cu(bpy)₂ and BF₄ groups positioned vertically with respect to the Cu ion [4]. The original structure of the Cu–organic crystal has isolated voids where N₂ molecules cannot access [4]. However, the crystal can adsorb a substantial amount of gas above a fixed pressure, called the gate pressure. For instance, adsorption isotherms of N₂ at 77 K and CO₂ at 303 K on the Cu–organic crystal have steep adsorption and desorption jumps named gate adsorption at gate pressures

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inherent to the adsorbate molecule [4]. The mechanism of gate adsorption has been studied using an adsorption measurement, powder X-ray diffraction (XRD), and IR spectroscopy. Although powder XRD patterns between Cu–organic crystals with and without adsorbed N₂ have different peaks, an exact structure change cannot be determined due to the pulverization after adsorption even using the diffraction simulation technique. The mechanism of this new type of adsorption should be elucidated for the design and for the synthesis of the MOF structures fit for a specific function.

Molecular simulation is quite effective in understanding the gas adsorption properties of rigid MOF materials [5, 6]. Grand canonical Monte Carlo (GCMC) simulation can evaluate the amount of equilibrium adsorption at an equilibrium pressure. However, molecules can be adsorbed even in closed pores by the GCMC simulation procedure. On the other hand, dynamic MC simulation is effective for the determination of accessibility of a given pore, although it cannot provide the amount of equilibrium adsorption [7, 8]. Recently, dynamic MC simulation extended to the grand canonical ensemble was applied to MOF systems. A combined study using GCMC and dynamic GCMC simulations should give us an insight into the gate adsorption mechanism of Cu–organic crystals.

Although CO₂ shows more vertical gate adsorption than N₂, the molecular simulation approach for N₂ is well established. In this article, GCMC and dynamic GCMC simulations have been executed for the prediction of the gate adsorption mechanism of N₂ on Cu–organic crystals.

2. Experiment and simulation

Cu–organic crystals were pretreated for 2 h at 373 K and 1 mPa prior to N₂ adsorption. The adsorption isotherm was measured over the pressure range of 10⁻⁶ to 0.1 MPa at 77 K.

GCMC and dynamic GCMC simulations were conducted at a fixed temperature and chemical potential (that is pressure) [9]. Each calculation for the Cu–organic crystals of a different expansion in the *c*-direction included 1 × 10⁶ configurations to ensure equilibrium in the GCMC simulation, and 450 ps in the dynamic GCMC simulation. We used a rectangular cell 2.261 nm × 2.293 nm × *l_c* for the calculation under periodic boundary conditions. Here, fixed *l_c* parameters were selected from 1.896 (original structure) to 2.844 nm (50% expansion) for each calculation. The cell size in the dynamic GCMC simulation was 2³ times larger than the unit cell in GCMC simulation.

An N₂ molecule is treated as a two-centred Lennard-Jones molecule with quadrupole represented by four Coulomb interactions [10]. The potential parameters of the Cu–organic crystal, which are based on the reference papers [11, 12], were determined by a universal force field calculation.

3. Results and discussion

Each layer in the Cu–organic crystal has coordination bonds between the Cu ion and bipyridine. The Cu²⁺–2 × BF₄⁻ bond is presumed to be a perfect ionic bond.

Dispersion forces are the main part of the interlayer interaction and the interlayer distance is varied in this simulation. The layer stability with an expansion percentage of the interlayer determined from the calculation of the layer potential shows that the potential energy profile has double minima at -4% and 4% expansion; in this way, the original structure fluctuates slightly in the interlayer distance. According to the potential profile, a slight expansion of more than 4% does not seriously increase the repulsive interaction. The thermal energy at 77 K can induce an expansion of the layer structure by at least 8% .

