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A Microporous Hydrogen-Bonded Organic Framework for Highly Selective C_2H_2/C_2H_4 Separation at Ambient Temperature

Yabing He, Shengchang Xiang, and Banglin Chen*

Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, United States

Supporting Information

ABSTRACT: The first microporous hydrogen-bonded organic framework with permanent porosity and exhibiting extraordinarily highly selective adsorptive separation of C_2H_2 and C_2H_4 at ambient temperature has been established.

Scientific and technological innovations have been always followed by new discoveries and the realization of novel functional materials. Because porous materials have very important and useful industrial applications in gas storage, separation, and catalysis,[1−4] there have been extensive research endeavors to target low-energy-consuming and cost-effective porous materials for highly efficient gas storage and separation. Such efforts eventually led to the discovery of the so-called "molecular gate" adsorbent Engelhard titanium silicate (ETS-4) for economical N_2 and CO_2 removal[5] and the emergence of porous metal−organic frameworks (MOFs) and/or porous coordination polymers (PCPs) as very promising energy storage (hydrogen and natural gas) materials for future vehicles.[6] In fact, a MOF methane/natural gas fuel tank has been already developed,[7] and several prototypical porous MOFs have been commercialized recently by BASF.[8] Because C_2H_2/C_2H_4 separation is a very important industrial process, porous MOF materials for highly selective adsorptive C_2H_2/C_2H_4 separation have recently attracted extensive attention.[15]

Although hydrogen-bonded organic frameworks (HOFs) have been proposed as potential porous materials and a series of HOFs were structurally characterized about two decades ago,[9,10] no example of such a framework with permanent porosity by gas/vapor sorption isotherms has been established. This is mainly because of the weak hydrogen bonding within HOFs, which makes the framework very difficult to stabilize, so the structurally "porous" HOFs typically collapse once the solvent guest molecules are removed after thermal and/or vacuum activation. Such a failure situation also happened at the early stage of porous MOF development before the realization of a few MOFs and/or PCPs with permanent porosity in 1997−1999.[11,12] Unlike the very strong covalent bonds and moderately strong coordination bonds holding together the frameworks in zeolites and MOFs, which feature their corresponding robustness and dual robustness/flexibility, respectively, the weaker hydrogen bonding is reasonably expected to stabilize HOFs with even more flexibility, whose functions for gas separation might even surpass those of some well-developed zeolite and MOF materials. Furthermore, HOFs also have some other advantages, such as solution processability and characterization, potential high thermal stability, easy purification, and regeneration by simple recrystallization. Motivated by the pioneering work of Wuest on the construction of HOFs,[10] we plan to explore HOFs for their potential applications in gas separation. Herein we report on HOF-**1**, the first microporous HOF for highly selective C_2H_2/C_2H_4 separation at ambient temperature.

The organic building block shown in Scheme 1 was synthesized according to the procedure in refs 10 and 13. As pointed out by Wuest, highly crystalline, colorless needlelike crystals of HOF-**1** can be easily obtained by vapor diffusion of dioxane into a formic acid solution of the organic building block, whose purity was confirmed by ^1H NMR spectroscopy, microanalysis, thermogravimetric analysis (TGA), and powder X-ray diffraction (PXRD). It needs to be mentioned that the guest solvent molecules can be readily released from room temperature to 170 °C, and the resulting desolvated HOF-**1a** is also highly crystalline; its PXRD pattern is right-shifted relative to the as-synthesized one (Figure S1 in the Supporting Information), indicating a certain degree of framework flexibility and shrinkage of the framework. HOF-**1a** is thermally stable up to 420 °C (Figure S2).

The single-crystal X-ray structure of HOF-**1** revealed that HOF-**1** is a three-dimensional porous HOF in which each organic building block is connected with four neighboring ones by eight strong hydrogen bonds involving the 2,4-diaminotriazine groups (Figure S3a).[10] There exist one-dimensional pores along *c* axis with a size of ~8.2 Å based on the van der Waals radii (Figure 1a). Topologically, the organic building blocks can be considered as 8-connected nodes that form a three-dimensional body-centered cubic bcu $\{4^{24}6^4\}$ network (Figure 1b). The framework is further enforced by multiple aromatic $\pi-\pi$ interactions among the organic building blocks (Figure S3b). The collaborative hydrogen bonding and aromatic $\pi-\pi$ interactions have featured the HOF-**1** as the rare example of a highly robust HOF, as established by Wuest.[10] One of the amine groups within the 2,4-diaminotriazine moieties is not involved in the hydrogen bonding and thus is exposed on the pore surfaces for potential interactions with gas molecules.

