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A novel Zn-based heterocycle metal-organic framework for high C_2H_2/C_2H_4, CO_2/CH_4 and CO_2/N_2 separations

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ABSTRACT

Efficient separation of the small gas molecules especially the hydrocarbons is essential to social economy. The microporous metal-organic frameworks (MOFs) are taking precedence in this respect by virtue of their irreplaceable advantages. Herein, the new organic linker 5-(5-carboxypyridin-3-yl)isophthalic acid simplified as H_3L-N has been excavated to construct successfully the novel Zn-based heterocycle metal-organic framework $ZnL\cdot(DMF)_{1.5}\cdot(H_2O)_{6.0}$ (**ZJU-197**, ZJU = Zhejiang University, DMF = N,N-dimethylformamide). **ZJU-197** has been structurally characterized and explored in details for gas separation. It is commendable that the activated **ZJU-197a** has exhibited excellent C_2H_2/C_2H_4, CO_2/CH_4 and CO_2/N_2 separations simultaneously with IAST selectivity of 137.8, 53.0 and 514.1 respectively at ambient conditions.

1. Introduction

The energy shortage and environment pollution are growing seriously along with the rapid development of economy and society [1,2]. Thus, the urgent affair to mitigate the intractable situation is to improve the energy efficiency or to explore the potential bridging fuels. Light hydrocarbons are generally recognized as important raw chemicals to the petrochemical industries. Among them, acetylene (C_2H_2) as an impurity, obstructs seriously the further polymerization of ethylene (C_2H_4). Methane (CH_4), the main component of the natural gas, is agreed to be a preferably alternative choice due to the cleaner and more efficient significance. However, CH_4 mainly produced from biomass won't combust sufficiently if there is superabundant carbon dioxide. Furthermore, the global warming, also known as greenhouse effect is an absolutely worrisome environment issue, caused mainly by the anthropogenic emission of CO_2. Obviously, high-efficiency separation of C_2H_2 from C_2H_4, CO_2 from CH_4 and N_2, are of significances for remitting the worrisome energy crisis and greenhouse effect.

Therefore, the demand for gas separation and purification is quite emergency. It's well established that the porous materials based on the physisorption are very likely to address the aforementioned puzzles. Among a variety of porous materials, the microporous metal-organic frameworks (MOFs) have attracted particular interest because of their high porosity as well as rich designability [3–5]. In this context, thousands of novel MOFs have been reported over the past few decades, along with their functionality and properties [6–20]. Besides the classical solvothermal method to synthesize the metal-organic frameworks, some new synthetic approaches, such as surfactant-thermal method, have been excavated in the preparation of crystalline inorganic materials [21–27]. Herein, tremendous potentials have been exhibited on gas separation and purification since MOF-5 was explored for the first time in 1999 [28]. Furthermore, Long and co-workers explored mmen-CuBTTri to successfully achieve the excellent CO_2 separations [29]. However, the chemisorptive interaction between CO_2 molecular and the framework accounted for the high heat of adsorption. The higher the heat of adsorption, the more troublesome the regeneration bill. Given that, the regeneration cost associated with gas separation and purification is one of the decisive criteria of practical application. Herein, our previously reported work, ZJU-198a was further demonstrated as a successful model equilibrating masterly the selectivity and the regeneration cost [30]. As for the separation of C_2H_2 versus C_2H_4, M'MOF-3a was explored for high C_2H_2/C_2H_4 selectivity through the sieving effects but relatively low C_2H_2 storage [31]. Lately, Chen and co-workers successfully conquered the major barrier about the trade-off between the adsorption capacity and the selectivity through the precise control of the pore chemistry in networks with $SiF6^{2-}$ [32]. Up to now, the main approaches of MOFs to achieve the effective gas separation and purification are the chemisorption through the functionalization and the physical adsorption through the size-sieving. Table 1 lists the empirical kinetic sizes of small gas

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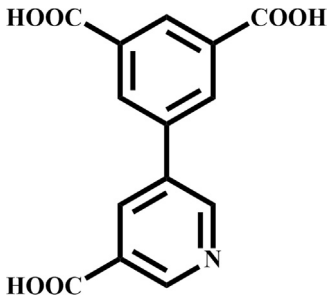
Table 1
The kinetic diameters of C_2H_2, C_2H_4, CO_2, CH_4 and N_2.

Molecules	Kinetic sizes
C_2H_2	3.32 Å × 3.34 Å
C_2H_4	3.28 Å × 4.18 Å
CO_2	3.18 Å × 3.33 Å
CH_4	3.82 Å × 3.94 Å
N_2	3.64 Å × 3.80 Å



Scheme 1. The Organic Linker 5-(5-carboxypyridin-3-yl)isophthalic acid (H_3L-N) Used to Construct ZJU-197.

molecules [33,34]. Note that there are relatively apparent discrepancy of kinetic sizes between CO_2 and CH_4, N_2 molecules while it is relatively different to distinguish C_2H_2 and C_2H_4 only in terms of sizes. However, it is still quite challengeable for MOFs to achieve the excellent CO_2 over CH_4, N_2 and C_2H_2 over C_2H_4 separations simultaneously.

