Pore chemistry and size control in hybrid porous materials for acetylene capture from ethylene

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The trade-off between physical adsorption capacity and selectivity of porous materials is a major barrier for efficient gas separation and purification through physiosorption. We report control over pore chemistry and size in metal coordination networks with hexafluorosilicate and organic linkers for the purpose of preferential binding and orderly assembly of acetylene molecules through cooperative host-guest and/or guest-guest interactions. The specific binding sites for acetylene are validated by modeling and neutron powder diffraction studies. The energies associated with these binding interactions afford high adsorption capacity (2.1 millimoles per gram at 0.025 bar) and selectivity (39.7 to 44.8) for acetylene at ambient conditions. Their efficiency for the separation of acetylene/ethylene mixtures is demonstrated by experimental breakthrough curves (0.73 millimoles per gram from a 1/99 mixture).

An urgent demand for efficient solutions to challenges in gas separation, sensing, and storage (1–7) has spurred research on custom-designed porous materials, termed metal-organic frameworks (MOFs) and/or porous coordination polymers (PCPs) (8), in which open lattices are formed from inorganic centers (nodes) and organic linking groups. These materials can be designed from first principles and, thanks to their inherent diversity, afford precise control over pore chemistry and pore size.

Ideal porous materials for gas separation should exhibit high selectivity and optimal adsorption capacity for the target gas molecules at relevant conditions. However, the design of new materials that improve upon existing benchmarks poses a daunting challenge to materials scientists (9–12). For example, porous materials are needed for acetylene (C2H2) capture and separation from ethylene (C2H4) (13–17), industrial processes that are relevant for the production of polymer-grade C2H2 and C2H4 (the most produced organic compound in the world, at over 140 million metric tons in 2014). The MOF-74 family of compounds has a high density of open metal sites that drive high uptake of C2H2 but displays low separation selectivities (18). The MMMOF (mixed metal-organic framework) family has microporosity that enables sieving effects and high separation selectivities but relatively low uptake of C2H2 (19).

We report that metal coordination networks with preformed inorganic and organic linkers—SIFSIX-2-Cu (SIFSIX = hexafluorosilicate (SiF6^2-); 2, 4,4'-dipyridylacetylene; i, interpenetrated) (20) and SIFSIX-1-Cu (1, 4,4'-bipyridine) (21)—can exhibit exceptional C2H2 capture performance because of the geometric disposition of SiF6^2- moieties enables preferential binding of C2H2 molecules. Both materials have pore spaces that enable extremely high C2H2 capture under low pressures, and they unexpectedly represent new benchmarks for the highly efficient removal of minor amounts of C2H2 from C2H4 gas (SIFSIX-2-Cu-i) and mass separation of C2H2/C2H4 mixtures under ambient conditions (SIFSIX-1-Cu). We attribute this unprecedented performance to the existence of “sweet spots” in pore chemistry and pore size that enable highly specific recognition and high uptake of C2H2 to occur in the same material.

In these SIFSIX materials, two-dimensional (2D) nets of organic ligand and metal node are pillared with SiF6^2- anions in the third dimension to form 3D coordination networks that have primitive cubic topology and, importantly, pore walls lined by inorganic anions (20–23). The pore sizes within this family of materials can be systematically tuned by changing the length of the organic linkers, the metal node, and/or the framework interpenetration. SIFSIX-1-Cu, SIFSIX-2-Cu, SIFSIX-2-Cu-i, SIFSIX-3-Cu (3, pyrazine), SIFSIX-3-Zn, and SIFSIX-3-Ni have already been studied for their exceptional CO2 capture performance, but here we report a study of their C2H2 and C2H4 adsorption from 283 to 303 K. Figure 1, A and B, and figs. S2 to S7 show dramatically different adsorption behaviors for C2H2 than those observed for CO2 (figs. S8 and S9) (24). SIFSIX-2-Cu-i rapidly adsorbs C2H2 at very low pressure (<0.05 bar). Its C2H2 uptake reaches 2.1 mmol/g at 298 K and 0.025 bar. In Fig. 1B, compared with an uptake of 1.78 mmol/g by UTSA-100a (17), this performance at low pressure indicates that SIFSIX-2-Cu-i has promise for capturing C2H2 when it is a minor component in a gas mixture. SIFSIX-1-Cu exhibits exceptionally high C2H2 uptake (8.5 mmol/g) at 298 K and 1.0 bar. This is not only the highest uptake of any of the SIFSIX materials, but is also even higher than that of the previous benchmark, FeMOF-74 (table S1) (18, 24). As detailed herein, we attribute the unprecedented performance of these materials to their hybrid pore chemistry and optimal pore sizes for binding C2H2.

