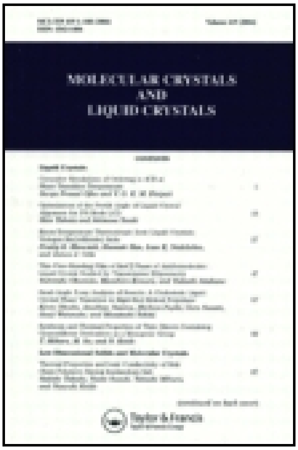

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Molecular Simulations of Argon, Nitrogen, and Hydrogen Adsorption in Microporous Complexes

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The gas-adsorption behavior in microporous transition-metal complexes was investigated by the use of Monte Carlo simulations. We prepared the models of Cu_3TMA_2 and Zn(BDC), which were crystallographically determined. The pressure dependence of the amount of adsorbed gases (argon, nitrogen, and hydrogen) was simulated at the boiling temperature of the gases. In the gas adsorption in Cu_3TMA_2, the effect of the charge distribution on the framework is negligible. However, the coordinating water narrows the cavity and stabilizes the adsorbed argon molecules. The amounts of adsorbed gases and the isosteric heats were calculated for Cu_3TMA_2 and Zn(BDC) and the pictures of probability distribution of gases in the cavity were obtained. The probability distributions indicated that the adsorbed gases tend to be distributed as a zig-zag column in the capillary of Zn(BDC) and as a shape like a four-leaf clover avoiding the four benzene rings in the narrow cavity of Cu_3TMA_2.

Keywords: molecular simulation; Monte Carlo calculation; gas adsorption; microporous transition-metal complex; argon; nitrogen; hydrogen

INTRODUCTION

The recent growth in the synthesis of porous materials based on building blocks of transition-metal complexes has provided new functions such as molecular adsorption. Previously, we reported that dinuclear transition-metal carboxylates (dicarboxylates (Cu(II)[1], Mo(II)[2], and Ru(II, III)[3]) and monocarboxylates (Rh(II)[4] and Cu(II)[5])) reversibly adsorb a large amount of gases such as N_2, O_2, Ar, and Xe. These are known as being a useful adsorbent for storing methane under low pressure.[6] In 1995, after we had applied to patent the microporous complexes, Kitagawa[7], Yaghi[8], and Williams[9] reported gas-adsorption phenomena of similar microporous complexes.

The Monte Carlo calculations give a view of gas-adsorption behavior on the molecular level. Herein, computer simulations of microporous transition-metal complexes were carried out.

EXPERIMENTAL

Model Preparation

Copper(II) trimesate (1,3,5-benzenetricarboxylate) (Cu_3TMA_2) reported by Williams[9] was selected as the adsorbent in the present simulation because this complex has a rigid three-dimensional structure and ideal symmetry (P_{21c}). The framework of the crystal structure was used after removal of water molecules from the cavity. A model with axial coordinating water was used after optimization. Additional computations were performed at the B3LYP by the use of the Tatewaki-Huzinaga MIDI plus Hays' diffuse d-basis set: (533(21)/53(21)/(41)) for Cu and 4-31G basis set for other atoms. The Gaussian94 program was used for this calculation.

In addition, the crystal structure of zinc(II) terephthalate (1,4-benzenedicarboxylate) (Zn(BDC)) reported by Yaghi[8] was also used for the simulation after the removal DMF molecules from the cavities.

Molecular Simulation of Gas Adsorption

The molecular simulation of gas-adsorption phenomena performed by MM, MC and MD calculations with the aid of a Cerius[2] program package introduced a general FF parameter set of "UNIVERSE-OFF 1.02"[10]. To enable the calculation of adsorption isotherms, the simulations werre performed in the grand-canonical ensemble. Smit reported that this operation gave comparable results to the experimental measurements for alkanes adsorbed in zeolites.[11] The simulations of the adsorption isotherms were performed in equilibration and production cycles (3 x 10^6 cycles) at the boiling temperatures of each gases.

We used simulation cubic boxes. The dimensions of the simulation box were a=b=c= 26.343 Å (1x1x1 cell) for Cu_3TMA_2 and 2a= 13.436, b= 15.488, c= 12.430 Å (2x1x1 cells) for Zn(BDC). Periodic boundary conditions were set during simulation. The potential in the complex is truncated at 20 Å for Cu_3TMA_2 and 6.0 Å for Zn(BDC).

RESULTS AND DISCUSSION

The microporous Cu_3TMA_2 has two types of channels as shown in Figure 1. The pressure dependence of the isosteric heat and the loading of argon molecules in the unit cell at the boiling temperature of argon are shown in Figure 2. The curves show two steps in the adsorption process. This step indicates the existence of two gas adsorbing processes for Cu_3TMA_2. The picture of the probability distribution revealed that argon gas molecules tend to be adsorbed in the narrow cavities in the first adsorbing process. The adsorbed gases tend to be distributed as a shape like a four leaf clover avoiding the four benzene rings in the narrow cavity of Cu_3TMA_2. (See Figure 1.) Accounting for the influence of the charge on the framework in this simulation, three models were prepared for dried Cu_3TMA_2 with different charges determined by *ab initio* calculations. (See Table 1.) The three models demonstrated highly

