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A microporous metal–organic framework with rare lvt topology for highly selective C₂H₂/C₂H₄ separation at room temperature†

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A new lvt-type metal–organic framework UTSA-60a with suitable pore channels and open metal sites has been developed for highly selective separation of C₂H₂/C₂H₄ at room temperature.

In steam cracking of ethane to produce ethene, ethyne is one of the small amounts of by-products, which has a deleterious effect on end-products of ethene such as polyethene; therefore, it is imperative to remove ethyne from ethene. Typically, the impurity level of 40 ppm C₂H₂ needs to be met for ethene feed for the polymerization reactor. The main commercial methods to eliminate ethyne from crude ethene include partial hydrogenation and solvent extraction which are costly and energy-intensive.¹ One of the alternative and energy-efficient strategies for this separation is adsorptive separation technology using porous materials. Although traditional porous zeolites and activated carbons have been extensively examined for this very important separation, no porous materials have been realized to significantly differentiate these two gas molecules.²

Porous metal–organic frameworks (MOFs), which can be readily self-assembled from metal ions/clusters with organic linkers,³ have been rapidly emerging as a new class of porous materials for gas storage and separation applications.^{4,5} Judicious selection of molecular building blocks can tune their structures, pore/window sizes, and functionalization at the molecular level to optimize and thus fulfill their specific separation of small molecules.⁶ Recently, the potential utility

of porous MOFs for separation of hydrocarbon mixtures has been explored by a number of independent groups.^{7,8} Among the diverse gas separations, separation of C₂H₂/C₂H₄ is one of the most challenging and difficult ones because of their similar sizes, volatilities, and electronic structures.⁹ To the best of our knowledge, only a few microporous MOFs have been realized for this separation so far.^{10–13} For example, our group realized a series of microporous mixed MOFs (MMOFs) for highly selective separation of C₂H₂/C₂H₄ by fine tuning of pore sizes.¹⁰ Long and Chen's groups independently reported that a series of MMOF-74 (M = Mg, Fe, and Co) with high density of open metal sites can separate C₂H₂ from the mixture well.^{11,12} However, the MMOFs suffer from the low C₂H₂ uptake capacities due to the narrow pore windows, while the MMOF-74 materials need significantly high regeneration energy costs to overcome the strong binding energy between open metal sites and gas molecules. Apparently, there is an increasing demand to develop better adsorbents with both high selectivity and C₂H₂ uptake but low regeneration cost to fulfill this challenging separation. With this in mind, we developed a novel tetracarboxylic acid ligand (H₄BTAA, Scheme 1), and reported herein the synthesis of its first porous MOF (termed as UTSA-60) with suitable window sizes and open Cu²⁺ sites for such a purpose.† This material exhibits not only higher C₂H₂/C₂H₄ selectivity and C₂H₄ productivity, but also lower regeneration energy costs compared to MMOF-74 (M = Mg, Fe, and Co), featuring it as one of the best adsorbents for selective separation of C₂H₂/C₂H₄ at room temperature.

The organic linker H₄BTAA, benzene-1,2,4,5-tetraacrylic acid, was simply synthesized by Heck cross-coupling reactions

Scheme 1 The organic ligand H₄BTAA for the construction of UTSA-60.

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† Electronic supplementary information (ESI) available: Synthesis and characterization of UTSA-60, PXRD, TGA, sorption isotherms, and breakthrough simulations. CCDC 1038935. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc09999k

of 1,2,4,5-tetraiodobenzene and methyl acrylate, followed by hydrolysis and acidification. Reactions of the organic linker with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in acidified DMF– H_2O at 60 °C for 24 h afforded green block crystals of UTSA-60. The as-synthesized UTSA-60 can be formulated as $[\text{Cu}_2\text{BTAA}(\text{H}_2\text{O})_2] \cdot 2\text{DMF} \cdot 2\text{H}_2\text{O}$, as determined by single-crystal XRD analysis, TGA and elemental analysis. The phase purity of the bulk material was also confirmed by powder X-ray diffraction (Fig. S3, ESI†).

Single-crystal X-ray diffraction analysis revealed that UTSA-60 crystallizes in the orthorhombic space group *Imma*. As frequently observed in MOFs, the framework nodes in UTSA-60 consist of paddle-wheel dinuclear $\text{Cu}_2(\text{COO})_4$ secondary building units (SBUs) with the organic linkers to form a three-dimensional (3D) framework (Fig. 1a). UTSA-60 shows a rarely observed lvt-type network of $4^2 \cdot 8^4$ topology which is different from the well-known nbo MOFs (Fig. 1b).¹⁴ There exist three types of open channels of about $4.8 \times 4.0 \text{ \AA}^2$ along the *b* axis, $3.6 \times 2.8 \text{ \AA}^2$ along the *c* axis, and $3.7 \times 10.5 \text{ \AA}^2$ along the *a* axis, respectively.

