

Research Article

High CO₂ Adsorption Enthalpy Enabled by Uncoordinated N-Heteroatom Sites of a 3D Metal-Organic Framework

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Received 11 October 2019; Accepted 28 November 2019; Published 21 December 2019

Guest Editor: Hu Li

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A 3D metal-organic framework (MOF), Mn₂L₂(H₂O)₂ · (DMF) {H₂L = 5-(Pyridin-2-yl)-3, 3'-bi (1H-1,2,4-triazole)} (**1**) with uncoordinated N-heteroatom sites, has been obtained through hydrothermal method and structurally characterized by X-ray structural analysis, powder X-ray diffraction (PXRD), and thermal analysis (TGA). The framework of compound **1** exhibits fascinating adsorption properties and shows high adsorption enthalpy of CO₂. The experimental results prove which uncoordinated nitrogen heteroatom sites can markedly increase the reciprocity between host frame and CO₂ at room temperature.

1. Introduction

Biomass is a sustainable material, which has been developed as a promising feedstock for producing biofuels, and carbon dioxide (CO₂) from the burning of biofuels, as well as fossil oil, is considered as the main component of all the gases that cause the greenhouse effect resulting in various kinds of environmental unsteadiness [1–4]. Captured CO₂ has industrial, economical, and social importance in decreasing CO₂ emissions and in alleviating greenhouse effect. Due to its high specific surface area and adjustable structures, MOFs are certainly very promising as CO₂ adsorbents materials have been investigated over the last couple of decades. Numerous types of research on MOFs have illustrated the great potential for storage and separation [5–12]. A recent effort to improve the ability of MOFs to capture CO₂ is that increase the number of uncoordinated nitrogen atoms in the metal-organic frame [13–16], the enthalpy of CO₂ can be augmented due to the uncoordinated N-heteroatom sites of ligands [17, 18].

We noticed an interesting framework Mn₂L₂(H₂O)₂ · (DMF) reported by Dong et al. [19], which is constructed by Mn salt and H₂L ligand. As shown in Figure 1, the Mn center is octahedrally coordinated by

one O atom from the terminal coordinated water and five N atoms from three different L ligands. Five of seven N atoms of the L ligand coordinate to three Mn centers, among which N1, N2, N4, and N6 atoms are in chelating mode, and N7 atom is in monodentate mode. Compound **1** has a 3D open framework including 1D channel and rich uncoordinated N-sites. Through the calculation of the PLATON program [20], the free solvent-accessible pore volume ratio in compound **1** is about 49.7% without taking into account the guest molecules. However, the microporosity of compound **1** has never been researched (the pore size distribution of the compound **1** is shown in Table 3S). Herein, we study the influence of uncoordinated N-heteroatom sites of compound **1** on the uptake and adsorption enthalpy of CO₂. As expected, it has high amusing adsorption properties and shows high adsorption enthalpy of CO₂ at ambient temperatures. In the conditions we adopted, the N-heteroatom which is uncoordinated can observably enhance the interaction between host framework and CO₂.

2. Experimental

2.1. Synthesis of Mn₂L₂(H₂O)₂ · (DMF). Compound **1** was synthesized according to the reported method [19]. The mixture of MnSO₄ · H₂O (0.0160 g, 0.1 mmol), H₂L (0.0213 g,

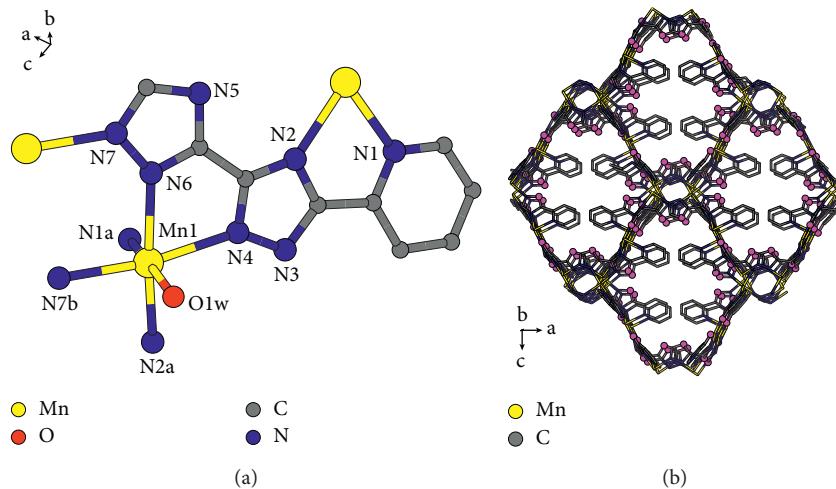


FIGURE 1: (a) Coordination environment of Mn (II) in compound 1; (b) the 1D channel of compound 1 (the pink atoms stand for uncoordinated N sites).

