

# An Ideal Molecular Sieve for Acetylene Removal from Ethylene with Record Selectivity and Productivity

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Realization of ideal molecular sieves, in which the larger gas molecules are completely blocked without sacrificing high adsorption capacities of the preferred smaller gas molecules, can significantly reduce energy costs for gas separation and purification and thus facilitate a possible technological transformation from the traditional energy-intensive cryogenic distillation to the energy-efficient, adsorbent-based separation and purification in the future. Although extensive research endeavors are pursued to target ideal molecular sieves among diverse porous materials, over the past several decades, ideal molecular sieves for the separation and purification of light hydrocarbons are rarely realized. Herein, an ideal porous material, SIFSIX-14-Cu-i (also termed as UTSA-200), is reported with ultrafine tuning of pore size (3.4 Å) to effectively block ethylene (C<sub>2</sub>H<sub>4</sub>) molecules but to take up a record-high amount of acetylene (C<sub>2</sub>H<sub>2</sub>, 58 cm<sup>3</sup> cm<sup>-3</sup> under 0.01 bar and 298 K). The material therefore sets up new benchmarks for both the adsorption capacity and selectivity, and thus provides a record purification capacity for the removal of trace C<sub>2</sub>H<sub>2</sub> from C<sub>2</sub>H<sub>4</sub> with 1.18 mmol g<sup>-1</sup> C<sub>2</sub>H<sub>2</sub> uptake capacity from a 1/99 C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixture to produce 99.9999% pure C<sub>2</sub>H<sub>4</sub> (much higher than the acceptable purity of 99.996% for polymer-grade C<sub>2</sub>H<sub>4</sub>), as demonstrated by experimental breakthrough curves.


Porous materials offer promise for the separation and purification of industrial commodity chemicals through adsorbent- and/or membrane-based separation technologies and thus might enable a transition from established separation technologies such as cryogenic distillation, which currently accounts for 10–15% of the world’s energy consumption.<sup>[1–4]</sup> Although such promise has not been fully fulfilled, extensive research efforts have indeed led to progress over the past several decades. For example, the discovery of the molecular gate adsorbent ETS-4 has initiated the industrial scale nature gas separation.<sup>[5,6]</sup>

Pore tuning and pore functionalization are two powerful approaches to introduce molecular sieving and preferential binding effects and thus are very important to target porous materials for the efficient gas separation and purification, as clearly demonstrated in ETS-4 series and zeolite LiX materials for CH<sub>4</sub>/N<sub>2</sub> and N<sub>2</sub>/O<sub>2</sub> separations, respectively.<sup>[5,7]</sup> Whereas