Of most interest are the small channels along the *b* axis, which present a large number of unsaturated Cu^{2+} centers for the recognition of gas molecules (Fig. 1d). As a result, the combined feature of small pore channels and open metal sites within UTSA-60a highlights its potential for highly selective adsorptive separation of C_2H_2 – C_2H_4 mixtures.

Prior to gas adsorption measurements, the as-synthesized UTSA-60 was solvent-exchanged with dry acetone, and then evacuated at 273 K for two days and at room temperature for 2 h under high vacuum to yield the activated UTSA-60a. The PXRD analysis indicates that the activated UTSA-60a retains its crystalline feature (Fig. S3, ESI†), although the peaks of UTSA-60a are slightly different from those of the as-synthesized UTSA-60 due to the flexible nature of double-bond spacers in the organic linker.¹⁵ The permanent porosity was established by nitrogen sorption at 77 K. The N_2 sorption isotherm at 77 K

Fig. 2 Single-component adsorption isotherms for C_2H_2 (blue) and C_2H_4 (green) of UTSA-60a at 296 K.

exhibits a typical Type-I sorption behaviour, characteristic of a microporous material (Fig. S6, ESI†). The Brunauer–Emmett–Teller (BET) and Langmuir surface areas were estimated to be 484 and $500 \text{ m}^2 \text{ g}^{-1}$, respectively.

The establishment of permanent microporosity in UTSA-60a prompted us to examine its potential as an adsorbent for the industrially important $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation. Single-component adsorption isotherms for acetylene and ethylene were measured up to 1 atm at 273 and 296 K, respectively. As shown in Fig. 2, UTSA-60a shows remarkably different adsorption behaviours with respect to C_2H_2 and C_2H_4 at 296 K. The adsorption isotherms of C_2H_2 in UTSA-60a display a rapid increase at low pressure and then saturation at around 30 kPa; however, the uptake of C_2H_4 increases slowly following this pressure. More importantly, UTSA-60a can take up a moderate amount of C_2H_2 ($70 \text{ cm}^3 \text{ g}^{-1}$) at 1 atm and 296 K, which is much higher than the amount of C_2H_4 ($46 \text{ cm}^3 \text{ g}^{-1}$) under the same conditions. These observed discrepancies between C_2H_2 and C_2H_4 absorption properties suggest that UTSA-60a might be a promising candidate for $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation, which encouraged us to examine its feasibility to selectively separate C_2H_2 from binary C_2H_2 – C_2H_4 mixtures in more detail.

Ideal Adsorbed Solution Theory (IAST) was utilized to calculate the adsorption selectivity of UTSA-60a for the binary C_2H_2 – C_2H_4 mixtures containing 1% C_2H_2 . Fig. 3a presents the IAST calculations of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ adsorption selectivities for UTSA-60a and three other representative MOFs (MMOF-74, *M* = Mg, Fe, and Co) at 296 K. The adsorption selectivity of UTSA-60a lies in the range of 5.5 to 16 at room temperature, which is significantly higher than those obtained in the range of 1.6 to 2.2 for FeMOF-74, CoMOF-74, and MgMOF-74 with high density of open metal sites. This is really remarkable, featuring UTSA-60a as the unique MOF having the highest adsorption selectivity for $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation except MMOF-3a.^{9,11} Besides adsorption selectivity, uptake capacity of C_2H_2 is also important in determining the performance of any given adsorbent in industrial fixed bed adsorbers. Fig. S8 (ESI†) compares the gravimetric uptake capacity of C_2H_2 for adsorption from mixtures containing 1% C_2H_2 . At a total gas phase pressure of 100 kPa, the hierarchy of uptake capacities

Fig. 1 X-ray single crystal structure of UTSA-60, indicating that (a) each tetracarboxylate ligand connects with four paddle-wheel $\text{Cu}_2(\text{COO})_4$ clusters; (b) the framework topology of the lvt net; (c) the structure viewed along the *c* axis, indicating the pore channels of about $3.6 \times 2.8 \text{ \AA}^2$; and (d) the pore channels viewed along the *b* axis indicating the pore channels of about $4.8 \times 4.0 \text{ \AA}^2$ in diameter (C, gray; H, white; Cu, blue).