Encouraged by the robustness and flexibility of HOF-**1**, we examined the permanent porosity of HOF-**1a** generated by activation under high vacuum at room temperature for 24 h and then at 100 °C for another 24 h. Such activation completely removed the guest molecules, as confirmed by ^1H NMR spectroscopy (Figure S4). The porosity was evaluated by CO_2 gas

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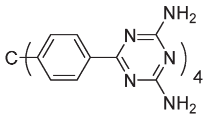
Scheme 1. Organic Building Block Used To Construct HOF-1



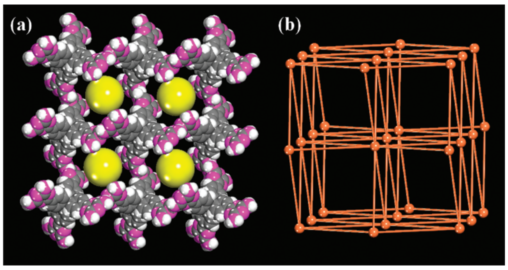


Figure 1. X-ray crystal structure of HOF-**1** featuring (a) one-dimensional channels along the *c* axis with a size of ~8.2 Å (yellow spheres) and (b) three-dimensional body-centered cubic bcu $\{4^{24}6^4\}$ network topology.

sorption at 196 K (Figure 2a). The isotherm shows a very sharp uptake at $P/P^\circ < 0.1$, indicative of a microporous material. Moreover, the isotherm exhibits a sudden increase at $P/P^\circ = 0.78$ and a large hysteretic desorption behavior, suggesting its framework flexibility and the existence of molecular gates. Such framework flexibility is attributed to the reversible transformation between the guest-free HOF-**1a** and guest-loaded HOF-**1**, which was also observed using PXRD (Figure S2) and has been observed in flexible MOFs.[14] Thus, the less porous HOF-**1a** can be expanded back to porous HOF-**1** once gas molecules have been gradually loaded into the pores. The isotherm gave an apparent Brunauer—Emmett—Teller (BET) surface area of 359.2 m^2 g^{-1} between relative pressures of 0.10 and 0.31 (Figure S5), which is moderate.

The establishment of permanent porosity and framework flexibility in HOF-**1a** prompted us to examine its gas separation capacity, particularly for the very important and challenging C_2H_2/C_2H_4 separation at ambient temperature. HOF-**1a** exhibits hysteretic sorption behaviors for C_2H_2 at both 273 and 296 K (Figure 2b and Figure S6). Accordingly, a higher pressure is needed to open the gate of HOF-**1a** at 296 K to maximize the C_2H_2 uptake. The most significant feature is that HOF-**1a** takes up a much larger amount of C_2H_2 than C_2H_4, indicating that HOF-**1a** is a very promising microporous material for the C_2H_2/C_2H_4 separation at ambient temperature. At 273 K, HOF-**1a** can take up acetylene up to 63.2 cm^3 g^{-1} (STP), which corresponds to 2.1 mol of C_2H_2 absorbed per mole of HOF-**1a**. The storage density of C_2H_2 is 0.17 g cm^{-3}, which is equivalent to the acetylene density at 16.4 MPa and 82 times greater than the compression limit for the safe storage of acetylene (0.2 MPa). On the other hand, HOF-**1a** can adsorb only 8.3 cm^3 g^{-1} (STP) of C_2H_4 at 1 atm. The C_2H_2/C_2H_4 molar ratio separation selectivity of 7.6 in HOF-**1a** is thus significantly higher than those previously reported (<2.5) in M′MOFs at 273 K.[15] Such high C_2H_2/C_2H_4 separation selectivity can be further increased up to 14.6 at 296 K for HOF-**1a**. To the best of our knowledge, HOF-**1a** is the best microporous material with such extraordinarily high C_2H_2/C_2H_4 separation selectivity. The moderately high C_2H_2 uptake of HOF-**1a** will make such C_2H_2/C_2H_4 separation practically feasible.