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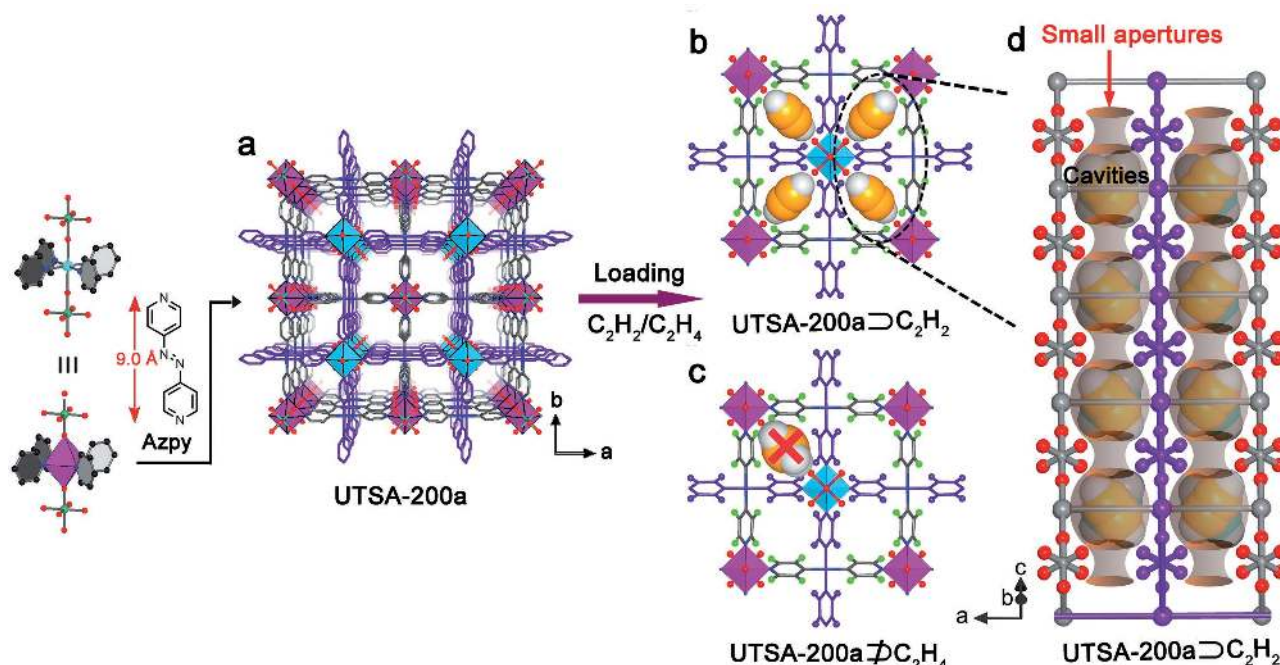
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traditional zeolite-type materials are quite limited in terms of tuning pore size and functionalization, basically through control of the thermal activation and substitutions of metal cations, microporous metal–organic frameworks, and related classes of materials have provided us the rich chemistry to realize fine pore tuning and functionalization, and thus target materials for gas separation and purification through the judicious choices of metal clusters and organic linkers, framework topology design, framework interpenetration control, and immobilization of specific functional sites.<sup>[8–16]</sup> Indeed, a number of microporous metal–organic frameworks (MOFs) have been realized to address a diverse range of gas separations over the past decades through a synergistic approach to pore tuning and functionalization.<sup>[17–27]</sup> Recent progress on this topic for the separation of  $C_2H_2/C_2H_4$  and  $C_3H_6/C_3H_8$  is of particularly interest.<sup>[28,29]</sup> In the former case of SIFSIX-2-Cu-i, the trade-off between adsorption capacity and selectivity for separating the challenging gas mixtures of  $C_2H_2/C_2H_4$  has been significantly minimized; in the latter case, NbOFFIVE-1-Ni exhibits a molecular sieving effect for  $C_3H_6/C_3H_8$  separation. Although these two porous materials exhibit benchmark performance for the above-mentioned gas separations, they still suffer from certain degree of the trade-off effects: the  $C_2H_2/C_2H_4$  selectivity ( $S_{ac}$ ) of SIFSIX-2-Cu-i does not preclude coadsorption of the larger molecule,  $C_2H_4$ , when  $C_2H_2$  is a minor impurity; NbOFFIVE-1-Ni can adsorb small amounts of the smaller molecule of  $C_3H_6$ , particularly under low pressure of 0.1 bar ( $\approx 5.3 \text{ cm}^3 \text{ g}^{-1}$ ), deviating from the ideal molecular sieves (ideal molecular sieves are defined as those which can completely block the larger gas

molecules and take up large amount of the smaller gas molecules from gas mixtures). Realization of ideal molecular sieves can certainly enable ultrahigh selectivity and working capacity for diverse gas separations and thus improve the product purity and adsorbent productivity in the adsorption-based separation process that is driven by pressure swing adsorption, thermal swing adsorption, or membrane-based operations, to result in the significant energy savings.<sup>[30–35]</sup> To the best of our knowledge, there are only a few reported molecular sieves for carbon capture and separation of olefin/paraffin.<sup>[29,36–41]</sup> We target this matter herein through the study of SIFSIX-14-Cu-i (UTSA-200), a new variant of SIFSIX-2-Cu-i, to realize the ideal molecular sieve for separation and purification of  $C_2H_2/C_2H_4$  mixtures with the record selectivity and  $C_2H_4$  productivity ever reported.

Structural and modeling studies have indicated that the pores of about 4.4 Å in SIFSIX-2-Cu-i remain slightly larger than the size of  $C_2H_4$  (kinetic dimensions 4.2 Å)<sup>[42]</sup> and thus cannot exhibit a sieving effect for  $C_2H_4$  (Figure S3, Supporting Information). We speculated that if a shorter organic linker of 4,4'-azopyridine (azpy, 9.0 Å) instead of 4,4'-dipyridylacetylene (dpa, 9.6 Å) is used to construct the isorecticular SIFSIX-14-Cu-i/UTSA-200 (Figure 1), the resulting microporous material was expected to exhibit a smaller pore size of  $\approx 3.3\text{--}4.0$  Å that might completely block  $C_2H_4$  molecules while enhance the affinity of the functional  $SiF_6^{2-}$  sites toward  $C_2H_2$ , thus targeting an ideal molecular sieve for the extremely highly efficient removal of  $C_2H_2$  from a 1/99  $C_2H_2/C_2H_4$  mixture to produce high purity of  $C_2H_4$  in a much higher production scale than SIFSIX-2-Cu-i. Our experimental and simulation studies verify this hypothesis,