Fig. 3 (a) IAST calculations of C_2H_2/C_2H_4 adsorption selectivities for UTSA-60a, MgMOF-74, FeMOF-74, and CoMOF-74 at 296 K; (b) the plot of pure C_2H_4 produced per L of adsorbent, during the time interval $0 - \tau_{\text{break}}$, plotted as a function of the time interval τ_{break} . The temperature is 296 K for all MOFs except FeMOF-74 for which the chosen temperature is 318 K; (c) comparison of isosteric heats of C_2H_2 adsorption, Q_{st} , in UTSA-60a, FeMOF-74, CoMOF-74 and MgMOF-74. The calculations of Q_{st} are based on the use of the Clausius–Clapeyron equation.

for C_2H_2 is $\text{MgMOF-74} > \text{FeMOF-74} \approx \text{UTSA-60a} > \text{CoMOF-74}$. Although the C_2H_2 uptake capacity of UTSA-60a is slightly lower than that of MgMOF-74, the much higher selectivity of UTSA-60a can outweigh its uptake capacity disadvantages. Taken together, UTSA-60a is superior to MMOF-74 in terms of C_2H_2/C_2H_4 separation.

To further validate the feasibility of using UTSA-60a for this separation, transient breakthrough simulations were carried out using the methodology developed and described in the literature (see the ESI† for details).¹⁶ The simulated breakthrough curve of UTSA-60a for the C_2H_2/C_2H_4 separation at 296 K is shown in Fig. S9 (ESI†). It is very clear that UTSA-60a can efficiently separate C_2H_2 from the C_2H_2/C_2H_4 (1/99) mixture at room temperature, in which ethylene breaks through first because of the lower adsorptivity relative to acetylene. The breakthrough time, τ_{break} of UTSA-60a, which satisfies the required purity level of 40 ppm, can be determined in Fig. S10 (ESI†). We note that pure C_2H_4 can be collected during the time interval, which can satisfy the feedstock requirements of the polymerization reactor in the polymer industry. From a material balance on the adsorber, the amount of C_2H_4 (of the required purity <40 ppm C_2H_2) produced during the time interval $0 - \tau_{\text{break}}$ can be determined. A plot of the amount of C_2H_4 produced as a function of the time interval τ_{break} is presented in Fig. 3b. Importantly, the hierarchy of the productivity of pure C_2H_4 is $\text{UTSA-60a} > \text{MgMOF-74} > \text{FeMOF-74} > \text{CoMOF-74}$, further highlighting that UTSA-60a shows better separation performance than MMOF-74. The superior performance of UTSA-60a is mainly attributable to the significantly higher C_2H_2/C_2H_4 adsorption selectivity as witnessed in Fig. 3a.

On the basis of the data presented in Fig. S10 (ESI†), the impurity level will meet the desired purity level of 40 ppm (indicated by the dashed line) after a certain time, τ_{break} . The adsorption cycle needs to be terminated at that time τ_{break} and the regeneration process needs to be initiated. In this context, the regeneration energy cost of the bed is another very important consideration. Fig. 3c presents a comparison of the heats of adsorption (Q_{st}) of C_2H_2 in UTSA-60a with three other selected MOFs. It is worthy of note that the value of Q_{st} in UTSA-60a is much lower than that of MgMOF-74, FeMOF-74 and CoMOF-74; this implies that the regeneration energy requirement of UTSA-60a will be less than those of MMOF-74, thus leading to significant energy saving. Such lower Q_{st} of C_2H_2 for UTSA-60a is probably attributed to its significantly lower concentration of open metal sites ($3.18 \text{ mmol cm}^{-3}$) relative to MgMOF-74 ($7.15 \text{ mmol cm}^{-3}$), FeMOF-74 ($7.28 \text{ mmol cm}^{-3}$), and CoMOF-74 ($7.25 \text{ mmol cm}^{-3}$).

In conclusion, we have developed and characterized a new porous MOF UTSA-60a with lvt topology for highly selective separation of C_2H_2 – C_2H_4 mixtures at room temperature. The foregoing results demonstrated that UTSA-60a shows not only much higher selectivity and C_2H_4 productivity, but also lower regeneration costs than those of MMOF-74 (M = Mg, Fe, and Co), highlighting its superior performance for this industrially important separation. Such high separation capacity of UTSA-60a is mainly attributed to the suitable pore windows and open metal sites around channel surfaces of the framework to differentiate both gas molecules. The breakthrough simulations further indicated that this material is able to separate C_2H_2 from the C_2H_2/C_2H_4 (1/99) mixture at room temperature, in which the purity requirement of 40 ppm in the outlet gas can be readily achieved using the fixed bed UTSA-60a adsorber.

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Notes and references

‡ Crystal data for UTSA-60: $C_{18}H_{14}Cu_2O_{10}$, $M = 517.37$, orthorhombic, space group *Imma*, $a = 18.8261(10)$ Å, $b = 22.1934(9)$ Å, $c = 10.0062(8)$ Å, $V = 4180.7(4)$ Å³, $Z = 4$, $D_c = 0.822$ g cm⁻³, $F(000) = 1040.0$, final $R_1 = 0.0639$ for $I > 2\sigma(I)$, $wR_2 = 0.1700$ for all data, GOF = 0.948, CCDC 1038935.

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