0.1 mmol), DMF (4.0 ml), and H₂O (4.0 ml) in a 25 ml Parr Teflon-lined stainless steel autoclave, heated at 160°C for 3 days, and then allowed to cool slowly to indoor temperature. Colorless octahedron crystals were acquired, rinsed with DMF, and dried at ambient temperatures. X-ray molecular structure analysis indicates that compound 1 in the orthorhombic I41, a space group, is identical to the reported one (crystal data of compound 1 are shown in Tables 1S and 2S). Elemental analysis (EA) for compound 1 C₂₁H₂₁Mn₂N₁₅O₃ (641.41) were given as follows: calculated: C 39.33, H 3.30, and N 32.76; found: C 39.14, H 3.43, and N 33.96; IR (KBr pellet, cm⁻¹) for compound 1: 3370 (m), 1656 (w), 1610 (w), 1495 (w), 1419 (w), 1120 (s), 818 (m), 646 (m), and 507 (m).

2.2. Preparation of Activated Sample. Supercritical CO₂ activation experiments were accomplished on Tousimis™ Samdri® PVT-30. Ahead of activation, samples were thoroughly washed with DMF. Sample 1 was wrapped with a toilet paper and fixed by Flament, and then the sample was put in a tube and placed into the chamber of the supercritical drier. The chamber was charged by dry liquid CO₂ (99.8%), and the sample tube was permitted to purge for 5 min every 30 min. During the process, the chamber temperature was kept at ~0–10°C. Four hours later, the temperature of the chamber was raised to ~38°C, and the same chamber temperature was kept for one hour followed by slow venting one night. As-synthesized samples were soaked in liquid CO₂ at high pressure over the course of hours and then under dynamic vacuum conditions to form activated sample.

3. Results and Discussion

3.1. The Powdered X-Ray Diffraction and Thermogravimetric Analysis. It can be known that the compound 1 is the pure phase because the experimental PXRD patterns confirm well with the graph simulated from the research results (Figure 2(a)). Thermal analysis (TGA) in N₂ ambience with a

heating rate of 10°C/min was done on a polycrystalline sample to study the thermostability of compound 1 from 25 to 800°C (Figure 3). The primary sample 1 indicated the first weight decrease in 6% takes place in the range of 30–100°C, corresponding to the release of surface solvent molecules and water molecules in the channel. The second weight decrease in 16% occurs at 100–200°C, which can owe to the loss of DMF molecules. The third weight decrease in 7% occurs at 200–450°C, which could be caused by the lost of coordinated water molecules. After this temperature, the framework starts to collapse.

3.2. The Study of Porosity. In order to evaluate the permanent porosity, N₂ adsorption and CO₂ adsorption experiments were carried out. Prior to gas adsorption, the sample was activated by supercritical CO₂ (SCD) methods. N₂ adsorption experiment at 77 K exhibits type I sorption isotherms, which is particular of porous materials. The maximum N₂ is 116.45 cm³/g at 744.6 mmHg (Figure 4), corresponding to Langmuir and BET surface areas which were 326.25 and 232.48 m²/g, severally. However, obvious hysteresis loop was observed. The possible reason is due to the flexibility of skeleton based on weak coordination bond because of Mn1 connection through monodentate coordination with N7, and the single bond between Mn1 with N7 can freely rotate. From the PXRD patterns between the as-synthesized and activated samples, we can see that the main peaks of compound 1 shift to high angles (Figure 2(b)), which reflected the flexibility of the framework.