**Figure 1.** Structure description of UTSA-200a. a) The channel structure of UTSA-200a reveals a pores size of  $\approx 3.4$  Å. b) DFT-D-calculated  $C_2H_2$  adsorption models in UTSA-200a, revealing that this pore size enables the passage of  $C_2H_2$  molecules. c) Simulated  $C_2H_4$  adsorption in UTSA-200a indicating that the  $C_2H_4$  molecule are too large to pass through the pores. d) Schematic illustration of ideal molecular sieves based on the structure of UTSA-200a  $\supset C_2H_2$ , in which larger cavities suitable for strongly binding  $C_2H_2$  molecules are interconnected by narrow apertures that serve as sieves for  $C_2H_4$  but not for  $C_2H_2$ . The different nets are highlighted in gray and purple for clarity. Color code: Cu (turquoise), Si (dark green), F (red), N (blue), C (gray), and H (green spheres).

and we report herein the structure, adsorption isotherms, simulated and experimental breakthrough curves of SIFSIX-14-Cu-i (UTSA-200). These data reveal that SIFSIX-14-Cu-i (UTSA-200) is the new benchmark porous material for the removal of  $C_2H_2$  from  $C_2H_4$  in a 1/99 mixture that mimics that present in large-scale industrial ethylene production processes.

Reaction of azpy with  $CuSiF_6$  afforded saffron prism-shaped crystals of  $[Cu(azpy)_2(SiF_6)]_n$  (see the Supporting Information for synthetic and crystallographic details). The single-crystal X-ray diffraction analysis revealed that UTSA-200 has doubly interpenetrated nets that are isostructural to the nets in SIFSIX-2-Cu-i.<sup>[18]</sup> After removing guest molecules, we further collected the desolvated structure, that is, UTSA-200a, by using neutron powder diffraction experiments at 200 K. As revealed by Figure 1a, the use of the shorter azpy instead of dpa as a linker offers: (i) a commensurate reduction on the pore size; and (ii) a certain degree of tilting of the pyridine moieties, which are rotated by around 28 degrees with respect to the crystal axis (Figure S4, Supporting Information). The  $SiF_6^{2-}$  pillars and pyridine rings are interconnected through a strong hydrogen bonding of  $C-H\cdots F$  (2.326 Å) to restrict the rotation of pyridine rings. This tilt of pyridine rings thereby results in the pore size of UTSA-200a being notably reduced to 3.4 Å. In addition, the channels of UTSA-200a exhibit the features of ideal molecular sieves, in which larger cavities functionalized with the  $SiF_6^{2-}$  binding sites are interconnected by narrow apertures of 3.4 Å (molecular sieving dimension, Figure 1d; Figure S5, Supporting Information). This narrow aperture size was further confirmed by the calculated pore size distributions, where the pore sizes of UTSA-200a are less than 3.6 Å (Figure S6, Supporting Information), in good agreement with the results of structural analysis. We note that the aperture size of 3.4 Å is much smaller than the kinetic diameter of  $C_2H_4$  molecule (4.2 Å) but slightly larger than that of  $C_2H_2$  (3.3 Å), consistent with the potential for selective molecular sieving in  $C_2H_2/C_2H_4$  separations.

