



A microporous metal–organic framework for selective C₂H₂ and CO₂ separation



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ABSTRACT

A quartzlike metal–organic framework with interesting one dimensional channel has been synthesized. It exhibits considerable acetylene and carbon dioxide uptake of 41.5 and 24.6 cm³ g⁻¹, respectively, and relatively high selectivity for separation of C₂H₂/C₂H₄, C₂H₂/CH₄, CO₂/CH₄ and CO₂/N₂ at ambient condition.

1. Introduction

Metal-organic frameworks (MOFs) are a new type of functional porous materials consisting of metal ions or metal clusters connected by multidentate organic linkers via coordination bonds. Compared to conventional porous materials such as activated carbons and zeolites, MOFs are unparalleled for their uniform pore structures, high porosities, designable structures and tunable pore sizes. Over the past two decades, MOFs have received widespread attentions due to their potential in the areas of gas storage [1–4], gas separation [5–11], sensing [12–18], catalysis [19–23], biomedicine [24,25] and so on [26,27].

Recently we mainly focus on porous MOFs for the storage and separation of light hydrocarbons that are very important for the industrial application [28–31]. Light hydrocarbons such as methane, ethane, acetylene, and ethylene are widely used as the energy resources and/or chemical raw materials in various chemical transformations. Although the application areas of each hydrocarbon specie is different, most of them are all produced simultaneously by thermal cracking of heavy hydrocarbons, making the separation processes required for obtaining high purity component. Commercial separations of binary gas mixtures such as ethylene/acetylene and acetylene/methane are very important but challenging due to their similar physical and chemical properties [32]. Furthermore, the coexistence impurity of CO₂ with CH₄ (the main component of natural gas steams) decrease the energy content of the natural gas and also result pipeline corrosion. Although traditional cryogenic distillation technology has been successfully used for these separations, its operating process is energy-

intensive, making the development of alternative technologies highly demanded. In recent years, considerable progress have been made on porous MOFs for the separation of C₂H₂/C₂H₄, C₂H₂/CH₄, CO₂/CH₄ and CO₂/N₂ at room temperature, emphasizing the trade-off between physical adsorption capacity and selectivity of MOFs for efficient gas separation, in which pore geometry and chemistry play an important role.

Therefore, the targeted MOFs for specific separation should be with suitable pore size and binding site. Isonicotinate acid (Hina), a multifunctional bridging ligand containing both O- and N-donors, has shown suitable linker length for self-assembly with transition metals ions into various microporous framework structures [33–39]. An earlier attempt to prepare low-density coordination polymers resulted in a porous lithium isonicotinate framework, which exhibits reversible gas uptake and release [40]. Recently, Vaidhyanathan et al. reported a nickel isonicotinate based ultramicroporous MOF, which has the lowest PE (the parasitic energy) for post-combustion CO₂ capture and exhibits high CO₂ diffusion coefficient for favorable adsorption/desorption kinetics [41]. These works indicate that the isonicotinate-based MOFs can be excellent materials for gas storage and separation applications. Herein we report a known MOF (QMOF-1) with quartz-like topology [33], assembled from isonicotinate ligands and zinc atoms giving considerable one dimensional channel (ca. 8.5 Å), for hydrocarbon separation.

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2. Experimental

2.1. Materials and methods

All reagents and solvents were used directly as received from the chemical supplier without further purification. QMOF-1 was prepared according to procedures reported in the literature [33]. TGA was performed by using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. PXRD patterns were recorded by using a Rigaku Ultima IV diffractometer operated at 40 kV and 44 mA with a scan rate of $1.0^{\circ}\text{ min}^{-1}$.

2.2. Gas sorption measurements

A Micromeritics ASAP 2020 surface area analyzer was used to obtain gas adsorption isotherms. To remove all guest solvents in the framework, a fresh sample of QMOF-1 was degassed under high vacuum at 423 K for several hours until the outgas rate reached to $6\text{ }\mu\text{mHg min}^{-1}$ prior to the gas sorption measurements. The measurement temperatures were maintained at 195, 273, and 298 K by using baths of dry ice/acetone slurry, ice/water mixture, and water bath in an air-conditioned laboratory ($25\text{ }^{\circ}\text{C}$), respectively.

2.3. IAST calculations

Adsorption isotherms and gas selectivities of mixed $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (50%: 50%), $\text{C}_2\text{H}_2/\text{CH}_4$ (50%: 50%), CO_2/CH_4 (50%: 50%), and CO_2/N_2 (15%: 85%) at 273 and 298 K were calculated based on the ideal adsorbed solution theory (IAST) proposed by Myers and Prausnitz [42]. To evaluate the performance of this MOF toward the separation of binary mixed gases, the parameters from the fitting of single-component C_2H_2 , C_2H_4 , CO_2 , CH_4 , and N_2 adsorption isotherms based on the Langmuir–Freundlich model were used in the IAST calculations [43]. The fitting parameters of the Langmuir–Freundlich equation are listed in Table S1.