The presence of the permanent porosity and oofy uncoordinated N-heteroatom sites indicates that compound 1 may have great potential for the CO₂ capture adhibition. Single-component CO₂ sorption isotherms were measured at 273 K and 298 K (Figure 5(a)). A hysteresis loop was also observed. The CO₂ uptake values were 32.4 cm³/g at 273 K, and 20.85 cm³/g at 298 K, respectively. The value of the uptake (32.4 cm³/g) is higher compared with numerous

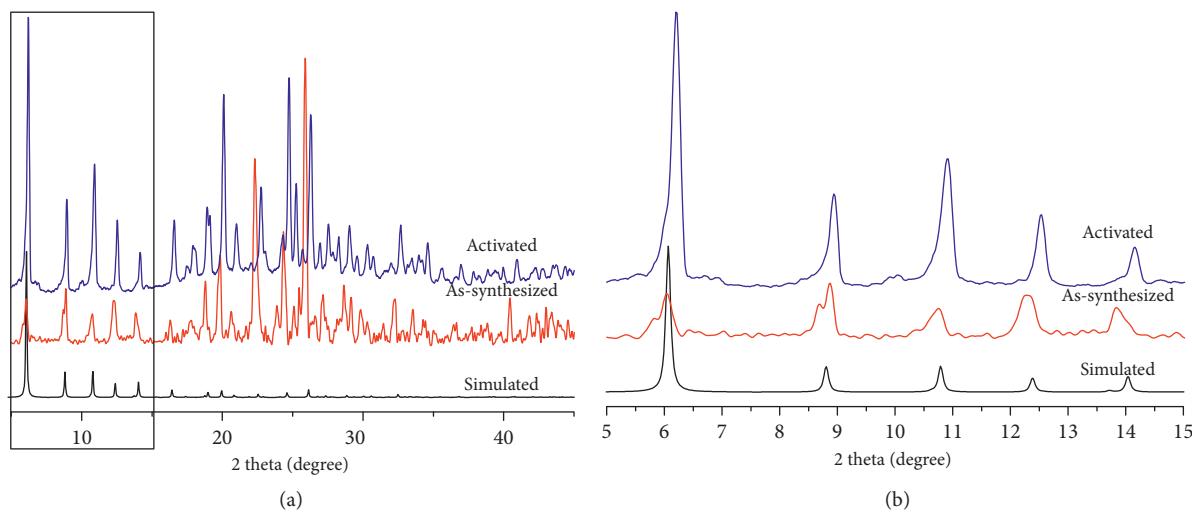


FIGURE 2: (a) The powder XRD patterns of compound **1** under different conditions. (b) The amplification of the 2theta in the range of 5–15 degrees.

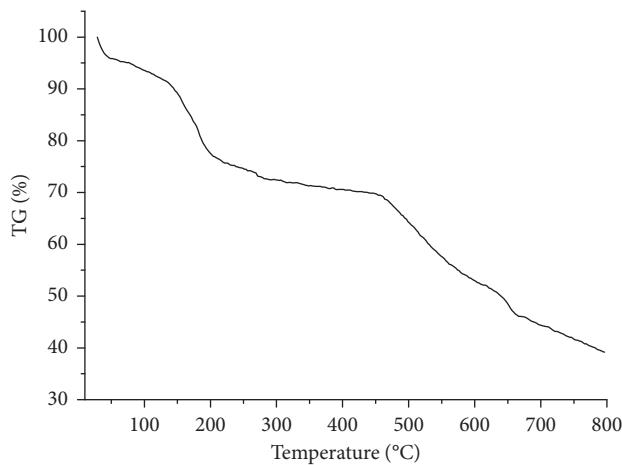


FIGURE 3: The TGA of compound **1**.

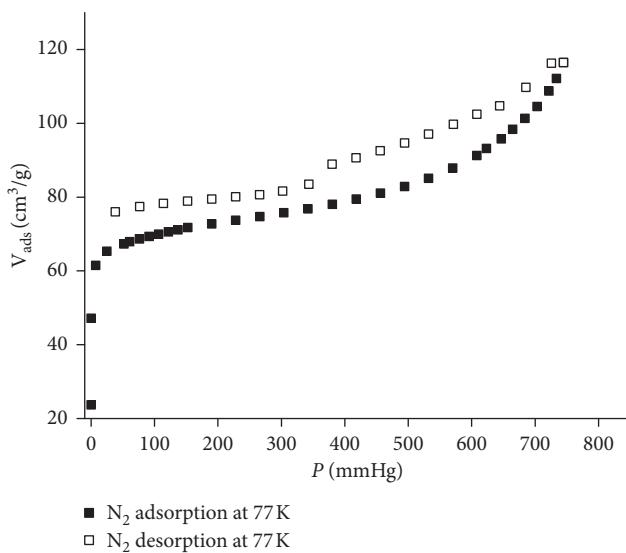


FIGURE 4: N₂ adsorption isotherms for compound **1** at 77 K.