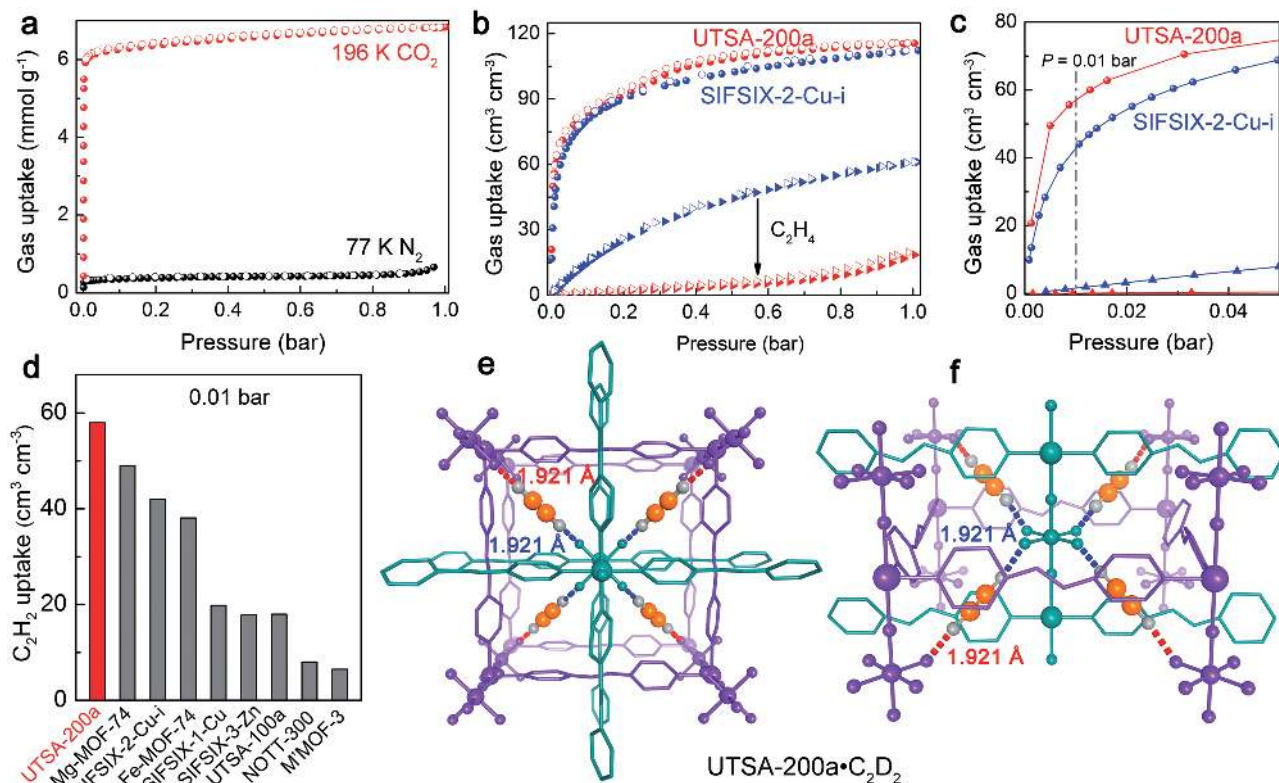
We first performed detailed modeling studies using first-principles dispersion-corrected density functional theory (DFT-D) method on UTSA-200a and compared the results with SIFSIX-2-Cu-i to evaluate the possible sieving effect on  $C_2H_2/C_2H_4$  molecules. In the 2-fold interpenetrated structure of SIFSIX-2-Cu-i, the window size of 4.4 Å is larger than both  $C_2H_2$  and  $C_2H_4$ , thereby allowing both  $C_2H_2$  and  $C_2H_4$  molecules to enter the cavities (Figure S3, Supporting Information). Each adsorbed  $C_2H_2$  or  $C_2H_4$  molecule is simultaneously bound by two  $SiF_6^{2-}$  sites from different nets through cooperative  $C-H\cdots F$  H-bonding (2.015 Å for  $C_2H_2$  and 2.186 Å for  $C_2H_4$ ).<sup>[28]</sup> When the aperture size was reduced to 3.4 Å in UTSA-200a, our computational results indicated that the contracted aperture size still allows  $C_2H_2$  molecules to enter the pore cavities and bind in the same fashion upon adsorption (Figure 1b). The calculated distance of  $C-H\cdots F$  H-bonding in UTSA-200a is shorter (1.900 Å) than that in SIFSIX-2-Cu-i (Figure S7, Supporting Information). In contrast, when loading a  $C_2H_4$  molecule into the pores, we found that the  $C_2H_4$  molecule would have inevitable space overlapping with the pore walls of UTSA-200a (Figure 1c), suggesting that the size of  $C_2H_4$  may mismatch with the host framework and thereby to be size excluded. These calculated studies support that the

contracted pore size of UTSA-200a (vs SIFSIX-2-Cu-i) might enable sieving of  $C_2H_2$  from  $C_2H_4$ .

The performance of UTSA-200a was determined by examining its gas sorption and separation properties. As illustrated in Figure 2a, UTSA-200a exhibits almost no  $N_2$  uptake at 77 K, indicating that even  $N_2$  (3.64 Å) is blocked at this low cryogenic temperature because of the small aperture size. On the other hand, for  $CO_2$  (kinetic diameter 3.3 Å), a high amount of  $CO_2$  is adsorbed ( $153\text{ cm}^3\text{ g}^{-1}$ ) at 196 K and 1 bar with type I sorption behavior characteristic of microporous materials. The Brunauer–Emmett–Teller (BET) surface area and pore volume were calculated to be  $612\text{ m}^2\text{ g}^{-1}$  and  $0.27\text{ cm}^3\text{ g}^{-1}$ , respectively, slightly lower than SIFSIX-2-Cu-i ( $735\text{ m}^2\text{ g}^{-1}$  and  $0.31\text{ cm}^3\text{ g}^{-1}$ ).