To understand the C2H2 adsorption isotherms in these materials, we conducted detailed modeling studies using first-principles DFT-D (dispersion-corrected density functional theory) calculations. In SIFSIX-1-Cu, C2H2 molecules are bound through strong C–H···F hydrogen (H) bonding (2.017 Å) and van der Waals (vdW) interactions with the 4,4'-bipyridine linkers (Fig. 1C and fig. S10) (24). The DFT-D–calculated static adsorption energy (AE) is 44.6 kJ/mol. Each unit cell of SIFSIX-1-Cu contains four equivalent exposed F atoms, and each exposed F atom binds one C2H2 molecule. The distance between neighboring adsorbed C2H2 molecules is ideal for them to synergistically interact with each other through multiple H···C–C dipole-dipole interactions (Fig. 1C), further enhancing the energy of adsorption. Because four C2H2 molecules are adsorbed per unit cell, the ΔE of C2H2 increases to 47.0 kJ/mol. The strong binding of C2H2 at F atoms and the geometric arrangement of SiF6^2- anions enable the efficient packing of four C2H2 molecules per unit cell and very high C2H2 uptake at 298 K and 1.0 bar (about 4.4 C2H2 molecules per unit cell).

C2H2 adsorption is weaker in the wider-pore material SIFSIX-2-Cu (10.5 Å × 10.5 Å cavity) than in SIFSIX-1-Cu (AE, 34.6 versus 44.6 kJ/mol) because the stronger C–H···F H-bonding interaction from SiF6^2- sites is of the same nature in these isoreticular networks (Fig. 1, C and D). However, the vdW interaction between C2H2 and the organic linker in SIFSIX-2-Cu is weak compared with that in SIFSIX-1-Cu. We attribute this difference to the former’s larger pore size and weaker vdW potential overlap (figs. S10 and S11) (24). Moreover, at high gas uptake, the C2H2 molecules adsorbed on adjacent F sites are too far separated to have synergistic guest-guest interactions. However, in the twofold interpenetrated structure of SIFSIX-2-Cu-i, one C2H2 molecule can be simultaneously bound by two F atoms from different nets through cooperative C–H···F H-bonding (2.013 and 2.015 Å; Fig. 1E), which enables the strongest energy of C2H2 binding yet observed in SIFSIX materials (AE, 52.9 kJ/mol). The strong adsorption energy of SIFSIX-2-Cu-i contributes to its extremely high uptake capacity at low pressure. In SIFSIX-3-Zn and SIFSIX-3-Ni, which are

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the strongest CO2 adsorbents, the pore size is smallest, and C2H2 molecules are primarily adsorbed at a different site in the 1D channel along the c axis (ΔE, 50.3 kJ/mol; Fig. 1F). The secondary adsorption site in SIFSIX-3-Zn (Fig. S12) exhibits a much smaller adsorption energy (25.9 kJ/mol), which results in lower C2H2 uptake compared with that of SIFSIX-2-Cu-i.