Herein, the novel Zn-based heterocycle metal-organic framework **ZJU-197** has been designed and successfully synthesized through the assembly of the organic linker 5-(5-carboxypyridin-3-yl)isophthalic acid (Scheme 1) with $Zn(NO_3)_2{\cdot}6H_2O$. Furthermore, **ZJU-197** has been structurally characterized and explored detailedly for gas separation. It is worth noting that the activated **ZJU-197a** has exhibited high C_2H_2/C_2H_4, CO_2/CH_4 and CO_2/N_2 separations with IAST selectivity of 137.8, 53.0 and 514.1 respectively at ambient conditions.

2. Experimental section

2.1. Materials and methods

All reagents and solvents were commercially available and used without further purification. The organic linker 5-(5-carboxypyridin-3-yl)isophthalic acid was obtained from Jinanhenghua company. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 5–40° range on an X'Pert PRO diffractometer with Cu Kα (λ = 1.542 Å) radiation at room temperature. Infrared spectrum (IR) was performed on Thermo Fisher Nicolet iS10 spectrometer using KBr pallets. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 10 °C/min in N_2 atmosphere.

2.2. Single-crystal X-ray crystallography

Crystallographic measurements for **ZJU-197** were taken on an Oxford Xcalibur Gemini Ultra diffractometer equipped with an Atlas detector using graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at 293 K. The determination of the unit cell and data collection for the crystal of **ZJU-197** was performed with CrysAlisPro. The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure of **ZJU-197** was determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 program package. The solvent molecules in the compound are highly disordered. The SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules. The new resulting files were used to further refine the structure. The composition of the as-synthesized **ZJU-197** was figured out based on the elemental analysis, TGA and single crystal structure. Crystallographic data are summarized in Table S1.

2.3. Gas sorption measurements

All gas sorption isotherms were obtained from the Micromeritics ASAP 2020 surface area analyzer. Before the gas sorption measurements, the fresh sample of **ZJU-197** was guest–exchanged with dry acetone at least 10 times, then filtered and degassed at 273 K for one day, 298 K for 12 h, and 323 K for 5 h under high vacuum to obtain the activated **ZJU-197a**. The measurements were maintained at 196 K with the mixture of drikold and acetone. The adsorption isotherms of C_2H_2, C_2H_4, CO_2, CH_4 and N_2 gases were obtained at 273 K and 298 K respectively. And the ice-water bath and water bath were used for adsorption isotherms at 273 K and 298 K, respectively.

2.4. Synthesis of ZJU-197

A mixture of the organic linker 5-(5-carboxypyridin-3-yl)isophthalic acid diacrylic acid (4.0 mg, 0.0125 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (10.0 mg, 0.0337 mmol) was dissolved into a 3.5 mL mixed solvent (DMF/acetonitrile/H_2O, 2.0 mL/1.0 mL/0.5 mL) in a screw-capped vial (20 mL), to which HBF_3 (80 μL) (50%, aq.) was added to the mixture, at 100 °C for 48 h. HBF_3 is a sort of inorganic acid. One hand, it could adjust the pH of the reaction solvent. On the other hand, it could lower the deprotonation rate of the ligand. Thus, it effectively avoided the occurrence of aggregate and further guaranteed the well dispersibility and crystallinity of crystal material. Colourless needle-like crystals were obtained by filtration and then washed with fresh DMF several times to afford **ZJU-197. ZJU-197** has a formula as $ZnL{\cdot}(DMF)_{1.5}{\cdot}(H_2O)_{6.0}$ obtained based on the single-crystal X-ray structure determination, elemental analysis and TGA. Anal. Calcd for $C_{19.1}H_{29.7}N_{2.72}O_{13.6}Zn$: C, 38.58; H, 5.00; N, 6.39; found: C, 38.59; H, 5.14; N, 6.46. IR (neat, cm^{-1}): 1626, 1576, 1462, 1412, 1353, 1284, 1249, 1190,1140,1080,1020,902,852,768,729,659.

2.5. Ideal Adsorbed Solution Theory (IAST)

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, can be formally defined as

$$S_{ads} = \frac{q1/q2}{p1/p2}$$

In above equation, q1 and q2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacity. We calculated the values of q1 and q2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

2.6. The isosteric heat, Qst

The isosteric heat of C_2H_2, C_2H_4, CO_2, CH_4 and N_2 adsorption, Q_{st}, defined as

$$Q_{st} = RT^2\left(\frac{\partial \ln P}{\partial T}\right)$$

was determined using the Clausius-Clapeyron equation by fitting the adsorption isotherms taken at 273 K and 298 K to a Langmuir expression.