Pure component equilibrium adsorption isotherms for  $C_2H_2$  and  $C_2H_4$  were measured at 298 K up to 1 bar, as presented in Figure 2b. Detailed analysis revealed that UTSA-200a exhibits a steep and high  $C_2H_2$  uptake of  $116\text{ cm}^3\text{ cm}^{-3}$  at 298 K and 1 bar. This value is comparable to the uptake of SIFSIX-2-Cu-i and is expected thanks to their similar pore chemistry. However, contraction of pore size in UTSA-200a was found to enable higher uptake than SIFSIX-2-Cu-i within the low pressure of 0.025 bar (Figure 2c). At 0.01 bar, which is an indicator of the  $C_2H_2$  capture ability of adsorbents from a  $C_2H_2/C_2H_4$  mixture (1/99, v/v), UTSA-200a exhibits notably enhanced  $C_2H_2$  uptake ( $58\text{ cm}^3\text{ cm}^{-3}$ ) versus SIFSIX-2-Cu-i ( $42\text{ cm}^3\text{ cm}^{-3}$ ). In comparison to other top-performing materials, UTSA-200a exhibits a new benchmark for  $C_2H_2$  uptake at 0.01 bar (Figure 2d), even higher than Mg- and Fe-MOF-74, indicating its ultrastrong  $C_2H_2$  capture capacity at low pressure. Conversely, as revealed by Figure 2b, the smaller static pore size of UTSA-200a can completely prevent the entrance of  $C_2H_4$  molecule below 0.2 bar and has very little uptake ( $\approx 0.25\text{ mmol g}^{-1}$ ) up to 0.7 bar at 298 K, which is dramatically lower than that of SIFSIX-2-Cu-i ( $2.28\text{ mmol g}^{-1}$ ). When the pressure was further increased to 1 bar,  $C_2H_4$  adsorption isotherm slopes up. This is because the N=N bond and the pyridine rings in the MOF linker have certain rotational flexibility, so the pore sizes were slightly enlarged under higher pressure (larger than 0.7 bar) to take up small amount of  $C_2H_4$  molecules (Figure S8, Supporting Information). Nevertheless, the  $C_2H_4$  uptake amounts of UTSA-200a in the entire range of 1 bar are still the lowest among the indicated materials (Figure S9, Supporting Information). Therefore, our adsorption findings demonstrated that the contracted pore size of UTSA-200a supports to efficiently block  $C_2H_4$  molecules without sacrificing its high  $C_2H_2$  adsorption capacity, rendering UTSA-200a an ideal candidate for  $C_2H_2/C_2H_4$  separation at ambient conditions.

To gain further insight into the ultrastrong  $C_2H_2$  adsorption and confirm the calculated  $C_2H_2$  binding sites, high-resolution neutron powder diffraction data were collected on  $C_2D_2$ -loaded samples of UTSA-200a and Rietveld structural refinements were conducted (Figure S11, Supporting Information). After the samples loaded with various amount of  $C_2D_2$  molecules, the MOF lattice can be slightly distorted from the tetragonal symmetry to a monoclinic lattice. As shown in Figure 2e,f, each adsorbed  $C_2D_2$  molecule interacts with two  $SiF_6^{2-}$  anions from different nets through cooperative  $C-D\cdots F$  H-bonding, which is consistent well with the previous calculated  $C_2H_2$  binding configuration. Because of the smaller pore size, the