The weakly basic nature of the SiF6 -2 sites (acid dissociation constant pKa, 1.92) and their geometric disposition enable strong binding with weakly acidic C2H2 molecules. Because C2H2 is more acidic than C2H4 (pKa, 25 versus 44) (17), and the geometry of the SIFSIX materials is more optimal for C2H2 binding, there are much stronger interactions with C2H2 than with C2H4 (ΔE in SIFSIX-1-Cu, 44.6 versus 27.2 kJ/mol; ΔE in SIFSIX-2-Cu-i, 52.9 versus 39.8 kJ/mol). The calculated H-bond distances between C2H4 and SiF6 -2 sites are 2.541 and 2.186 Å in SIFSIX-1-Cu and SIFSIX-2-Cu-i, respectively, which are longer than those between C2H2 and SiF6 -2 sites (figs. S13 and S14) (24).

To establish the structure of the C2H2 binding sites through Rietveld structural refinements, high-resolution neutron powder diffraction data were collected on C2D2-loaded samples of SIFSIX-1-Cu·4C2D2 and SIFSIX-2-Cu-i·1.7C2D2 at 200 K (figs. S15 and S16) (24). Each unit cell of SIFSIX-1-Cu is filled with four C2D2 molecules that are arranged in an ordered planar structure (Fig. 1, G and H), consistent with the DFT-D modeling results. C-D···H bonding occurs between C2D2 and SiF6 -2 anions (2.063 Å), and D···C distances between neighboring C2D2 molecules are 3.063 and 3.128 Å. In SIFSIX-2-Cu-i, each C2H2

Fig. 1. C2H2 and C2H4 adsorption isotherms of the MOFs, DFT-D–simulated optimized C2H2 adsorption sites of the MOFs, and neutron crystal structure of SIFSIX-1-Cu·4C2D2. (A and B) Adsorption isotherms of C2H2 (filled circles) and C2H4 (triangles) in SIFSIX-1-Cu (red), SIFSIX-2-Cu (green), SIFSIX-2-Cu-i (blue), SIFSIX-3-Zn (light blue), and SIFSIX-3-Ni (orange) at 298 K in two pressure regions, 0 to 1.0 bar (A) and 0 to 0.05 bar (B). Open circles in (A) are desorption isotherms of C2H2 (C to F) DFT-D–calculated C2H2 adsorption binding sites in SIFSIX-1-Cu (C), SIFSIX-2-Cu (D), SIFSIX-2-Cu-i (E) (the different nets are highlighted in magenta and green for clarity), and SIFSIX-3-Zn (F). Color code: F, red; Si, light blue; C, gray; H, light gray; N, sky blue; Cu, dark teal; Zn, violet; C (in C2H2 or C2D2), orange. (G and H) Neutron crystal structure of SIFSIX-1-Cu·4C2D2 at 200 K, determined from Rietveld analysis.

Fig. 2. IAST calculations for MOF performance with C2H2/C2H4 mixtures. (A and B) Comparison of the IAST selectivities of SIFSIX materials versus those of previously reported best-performing materials for C2H2/C2H4 mixtures. Results for varying C2H2 molar fractions at 100 kPa are shown in (A), and results at varying pressures for a 1% C2H2 mixture are shown in (B). (C and D) MOF capacity to uptake C2H2 from C2H2/C2H4 mixtures. Results for varying C2H2 molar fractions at 100 kPa are shown in (C), and results at varying pressures for a 1% C2H2 mixture are shown in (D).
interacts with two SIF$_6^-$ anions via dual C–D···F H-bonding (2.134 Å; fig. S17) (24).