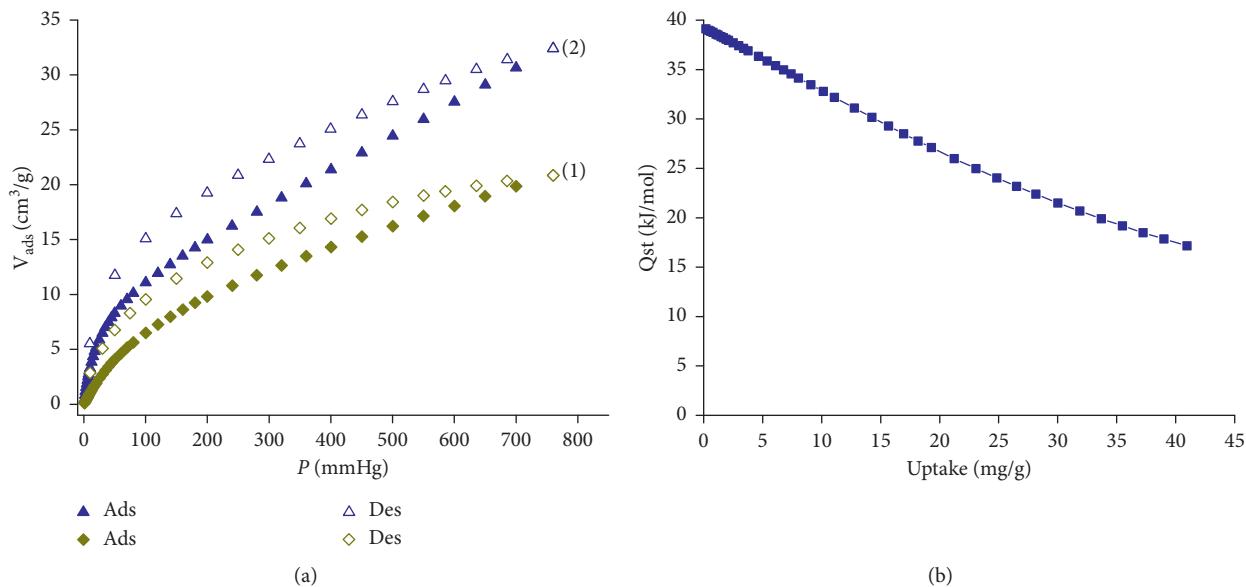


FIGURE 5: (a) CO₂ adsorption isotherms for compound 1 at 298 K (1) and 273 K (2) (b).

famous porous materials without uncoordinated N-sites, for instance ZIF-8, ZIF-68, ZIF-69, and ZIF-71 [21, 22].

In order to measure the powerful affinities to CO₂, the enthalpy of CO₂ adsorption for compound 1 was calculated by using the virial equation from the adsorption isotherms at two different temperatures (273 and 295 K). At zero loading, the enthalpy of CO₂ adsorption is 39.1 kJ/mol for compound 1 (Figure 5(b)), which is also higher than most of the famous MOFs, such as MOF-5, IR-MOF-3, MOF-253, and bio-MOF-1 [23–26]. These results suggest the N-heteroatom which uncoordinated can markedly enhance the binding strengths of CO₂ gas molecules with the framework.

4. Conclusion

In summary, here, we reported the gas adsorption of a microporous MOF containing N-heteroatom. In the conditions we adopted that the N-heteroatom which is uncoordinated can markedly enhance the interaction between the host framework and CO₂ under ambient conditions.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was financially supported by the Youth Growth Science and Technology Personnel Foundation of Guizhou Education Department (no. KY[2018]331).

Supplementary Materials

Crystal data and structure refinement parameters for compound 1 is shown in Table 1S, and the selected bond lengths (Å) and angles (°) for compound 1 are shown in Table 2S. The X-ray molecular structure analysis indicates that compound 1 is in the orthorhombic I41, a space group. The pore size distribution of the compound 1 is shown in Table 3S. (*Supplementary Materials*)

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