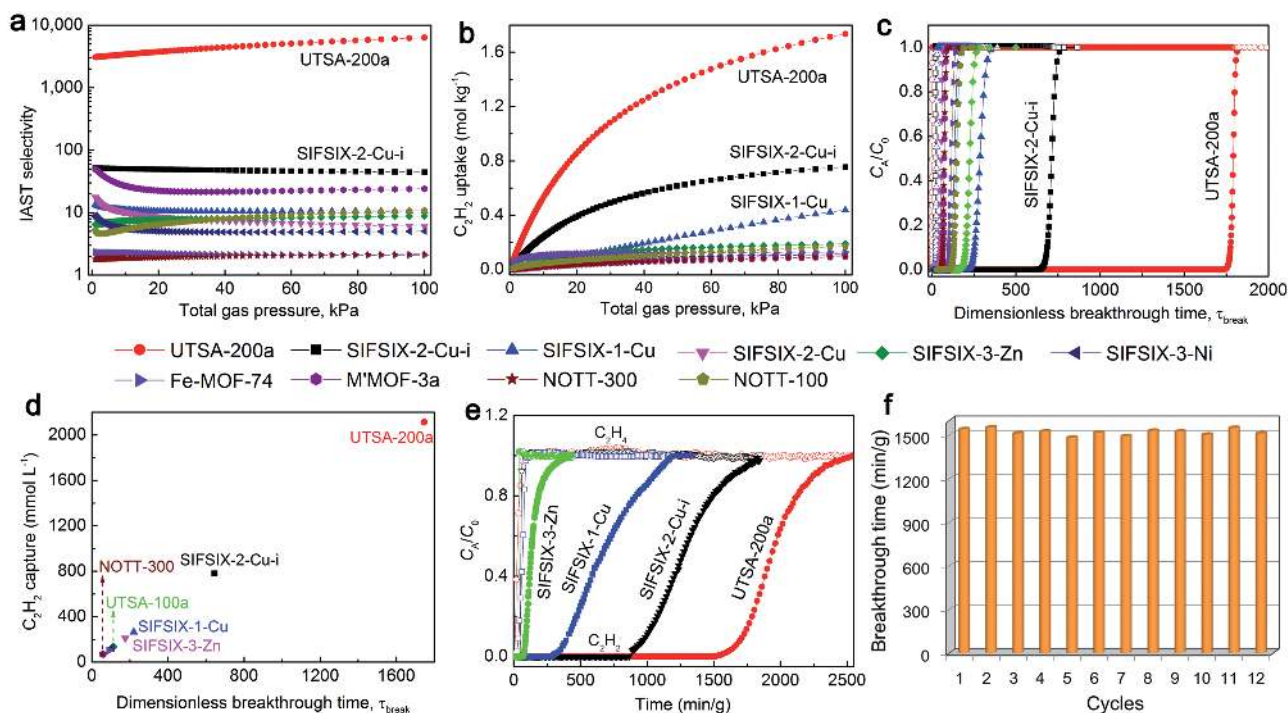
**Figure 2.** Gas adsorption isotherms and neutron crystal structure of UTSA-200a-C<sub>2</sub>D<sub>2</sub>. a) Gas adsorption isotherms of UTSA-200a for CO<sub>2</sub> at 196 K and N<sub>2</sub> at 77 K. Adsorption isotherms of C<sub>2</sub>H<sub>2</sub> (circles) and C<sub>2</sub>H<sub>4</sub> (triangles) for UTSA-200a and SIFSIX-2-Cu-i at 298 K in two pressure regions, b) 0–1.0 bar and c) 0–0.05 bar. Filled/empty circles represent adsorption/desorption. d) Comparison of C<sub>2</sub>H<sub>2</sub> uptake for UTSA-200a and other best-performing materials at 0.01 bar. Neutron crystal structure of UTSA-200a-C<sub>2</sub>D<sub>2</sub> at 200 K viewed along the f) *b* and e) *c* axis, determined from Rietveld analysis (the different nets are highlighted in purple and dark green for clarity). Color code: D, white; C (in C<sub>2</sub>H<sub>2</sub>) orange.

experimentally determined H-bonding length in UTSA-200a (1.921 Å) is notably shorter than that observed in SIFSIX-2-Cu-i (2.015 Å), further indicating that there are stronger interactions with C<sub>2</sub>H<sub>2</sub> molecules. Consistent with this, the calculated static binding energy ( $\Delta E$ ) of C<sub>2</sub>H<sub>2</sub> for UTSA-200a (56.0 kJ mol<sup>-1</sup>) is larger than that of SIFSIX-2-Cu-i (52.9 kJ mol<sup>-1</sup>), making it the strongest C<sub>2</sub>H<sub>2</sub> adsorption observed in SIFSIX and related materials. This is the primary factor for the ultrahigh C<sub>2</sub>H<sub>2</sub> adsorption capacity of UTSA-200a at very low pressures. Further diffraction measurement shows that the MOF structure can be completely restored after removing C<sub>2</sub>D<sub>2</sub> from the sample, suggesting that the adsorption-induced lattice distortion is a temporary effect, and thus the sample does not lose crystallinity.