3. Results and discussion

3.1. Crystal structure of QMOF-1

The sample of QMOF-1 was synthesized according to reported method [33]. The phase purity of the bulk material was confirmed by powder X-ray diffraction (PXRD) analysis (Fig. S1). Thermogravimetric analysis (TGA) revealed that all the solvent H_2O molecules in QMOF-1 were completely released before $190\text{ }^{\circ}\text{C}$ (Fig. S2). For this compound, each Zn atom coordinates to two nitrogen atoms from two different isonicotinate ligands, and two oxygen atoms from carboxylate groups of another two ligands, while isonicotinate

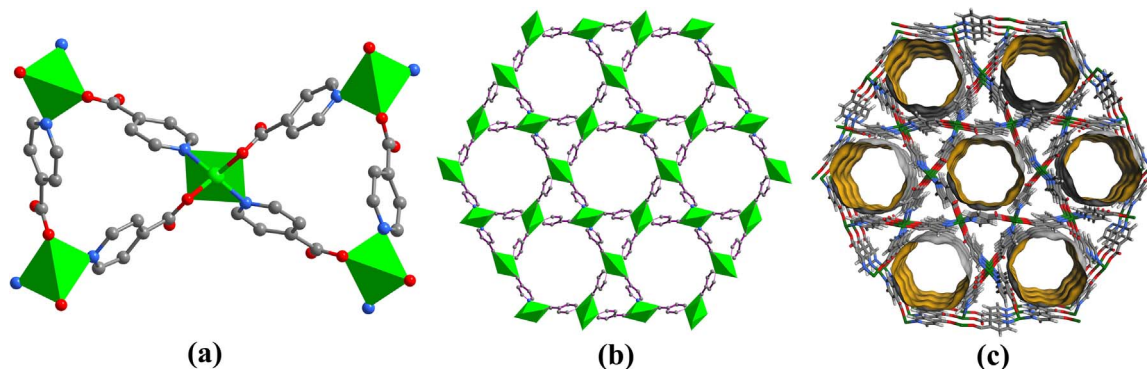


Fig. 1. (a) The coordination environment of QMOF-1; (b) The crystal structure projection of QMOF-1 in the [001] direction; (c) Packing diagram along the [001] direction, showing the pore surfaces of 1D channels highlighted as grey/yellow (outer/inner) curved planes with pore window. Zn, green; C, grey; H, light grey; O, red; N, light blue. The solvent (water) molecules are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

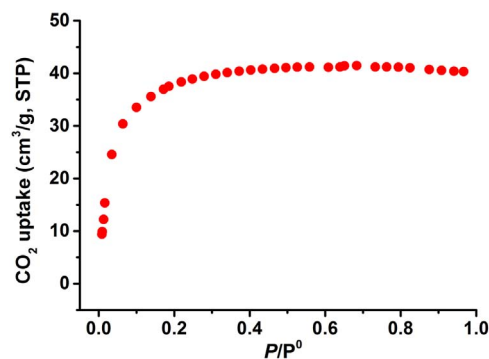


Fig. 2. Carbon dioxide sorption isotherm of QMOF-1a at 195 K.

ligand serves as a two-connection linker to form a 4-connect net with the quartz topology (Fig. 1). Disordered water molecules are observed in the hexagonal 1D channels, showing pores size of $\sim 8.5\text{ }\text{\AA}$ (the van der Waals radii are considered) in diameter. Such hexagonal framework structures (along c axis) can be simplified as a set of tetrahedral nodes (Zn^{2+}), linked via isonicotinate linkers to form two-fold interpenetrated quartz nets (Fig. 1). The potential accessible volume determined by PLATON [44] calculation, is $473\text{ }\text{\AA}^3$ per unit cell volume ($1305\text{ }\text{\AA}^3$), that is 36% void per unit volume for QMOF-1. The interesting structural features observed in QMOF-1 suggest that it might be a promising candidate for gas sorption and separation.

3.2. Establishment of permanent porosity

The permanent porosity of QMOF-1 was firstly checked by the CO_2 gas sorption at 195 K by using a Micromeritics ASAP 2020 surface area analyzer. Prior to gas sorption analysis, freshly prepared QMOF-1 sample was degassed under high vacuum at 423 K for several hours until the outgas rate reached to $6\text{ }\mu\text{mHg min}^{-1}$ to afford activated QMOF-1a. The TGA curve reveals that all solvent molecules are completely lost (Fig. S2). As observed in Fig. S1, the PXRD pattern shows that the activated phase QMOF-1a is still highly crystalline. The CO_2 gas sorption isotherm at 195 K clearly demonstrates its microporosity (see Fig. 2). The Brunauer–Emmett–Teller (BET) surface area of QMOF-1a was calculated to be $140\text{ m}^2\text{ g}^{-1}$, and the pore volume measured from the CO_2 sorption is $0.07\text{ cm}^3\text{ g}^{-1}$, which is clearly lower than the theoretical one of $0.32\text{ cm}^3\text{ g}^{-1}$. This can be due to certain flexibility of the host framework, which can only be partly opened by CO_2 molecules.

3.3. Gas sorption and separation

Since the storage and separation of light hydrocarbons are very

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