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A novel metal-organic framework for high storage and separation of acetylene at room temperature

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ABSTRACT

A novel 3D microporous metal-organic framework with NbO topology, $[Cu_2(L)(H_2O)_2]\bullet(DMF)_6\cdot(H_2O)_2$ (**ZJU-10**, ZJU = Zhejiang University; H_4L = 2′-hydroxy-[1,1′:4′,1″-terphenyl]-3,3″,5,5″-tetracarboxylic acid; DMF = *N,N*-dimethylformamide), has been synthesized and structurally characterized. With suitable pore sizes and open Cu^{2+} sites, **ZJU-10a** exhibits high BET surface area of 2392 m^2/g, as well as moderately high C_2H_2 volumetric uptake capacity of 132 cm^3/cm^3. Meanwhile, **ZJU-10a** is a promising porous material for separation of acetylene from methane and carbon dioxide gas mixtures at room temperature.

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1. Introduction

Metal-organic frameworks (MOFs), composed of metal ions or metal clusters connecting polydentate organic ligands, have attracted remarkable attention as the most promising class of porous functional materials in the gas storage and separation field [1,2]. This is because (i) such porous framework materials possess unparalleled permanent porosities after removing solvent molecules in the pore; (ii) MOFs have high surface areas and pore volumes; and (iii) the pore size can be systematically tuned/controlled and pore surfaces can be functionalized such as open metal sites and some functional groups for enhancing the interaction between gas molecule and host frameworks [3–10].

The various factors such as pore spaces/structure (pore size and pore shape), framework densities and open metal sites have been proved to impact on the performance of MOFs materials for gas storage and separation [11–29]. HKUST-1 with high density open Cu^{2+} sites exhibits an exceptionally high gravimetric acetylene storage capacity of 201 cm^3(STP)/g at room temperature and atmospheric pressure [30]. The breakthrough simulations experiments has demonstrated the micro-porous UTSA-33a with suitable pore sizes has potential applications for the separation of C_2H_2 from methane at room temperature [31]. So open metal sites and suitable aperture sizes play an important role in the aspect of acetylene storage and separation. The open metal sites can be straightforwardly generated through removing coordinative water or solvent molecules, followed by the vacuum activation and/or in situ thermal. The considerable researches have testified that NbO-type series of MOFs constructed from copper paddle-wheel $Cu_2(COO)_4$ cluster and a variety of tetra-carboxylates show attractive application prospects in the field of acetylene storage and separation due to the open Cu^{2+} sites and suitable pore sizes [14–26]. Herein, we report a novel NbO-type metal-organic framework $[Cu_2(L)(H_2O)_2]\bullet(DMF)_6\cdot(H_2O)_2$ (**ZJU-10**, ZJU = Zhejiang University; DMF = *N,N*-dimethylformamide) constructs from the tetra-carboxylate ligand H_4L (Scheme 1) (H_4L = 2′-hydroxy-[1,1′:4′,1″-terphenyl]-3,3″,5,5″-tetracarboxylic acid). The activated **ZJU-10a** exhibits moderately high porosity with a Brunauer-Emmett-Teller (BET) surface area of 2392 m^2/g. With suitable pore sizes, open Cu^{2+} sites and moderately high permanent porosity, **ZJU-10a** shows a moderately high C_2H_2 gravimetric (volumetric) uptake capacity of 174 (132) cm^3/g at 298 K and 1 bar; Meanwhile **ZJU-10a** can separate acetylene from methane and carbon dioxide gas mixtures at room temperature.

2. Experimental

2.1. Gas sorption measurements

The gas sorption isotherms of C_2H_2, CO_2 and CH_4 were measured by a Micromeritics ASAP 2020 surface area analyzer. In order to obtain a desolvated framework, the as-synthesized sample of

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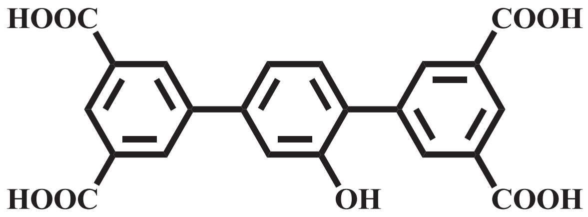

Scheme 1. The organic linker H_4L used to construct **ZJU-10**.

ZJU-10 was dry acetone-exchanged for 3 days, filtered and then vacuumed for 24 h at 273 K, for 12 h at 298 K and at 373 K until the outgas rate was < 5 μm Hg/min prior to measurements.

2.2. Derivation of the isosteric heats of adsorption

A virial-type expression of the following form was employed to calculate the enthalpies of adsorption of C_2H_2, CO_2 and CH_4. The data were fitted using the equation:

$$\ln P=\ln N+\frac{1}{T\sum_{i=0}^{m}a_iN^i}+\sum_{i=0}^{n}b_iN^i \tag{1}$$

where the p is pressure expressed in mmHg, N is the capacity adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, m, n represents the number of coefficients required to adequately describe the isotherms. The isosteric heat of adsorption, Q_{st}, defined as

$$Q_{st}=RT^2(\partial \ln P/\partial T) \tag{2}$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant of 8.3147 J/K/mol.

2.3. Fitting of pure component isotherms

The adsorption isotherms for C_2H_2, CO_2 and CH_4 in **ZJU-10a** were measured at 273 and 298 K and fitted on the basis of the dual site Langmuir-Freundlich equation:

$$N=N_1^{max}\times\frac{b_1p^{1/n_1}}{1+b_1p^{1/n_1}}+N_2^{max}\times\frac{b_2p^{1/n_2}}{1+b_2p^{1/n_2}} \tag{3}$$

where p is the pressure of the bulk gas at equilibrium with the adsorbed phase in kPa, N is the adsorbed amount per mass of adsorbent in mol/kg, N_1^{max} and N_2^{max} are the saturation capacities of sites 1 and 2 in mol/kg, b_1 and b_2 are the affinity coefficients of sites 1 and 2 in 1/kPa, and n_1 and n_2 represent the deviations from an ideal homogeneous surface. The fitting parameters of DSLF equation are presented in Table S1.