The separation of C$_2$H$_4$ from C$_2$H$_4$ is necessary for the production of high-purity C$_2$H$_4$ and C$_2$H$_2$. In the production of polymer-grade C$_2$H$_4$ removal of trace C$_2$H$_2$ (about 1%) from C$_2$H$_4$ gas must meet the requirement of <40 parts per million (ppm) C$_2$H$_2$ in the downstream polymerization reaction (17). Similarly, in the production of polymer-grade C$_2$H$_4$ by pyrolysis of coal and biomass, the capture of C$_2$H$_2$ from C$_2$H$_4$ is of great importance (90/10 to 50/50, v/v) is a crucial step. Existing methods, such as solvent absorption and partial hydrogenation of C$_2$H$_2$, are energy intensive, so there is an urgent need to develop efficient porous materials for C$_2$H$_2$ capture from C$_2$H$_4$.

To address gas mixture separations, we first determined the C$_2$H$_2$/C$_2$H$_4$ separation selectivities of the SIFSIX materials by means of ideal adsorbed solution theory (IAST) calculations (Fig. 2 and fig. S20) (24, 26). SIFSIX-2-Cu-i exhibits record selectivity (39.7 to 44.8; Fig. 2A), even compared to recently reported best-performing materials (A). The separation of C$_2$H$_2$ from C$_2$H$_4$ was, from longest to shortest, SIFSIX-2-Cu-i, SIFSIX-1-Cu, then SIFSIX-3-Zn (E), open circles are for C$_2$H$_2$, and filled circles are for C$_2$H$_4$. C$_2$/C$_2$H$_4$/C$_2$H$_2$, outlet concentration/feeding.

Fig. 3. Simulated and experimental column breakthrough results. (A) and (B) Simulated column breakthrough curves for C$_2$H$_2$/C$_2$H$_4$ separations with SIFSIX materials and previously reported best-performing materials [(A), 1/99 mixture; (B), 50/50 mixture]. (C) and (F) Plots of the amount of C$_2$H$_2$ captured as a function of t$_{break}$ in the simulated column breakthrough [(C), 1/99 mixture; (F), 50/50 mixture]. (D) and (E) Experimental column breakthrough curves for C$_2$H$_2$/C$_2$H$_4$ separations with SIFSIX-1-Cu, SIFSIX-2-Cu, and SIFSIX-3-Zn at 298 K and 1.01 bar [(D), 1/99 mixture; (E), 50/50 mixture]. In (A), (B), (D), and (E), open circles are for C$_2$H$_2$, and filled circles are for C$_2$H$_4$. C$_2$/C$_2$H$_4$/C$_2$H$_2$, outlet concentration/feeding.

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amounts of C$_2$H$_2$. These experiments indicate that the presence of CO$_2$ has only a slight (1000 ppm CO$_2$) or no (10 ppm CO$_2$) effect on the separation of C$_2$H$_2$ from C$_2$H$_4$ (fig. S24) (24). Moisture (6 to 1340 ppm) and oxygen (2200 ppm) do not affect the C$_2$H$_2$ capture ability of SIFSIX-2-Cu-i (figs. S25 and S26) (24). The breakthrough performances of SIFSIX-2-Cu-i and SIFSIX-3-Zn at 1/99 mixture did not decline during 16 and 3 cycles, respectively (figs. S28 and S29) (24), and the SIFSIX materials retained their stability after breakthrough experiments (figs. S1 and S30) (24).

The SIFSIX materials that we studied exhibit excellent C$_2$H$_2$ storage performance. The volumetric uptake of C$_2$H$_2$ by SIFSIX-1-Cu at 298 K and 1.0 bar is the highest among these SIFSIX materials (0.391 g/cm$^3$; table S14) (24). The C$_2$H$_2$ storage densities in the pores of SIFSIX-1-Cu, SIFSIX-2-Cu-i, and SIFSIX-3-Zn at 298 K are 0.388, 0.403, and 0.499 g/cm$^3$, respectively.

The basic principles outlined here are likely to be applicable to other gas mixtures. Primary binding sites will be necessary for recognition of specific gas molecules, whereas suitable pore sizes and spacing will be needed to enforce synergistic binding to multiple sites in order to form the so-called “gas clusters” through intermolecular guest-guest interactions. This work not only reveals a path forward for industrial C$_2$H$_2$/C$_2$H$_4$ separations, but also facilitates a design or crystal engineering approach to the development of porous materials for other gas separations.