Given the observations of molecular exclusion of C<sub>2</sub>H<sub>4</sub> and ultrastrong C<sub>2</sub>H<sub>2</sub> capture capacity, UTSA-200a was found to exhibit an extraordinary ideal adsorbed solution theory (IAST) selectivity of over 6000 at 1 bar and 298 K for binary C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99, v/v) mixtures, significantly higher than the previous top-performing materials (Figure 3a). It should be pointed out that this value is only for the qualitative comparison purpose. We also calculated the uptake ratios of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (at 0.01/0.01 or 0.01/0.99 bar) determined from single-component isotherms<sup>[40]</sup> and compared with other reported MOFs (Figure S12, Supporting Information). These data also clearly demonstrate the superior selectivity of UTSA-200a for the separation of

C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures. In addition, UTSA-200a also exhibits the highest C<sub>2</sub>H<sub>2</sub> uptake (1.74 mol kg<sup>-1</sup>) for adsorption from this gas mixture, which is much higher than the benchmark MOFs evaluated in Figure 3b. UTSA-200a is to our knowledge the first example of a porous material that fully overcomes the trade-off between selectivity and uptake capacity in which it exhibits not only the unprecedented high selectivity but also record-high uptake capacity in the context of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation.

Next, transient breakthrough simulations were performed to validate the feasibility of using UTSA-200a in a fixed bed for the separation of 1/99 C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixture that mimics the industrial process. Figure 3c reveals the molar concentrations of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> exiting the adsorber packed with UTSA-200a as a function of the dimensionless time,  $\tau$ , at 1 bar and 298 K. Complete separation was accomplished by UTSA-200a, whereby C<sub>2</sub>H<sub>4</sub> breakthrough occurred first within seconds to yield the polymer-grade gas, and then C<sub>2</sub>H<sub>2</sub> passed through the fixed bed after a certain time ( $\tau_{\text{break}}$ ). Attributed to the record-high selectivity and C<sub>2</sub>H<sub>2</sub> uptake capacity, the  $\tau_{\text{break}}$  value for UTSA-200a is more than twice as long as that observed in the previous benchmark, SIFSIX-2-Cu-i. Further, during the time 0– $\tau_{\text{break}}$ , the C<sub>2</sub>H<sub>2</sub> amount captured by UTSA-200a reaches up to 2133.3 mmol L<sup>-1</sup>, which is 3–30 times higher than SIFSIX-2-Cu-i (780.0 mmol L<sup>-1</sup>) and other benchmark materials (Figure 3d). Overall, the separation performance of UTSA-200a far surpasses other SIFSIX materials and MOFs reported to date.



**Figure 3.** IAST calculations, simulated and experimental column breakthrough studies of UTSA-200a for  $C_2H_2/C_2H_4$  (1/99) mixtures. Comparison of the a) IAST selectivity and b)  $C_2H_2$  uptake capacity of UTSA-200a versus the other best-performing materials. c) Simulated column breakthrough curves for  $C_2H_2/C_2H_4$  separation with respect to various MOF materials as indicated. d) Plots of the amount of  $C_2H_2$  captured as a function of  $\tau_{break}$  in the simulated column breakthrough for UTSA-200a and the other indicated materials. e) Experimental column breakthrough curves for  $C_2H_2/C_2H_4$  separations with UTSA-200a, SIFSIX-2-Cu-i, SIFSIX-1-Cu, and SIFSIX-3-Zn at 298 K and 1.01 bar. f) The recyclability of UTSA-200a under multiple mixed-gas column breakthrough tests.

These simulated results prompted us to further evaluate the separation performance of UTSA-200a in the actual separation. Experimental breakthrough studies were conducted for a  $C_2H_2/C_2H_4$  (1:99, v/v) mixture at room temperature. As illustrated in Figure 3e, highly efficient separation for  $C_2H_2/C_2H_4$  mixture was achieved by UTSA-200a: the  $C_2H_4$  gas eluted through the adsorption bed immediately in a high-purity grade (Figure S14, Supporting Information), whereas  $C_2H_2$  was retained in the packed column over 1500 min (the concentration in the outlet below 40 ppm). This  $C_2H_2$  breakthrough time is 2 times longer than SIFSIX-2-Cu-i ( $\approx 800$  min), in good agreement with the simulated breakthrough results. Detailed gas chromatography data revealed that the purity of  $C_2H_2$  in the outlet effluent was below 1 ppm up to 1300 min, affording high  $C_2H_4$  purity of  $>99.9999\%$  (Figure S15, Supporting Information). The  $C_2H_2$  concentration is notably less than the acceptable level of  $<40$  ppm for polymer-grade  $C_2H_4$  gas. During the breakthrough process, the  $C_2H_4$  production from the outlet effluent and the  $C_2H_2$ -captured amount for a given cycle were analyzed to be record high of 85.7 and 1.18  $mmol\ g^{-1}$ , respectively, which is much higher than the 47.4 and 0.73  $mmol\ g^{-1}$  observed in SIFSIX-2-Cu-i. The adsorbed  $C_2H_2$  can be further recovered in a two-step process via adsorption followed by desorption at 338 K, offering a 93.6% recovery of a  $C_2H_2$  capacity of 1.105  $mmol\ g^{-1}$  per cycle, with a 97% purity (Figures S16 and S17, Supporting Information). This recovered  $C_2H_2$  purity is notably higher than the 89% obtained in SIFSIX-2-Cu-i. These results indicate that

UTSA-200a offers the potential to effectively separate  $C_2H_2$  from  $C_2H_4$  and simultaneously produce both gases in high purity.