Figure 1(a) shows an experimental adsorption isotherm of N_2 on Cu-organic crystals. The experimental isotherm indicates that N_2 molecules are not adsorbed below the gate pressure of $P/P_0=0.1$ and a steep rise in adsorption begins at the gate pressure of the adsorption branch. The adsorbed amount changes with the expansion of the interlayer distance of the Cu-organic crystal, as shown by GCMC and dynamic GCMC simulations (figure 1b). The adsorbed amount in GCMC simulations linearly increases with the expansion percentage. A comparison of the simulated adsorbed amount and the experimental saturated adsorption amount indicates 30% expansion for the complete filling of the internal void spaces. However, the GCMC simulation cannot provide information on connectability of the internal void to the surroundings. Consequently we need more information from the dynamic GCMC simulations. There are two jumps in adsorption at 8% and 20% expansion (figure 1b). The first jump at 8% expansion should be a trigger for the gate adsorption. Although the original structure of the Cu-organic crystal has no open pore spaces for N_2 molecules, the thermal fluctuation of the structure under sufficient gas pressure should induce the first jump at 8% expansion, following a further adsorption jump; finally a more stable structure is constructed after further N_2 adsorption and a 30% expansion of the Cu-organic crystal. The corresponding adsorption behaviour was suggested in the observed adsorption branch.

Snapshots of the N_2 molecules in the Cu-organic crystals are shown in figure 2 as a function of the expansion percentage from the dynamic GCMC simulations. Cu-organic

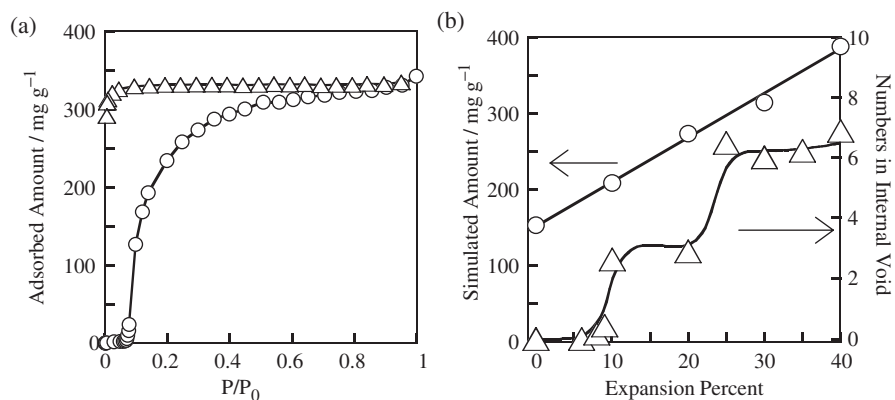


Figure 1. Adsorption isotherm of N_2 for adsorption (\circ) and desorption (\triangle) courses from experiment (a). Simulated adsorption amounts versus expansion percentage using GCMC simulation (\circ) and dynamic GCMC simulation (\triangle) (b).