REFERENCES AND NOTES


Materials and methods are available as supplementary materials on Science Online.


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The authors and their affiliated institutions have filed a patent application related to the results presented here.

SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S32

Tables S1 to S15

References (26–34)

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ORGANIC CHEMISTRY

Copper-catalyzed asymmetric addition of olefin-derived nucleophiles to ketones

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Enantioenriched alcohols found in an array of bioactive natural products and pharmaceutical agents are often synthesized by asymmetric nucleophilic addition to carbonyls. However, this approach generally shows limited functional-group compatibility, requiring the use of preformed organometallic reagents in conjunction with a stoichiometric or substoichiometric amount of chiral deliverer to deliver optically active alcohols. Herein we report a copper-catalyzed strategy for the stereoselective nucleophilic addition of propargylic and other alkyl groups to ketones, using easily accessible (poly)unsaturated hydrocarbons as latent carbonyl equivalents. Our method features the catalytic generation of highly enantioenriched organocopper intermediates and their subsequent diastereoselective addition to ketones, allowing for the effective construction of highly substituted stereochemical dyads with excellent stereoselectivity. Moreover, this process is general, scalable, and occurs at ambient temperature.

Stereocchemically pure complexes in optically pure form are commonly encountered structural elements in a diverse range of pharmaceutical drugs and biologically active natural products (Fig. 1A). Consequently, general methods that allow for the stereoselective assembly of highly substituted alcohol have long been sought (7). The discovery of Grignard reagents and their subsequent addition to ketones and aldehydes have been widely considered as milestones in synthetic chemistry, giving rise to a general synthesis of alcohols from preformed organo-magnesium reagents and broadly available carbonyl compounds (2). Since then, extensive efforts have been devoted to the development of asymmetric variants of nucleophilic addition reactions to carbonyls, using preformed organometallic reagents (1, 3–7). These synthetic endeavors have proven to be exceptionally fruitful, culminating in a variety of protocols for enantioselective additions to carbonyls, using either a chiral auxiliary-modified organometallic reagent or a substoichiometric amount of chiral deliverer to achieve excellent levels of stereocontrol. Compared with aldehydes, however, the asymmetric nucleophilic addition to ketones has been studied to a lesser extent (5–7).

Although numerous advances have been made in this area, considerable hurdles have impeded the further adaptation of these methods by the synthetic community. The requirement to prepare and use a stoichiometric quantity of an organometallic reagent complicates most of the existing methods. In addition, the highly nucleophilic and basic nature of organometallic reagents has posed substantial limitations with respect to the functional-group compatibility of these processes. As a consequence, these methods are typically not amenable to the transformation of late-stage intermediates and other highly functionalized molecules. Furthermore, an additional synthetic operation is required to prepare these organometallic reagents from organic halide or unsaturated hydrocarbon precursors, imposing further constraints on the types of nucleophiles suitable for carbonyl addition.

In this context, a catalytic method for stereoselective additions to carbonyls, using easily accessible olefins as latent carbonyl equivalents in

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Pore chemistry and size control in hybrid porous materials for acetylene capture from ethylene
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Editor's Summary

Separating one organic from another

Separating closely related organic molecules is a challenge (see the Perspective by Lin). The separation of acetylene from ethylene is needed in high-purity polymer production. Cui et al. developed a copper-based metal-organic framework with hexafluorosilicate and organic linkers designed to have a high affinity for acetylene. These materials, which capture four acetylene molecules in each pore, successfully separated acetylene from mixtures with ethylene. Propane and propylene are both important feedstock chemicals. Their physical and chemical similarity, however, requires energy-intensive processes to separate them. Cadiau et al. designed a fluorinated porous metal-organic framework material that selectively adsorbed propylene, with the complete exclusion of propane.

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