Adsorption isotherms and gas selectivities calculated by Ideal Adsorbed Solution Theory (IAST) for mixed C_2H_2/CH_4 (50/50) and C_2H_2/CO_2 (50/50) in the **ZJU-10a.** The adsorption selectivities, S_{ads}, are defined by the following equation:

$$S_{ads}=\frac{q_1/q_2}{p_1/p_2} \tag{4}$$

in which p_i the bulk gas pressure of species i, and q_i the component molar loading of species i. The IAST selectivities are presented in Table S2.

2.4. Synthesis and characterization of ZJU-10

A mixture of the organic link H_4L (15 mg, 0.0355 mmol) and Cu $(NO_3)_2$•2 · $5H_2O$ (30 mg, 0.129 mmol) was dissolved into 6 mL DMF solvent, then added H_2O of 2 mL and 100 μL HCl (37%, aq.) in a 20 mL screw-capped vial, the mixture was sonicated until homogenous. The vial was capped and placed in a precise oven at 80 °C for 2 day. The resulting blue rhombic shaped crystals were washed with DMF three times to afford **ZJU-10** materials. Yield: 68%, calculated from ligand. According to the single-crystal structure determination, elemental analyses and thermogravimetric analysis, **ZJU-10** can be formulated as $[Cu_2(C_{22}H_{10}O_9)(H_2O)_2]$•$(DMF)_6\cdot(H_2O)_2$, Elemental analysis: Calcd. ($C_{40}H_{60}Cu_2N_6O_{19}$, %): C, 45.79; H, 5.74; N, 7.96; Found: C, 45.75; H, 5.37; N, 7.74. The FT-IR of **ZJU-10** was shown in Fig. S1.

3. Result and discussion

Solvothermal reactions between the organic linker with Cu $(NO_3)_2$•2 · $5H_2O$ in a N,N′-dimethylformamide (DMF)/water solution in the presence of HCl at 80 °C for 72 h yielded blue rhombic shaped crystals, formulated by single-crystal X-ray diffraction (SCXRD) analysis and elemental analysis as $[Cu_2(C_{22}H_{10}O_9)(H_2O)_2]$•$(DMF)_6\cdot(H_2O)_2$. The phase purity of the bulk crystal material was independently confirmed by consistency between the simulated and as-synthesized powder X-ray diffraction (PXRD) patterns (Fig. S2) and thermogravimetric analysis (TGA, Fig. S3). The desolvated **ZJU-10a** for the gas adsorption studies was acquired from dry acetone-exchanged samples by the activation under high vacuum at 373 K for 2.5 h. The PXRD pattern of activated **ZJU-10a** is consistent with as-synthesized PXRD pattern, which indicates that it does not influence the crystalline framework structure that the removal of the guest molecules and coordinated water (Fig. S2).

Single-crystal X-ray diffraction analysis reveals **ZJU-10** adopts a 3D network that crystallizes in a trigonal space group R-3m. As expected, **ZJU-10** adopts the paddle-wheel $Cu_2(COO)_4$ clusters as secondary building units (SBUs), to construct the NbO-type metal organic frameworks with hydroxy-decorated tetracarboxylates. The pairs of copper centers are coordinated with four carboxylate groups to constitute octahedron. Two water molecules bind to Cu^{II} centers along the octahedron normal direction. The copper atoms of $Cu_2(COO)_4$ clusters will become open Cu^{2+} sites after removing axial aqua. Furthermore, there exist two types of cages in the framework of **ZJU-10** which are alternately stacked along the c axis. The size of small cage with a spherical pore is about 11 Å in diameter, taking into account of the van der Waals radii; while the dimensions of large shuttle-shaped cage is approximately 9.5 × 14 Å (Fig. 1(a)). Meanwhile, the triangular windows of 5.0 Å along c axis can be observed (Fig. 1(b)). The total accessible free volume is 7482 $Å^3$, or 65.0% of the unit volume 11510.7 $Å^3$ by PLATON analysis. The framework density is 0.757 g/cm^3 after removing the coordinated water and guest molecules.

N_2-gas sorption-desorption studies performed on the **ZJU-10a** show fully a reversible type-I isotherms, representative of microporous MOFs materials with permanent porosity (Fig. 2). The saturation uptake of N_2 of **ZJU-10a** is 625 cm^3/g and the corresponding pore volume is 0.9666 cm^3/g at $P/P_0=0.99$. The BET (Brunauer-Emmett-Teller, Fig. S4) and Langmuir surface areas based on the N_2 adsorption at 77 K are 2392 m^2/g and 2591 m^2/g. Although the BET value is slightly smaller than those of prototype NOTT-101 [7,20] because of the presence of the hydroxy groups inside the pore, it are comparable to those of these NbO-type MOFs such as ZJNU-40 [14], NJU-Bai14 [15], HNUST-2 [16], ZJU-26 [17], ZJU-9 [18], PCN-16 [19], NOTT-105 [20], NOTT-125a [21]. **ZJU-10** has a wide pore size distribution with the range from 5 Å to 14 Å which is consistent with the pore sizes from the single-crystal X-ray diffraction (Fig. S5).

The acetylene is very important raw material for the synthesis of various consumer and industrial chemicals products, petrochemical industry, oxy-acetylene cutting in metal fabrication, electric materials. Meanwhile, the acetylene is also a kind of

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