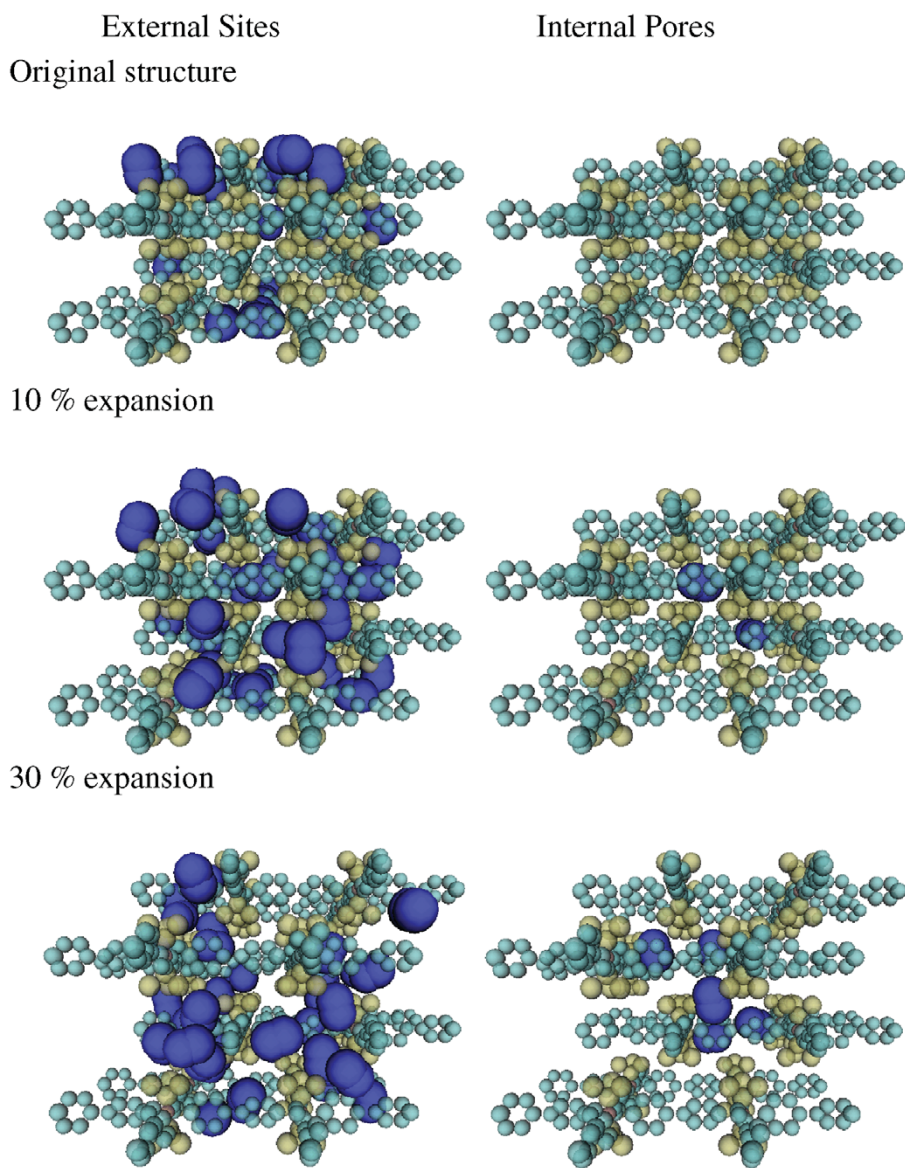


Figure 2. Snapshots of N_2 at 0%, 10%, and 30% expansion of Cu-organic crystals from dynamic GCMC simulations. This figure is available in colour online.

crystals with expansion of 10% and 30% can adsorb N_2 in the internal pores, while the N_2 molecules do not penetrate into the internal pores of the original structure of the Cu-organic crystal. Figure 3 shows snapshots of molecules in an equilibrium state in the Cu-organic crystals expanding by 30% from the GCMC simulations. N_2 molecules are highly packed in the framework to form a new stable structure, corresponding to the $[Cu(bpy)_2(BF_4)_2](N_2)_6$ formula. Thus, the critical expansion brings about the formation of a clathrate compound with adsorbed N_2 molecules.

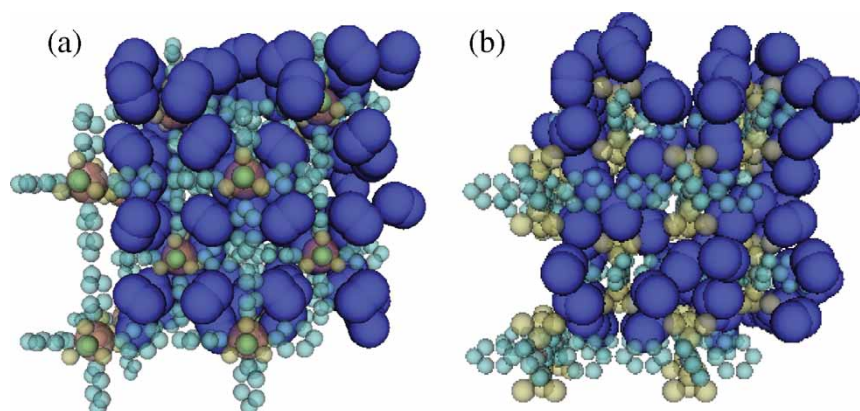


Figure 3. Snapshots of N_2 at 30% expansion of Cu-organic crystals from GCMC simulations from the *c*-axis (a) and *a*-axis (b) viewpoints. This figure is available in colour online.

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