The feed gases in the practical  $C_2H_2$  removal unit are often contaminated by trace levels of  $CO_2$  ( $<50$  ppm),  $H_2O$  ( $<5$  ppm), and  $O_2$  ( $<5$  ppm),<sup>[43]</sup> so the amenability to recycling and efficacy in the presence of these gases must be also addressed. To investigate the influence of these other gases, we conducted a series of breakthrough experiments on UTSA-200a for the 1/99 mixtures containing trace amounts of  $CO_2$ ,  $H_2O$ , and  $O_2$ , respectively. The presence of  $CO_2$  (100 ppm) and  $O_2$  (up to 2200 ppm) has a negligible effect on the separation capacity of UTSA-200a (Figures S18 and S19, Supporting Information). Similarly, the moisture (from 6 to 1340 ppm) also did not affect the separation of  $C_2H_2$  from  $C_2H_4$  (Figure S20, Supporting Information). Subsequently, we performed multiple mixed-gas ( $C_2H_2/C_2H_4$  at 1/99) column breakthrough tests to examine the preservation of separation performance of UTSA-200a at ambient conditions. The recycling measurements revealed that UTSA-200a retains the  $C_2H_2$  capture capacity and its molecular sieving over 12 cycles (Figures S21 and S23, Supporting Information). The breakthrough time remains almost unchanged during 12 breakthrough experiments, confirming the recyclability of this material for  $C_2H_2/C_2H_4$  separation (Figure 3f). As inferred from the PXRD performed on associated samples, the framework of UTSA-200a remains stable after multiple adsorption and breakthrough experiments (Figure S27, Supporting Information).

Removal of acetylene from ethylene/acetylene mixture (1/99) is one of the most important but challenging industrial-scale gas separations and is currently affected by energy- and cost-intensive processes.<sup>[44–46]</sup> Although adsorption-based porous materials offer promise to create cost-effective and energy-efficient separation technologies, porous materials reported so far suffer from a trade-off between adsorption capacity and selectivity.<sup>[47–50]</sup> We have demonstrated the first example of nearly ideal molecular sieve, UTSA-200a, with the required characteristics (molecular-sieving size of  $\approx 3.4$  Å and strong binding sites toward  $C_2H_2$ ), that afford the selective molecular exclusion of  $C_2H_4$  and record-high amount of  $C_2H_2$  adsorption, thus overcoming the trade-off effect for achieving highly efficient separation of  $C_2H_2/C_2H_4$  mixtures. The molecular sieving of  $C_2H_2$  from  $C_2H_4$  is supported by detailed structural analysis, gas adsorption isotherms, simulated and experimental breakthrough studies. The resulting separation performance includes record-high  $C_2H_4$  productivity of  $87.5$  mmol  $g^{-1}$  per cycle with purity higher than 99.9999% and simultaneous production of the high purity  $C_2H_2$  (97%) via a simple recovery operation.

Ideal molecular sieves, while very difficult to achieve, indeed can provide a promising energy-efficient route to address the industrially important gas separations. Through fine tuning of pore size in molecular sieves to selectively exclude the  $C_2H_4$  but to retain the strong binding sites for the record-high  $C_2H_2$  adsorption capacity, our findings demonstrated, for the first time, that it is possible and feasible to target microporous MOFs with ideal molecular sieve performance through the elaborated fine tuning of the pore sizes and the introduction of specific binding sites for the preferred gas molecules. SIFSIX-14-Cu-i/UTSA-200 can readily remove trace amount of  $C_2H_2$  from 1/99  $C_2H_2/C_2H_4$  mixture, affording benchmark high selectivity as well as benchmark  $C_2H_2$  capture capacity and thus record-high  $C_2H_4$  production scale as demonstrated in the breakthrough experiments. Combined with the excellent recyclability and resistance to other gases, SIFSIX-14-Cu-i/UTSA-200 represents an ideal microporous solid material that has the potential to be applied in the industry as an adsorbent for removing trace acetylene from ethylene using a relatively simple and energy-efficient process. The principle revealed in this work is general, which will provide some guidance to facilitate the design and implementation of ideal molecular sieves for other important gas separations and purification as well.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

acetylene, ethylene purification, gas separation, molecular sieves, porous materials

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