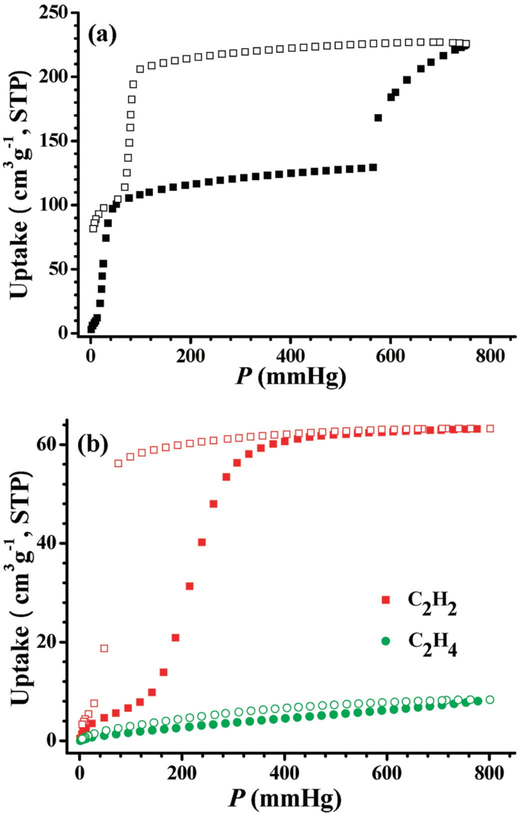


Figure 2. (a) CO_2 sorption isotherm at 196 K and (b) C_2H_2 and C_2H_4 sorption isotherms at 273 K.

To understand the high C_2H_2/C_2H_4 separation selectivity, adsorption enthalpies based on the virial equation were calculated (Figures S7 and S8; the virial parameters are summarized in Table S1). The adsorption enthalpies at zero coverage (calculated from the A_0 virial coefficients) are 58.1 and 31.9 kJ mol^{-1} for C_2H_2 and C_2H_4, respectively. The adsorption enthalpy of 31.9 kJ mol^{-1} for C_2H_4 in HOF-**1a** is comparable to those in microporous MOFs.[16] However, the adsorption enthalpy of 58.1 kJ mol^{-1} for C_2H_2 in HOF-**1a** is much higher than those found in microporous MOFs,[17] indicating that the interactions between the guest C_2H_2 molecules and host HOF-**1a** framework are very strong. Such very strong interactions might be attributed to the narrow pore spaces within HOF-**1a** (the pores in this activated HOF-**1a** are much smaller than those of 8.2 Å in the as-synthesized HOF-**1** as shown by PXRD) and hydrogen-bonding interactions of acidic H atoms of the guest acetylene molecules and the basic amine groups of HOF-**1a**.[18] The calculated Henry C_2H_2/C_2H_4 separation selectivities in HOF-**1a** are 19.3 and 7.9 at 273 and 296 K, respectively, which are much higher than the values of 4.1 and 5.2 in the recently discovered M′MOF-**3a**.[15] Therefore, the collaborative size-exclusive effect (3.32 Å × 3.34 Å × 5.70 Å for C_2H_2 vs 3.28 Å × 4.18 Å × 4.84 Å for C_2H_4)[19] confined by the small narrow pores and the preferential stronger interactions of C_2H_2 with the basic amine groups of the host framework enable HOF-**1a** to act as an extraordinarily highly selective microporous material for the separation of C_2H_2 and C_2H_4 at ambient temperature.

Ethylene obtained from natural gas cracking contains a small amount of acetylene as an impurity, which can serve as a catalyst poison during ethylene polymerization and also lower the quality of the resulting polyethylene. In addition, acetylene can form explosive metal acetylides. It is thus imperative that acetylene in the ethylene product be reduced to an acceptable level. Current main commercial approaches to eliminate acetylene in crude ethylene include partial hydrogenation and solvent extraction. The former process suffers from the need for a noble-metal catalyst and the loss of olefins due to the overhydrogenation to paraffins, while the latter is also disadvantageous in terms of technical and economical aspects because of the low selectivities for acetylene over olefins and the significant loss of solvent after multiple operations. The realization of microporous HOF-**1a** with its extraordinarily high capability for C_2H_2/C_2H_4 separation might lead to the development of revolutionary C_2H_2/C_2H_4 gas separation processes with the implementation of pressure-swing adsorption (PSA) and temperature-swing adsorption (TSA) in the near future.

In summary, we have reported the first example of a microporous hydrogen-bonded organic frameworks (HOF) with permanent porosity and the capacity for extraordinarily highly selective adsorptive separation of C_2H_2 and C_2H_4 at ambient temperature. Although it is very difficult to stabilize HOFs and thus to establish their permanent porosities, the unique features of such microporous HOFs, such as framework flexibility, easy purification and regeneration, and high thermal stability, might surpass those of traditional microporous zeolite and metal—organic framework materials for use in industrial gas separation. It is expected that this work will generate a resurgence of the extensive interest in microporous HOFs for their recognition of small molecules and thus applications in gas separation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, TGA data, PXRD patterns, NMR characterization, and virial analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

banglin.chen@utsa.edu

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