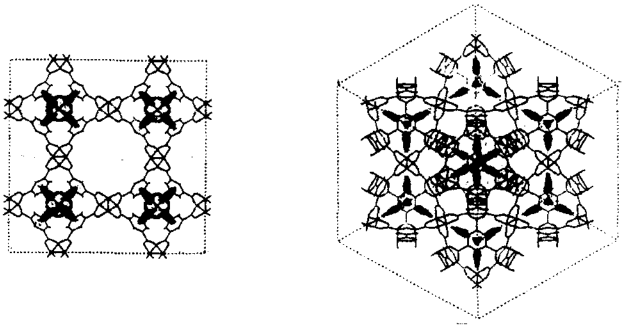
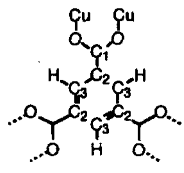


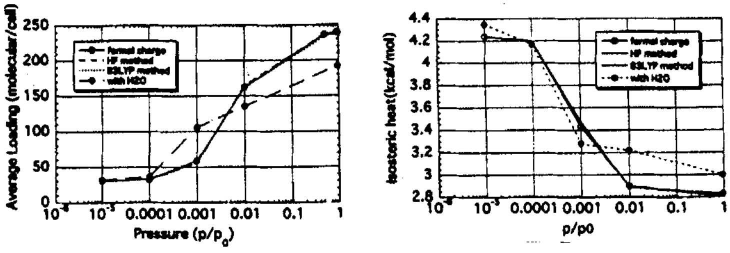
FIGURE 1. Crystal model of Cu_3TMA_2. (The probability distribution of loaded gas molecules is pictured as a cloud of dots)

TABLE I. Charge distribution for three models.

	Cu	O	C_1	C_2	C_3	H
formal charge	+2	-0.5	0	0	0	0
HF	+1.22	-0.82	+1.01	-0.82	-0.00	+0.25
B3LYP	+0.63	-0.53	+0.65	+0.01	-0.07	+0.16



similar adsorption behavior. However the effect of axial coordinating water is obvious in the pressure dependence of the amount of adsorbed gas. The amount of loaded argon molecules increased early at $p/p_0 = 1.0 \times 10^{-2}$ and the saturated amount is smaller than that for dried Cu_3TMA_2. In the high-pressure region, the larger isosteric heat of adsorbed argon is observed for Cu_3TMA_2 with axial coordinating water. Judging from these results, the coordinating water narrows the cavity and stabilizes the adsorbed argon molecules. In this simulation, the argon adsorption phenomenon for the microporous complex predominantly depends not on the charge distribution on the framework but on the cavity structure.



(a) (b)

FIGURE 2. Pressure dependence of amount of adsorbed argon molecules (a) and isosteric heat of adsorption (b).

The simulations for zinc(II) 1,4-benzenedicarboxylate were also carried out. This complex has one-dimensional channels made by the stacking of two-dimensional lattices. The probability distributions indicated that the adsorbed gases tend to be distributed as zig-zag columns in the capillary of Zn(BDC). (See Figure 3.)

The partial results of adsorption simulations for argon, nitrogen, and hydrogen are summarized in Table 2. The isosteric heats in all cases are small in the range of the values for the phisisorption (< 10 kcal mol^{-1}). In the simulation for Zn(BDC), no significant change of isosteric heat of adsorption is observed under different pressures. (See Table II.) This result indicates the adsorbing site of Zn(BDC) homogenity to gas adsorbates due to the capillary structure.

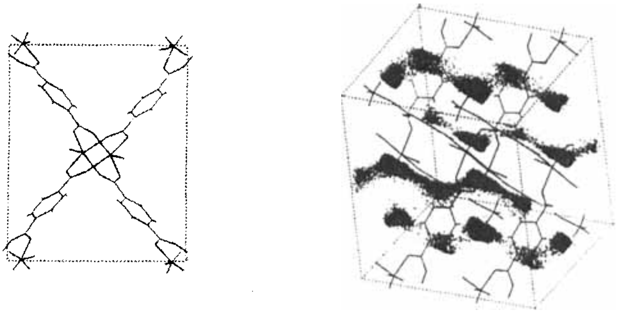


FIGURE 3. Crystal model of Zn(BDC). (The probability distribution of loaded gas molecules is pictured as a cloud of dots)

TABLE II. Amount of loaded gas molecules and isosteric heat of adsorption at the boiling temperature of gases.

Complex	Loaded gas	Pressure (p/p_0)	
		9.87 x10^{-6}	0.95
Cu$_3$TMA$_2$	Ar (at 87.28 K)	30.47[a] (4.24)[b]	239.82 (2.83)
	N$_2$ (at 77.35 K)	—[c]	210.14 (2.65)
	H$_2$ (20.28 K)	—[c]	451.02 (1.61)
Zn(BDC)	Ar (at 87.28 K)	6.24 (3.52)	23.22 (3.51)
	N$_2$ (at 77.35 K)	9.87 (3.44)	16.98 (3.43)
	H$_2$ (20.28 K)	41.93 (2.14)	43.34(2.14)

[a]The averaged amount of loaded gas molecules in the box, [b]isosteric heat of adsorption gas (kcal mol^{-1}), [c]not simulated.

The saturated amounts of loaded nitrogen are 210.14 for Cu$_3$TMA$_2$ and 16.98 for Zn(BDC) at p/p_0= 0.95. These amounts are translated to 440 cm^{3}g^{-1} and 180 mgg^{-1}, respectively. The amounts are about twice the amounts of 215 cm^{3}g^{-1} and 75 mgg^{-1} experimentally observed for Cu$_3$TMA$_2$[8] and Zn(BDC) [8], respectively. The amount of adsorbed hydrogen is about twice of argon and nitrogen in all cases.

The novel adsorbent system of transition-metal complexes is an exciting area of complex chemistry. Considering the nature of a transition-metal complex, synthetic efforts can provide new research areas in solid state physics and chemistry. Further investigations are underway in our group.

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