

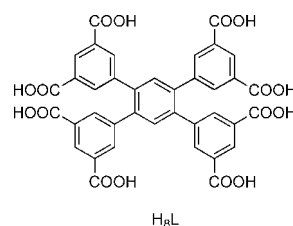
High Separation Capacity and Selectivity of C₂ Hydrocarbons over Methane within a Microporous Metal–Organic Framework at Room Temperature

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Separation of C₂ hydrocarbons (C₂s) from methane (C₁) is a very important industrial process.^[1] This is because the recovery of C₂ hydrocarbons from methane not only upgrades the quality of natural gas (NG) for its efficient usage, but can also provide an alternative chemical source of C₂s for further chemical processing and transformation. Furthermore, C₂s are the main products of oxidative coupling of methane (OCM) in the process for converting NG into a more useful chemical feedstock, thus they certainly need to be separated out from the unreacted methane. The conventional cryogenic distillation for such a separation is very energy-consuming, while no significant breakthrough has been made to target porous adsorbents for the efficient adsorptive separation of C₂s from C₁ over the past two decades.^[2]

ExxonMobil started to search for porous metal–organic frameworks (MOFs)^[3,4] for such a C₂s/C₁ separation back in 2006.^[5] The examined porous **ZIF-8** (Zn(MeIM)₂, MeIM = 2-methylimidazole) exhibits quite a low separation capacity and selectivity. Recently, Kitagawa and we have tried to

tune the pore and cavity sizes within several microporous MOFs to enhance their separation capacity up to about 1.9 mol kg⁻¹ and selectivity up to 20.^[6] Given the fact that higher separation capacity and selectivity for this C₂s/C₁ separation can significantly save the energy cost, there is a great need to explore new porous MOFs for such a purpose. The ideal ones are those with moderately high porosities and optimised pore/cage sizes to maximise their hydrocarbon uptake and thus separation capacity; and with immobilised functional sites, such as open metal sites, to direct their stronger interaction with C₂s. Herein we report a novel copper–organic framework [Cu₃(H₈L)(H₂O)₃]₃DEF·2.5H₂O (which we termed as **UTSA-34**, UTSA = University of Texas at San Antonio; H₈L = 1,2,4,5-tetra(5-isophthalate)benzene;



H₈L

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DEF = *N,N'*-diethylformamide) constructed from the paddle-wheel Cu₂(CO₂)₄ secondary building units (SBUs) and the expanded octacarboxylate organic linkers H₈L. The resulting desolvated **UTSA-34b**, which has cage sizes of about 12.8 Å, BET surface area of 991.4 m² g⁻¹ and high-density open copper sites of 3.3 mmol g⁻¹, meets the above-mentioned prerequisites, exhibiting the highest separation capacity of 3.0 mol kg⁻¹ and selectivity of 35 ever reported for the separation of C₂ hydrocarbons from methane at room temperature.

The organic linker H₈L was readily synthesised by cross-coupling between 1,2,4,5-tetrabromobenzene and dimethyl 5-(pinacolboronyl)isophthalate followed by hydrolysis. **UTSA-34** was obtained as small rod-like crystals from the solvothermal reaction of H₈L and Cu(NO₃)₂·2.5H₂O in DEF/H₂O mixed solvents at 90 °C under acidic conditions. The phase purity of the bulk material was confirmed by powder X-ray diffraction (PXRD, Figure S1 in the Supporting Information.). The formula was established based on a single-crystal X-ray structure determination, thermogravimetric analysis

(TGA, Figure S2 in the Supporting Information), and micro-analysis.

The single-crystal X-ray structure analysis reveals that **UTSA-34** adopts a three-dimensional framework in which six carboxylates are connected to the paddle-wheel $\text{Cu}_2(\text{COO})_4$ SBUs (Figure S3 in the Supporting Information) to form a topologically novel non-interpenetrated binodal (4,6)-connected **ybh** network^[7] (topologically, each binuclear $\text{Cu}_2(\text{COO})_4$ unit and each organic linker can be considered as the four-coordinate and six-coordinate nodes, respectively, Figure 1 a). Large interconnected cages of about 12.8 Å in diameter exist that are surrounded by 24 isophthalate moieties (Figure S4 in the Supporting Information). The pore structure of **UTSA-34** can be approximately regarded as a face-centred cubic (fcc) close-packing of spherical cages, each connected to 12 nearest neighbouring cages (Fig-

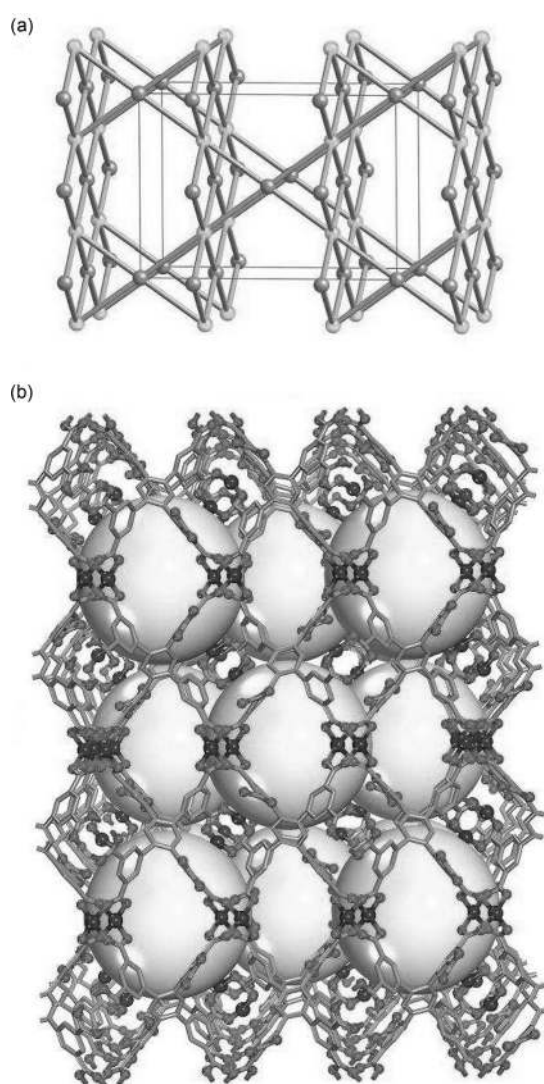


Figure 1. Single-crystal X-ray structure of **UTSA-34** showing a) the novel non-interpenetrated binodal (4,6)-connected **ybh** topology, and b) the interconnected cages of about 12.8 Å viewed along *c* axis. The terminal water molecules and hydrogen atoms were omitted for clarity.

ure 1 b). PLATON calculations indicate that **UTSA-34** contains 64.7% void space that is accessible to the solvent molecules after removal of the terminal H_2O molecules from the Cu centres.^[8]

The permanent microporosities were established with N_2 adsorption measurement at 77 K for both partially and completely desolvated MOFs **UTSA-34a** and **UTSA-34b**. The fresh samples were guest-exchanged with dry acetone and then evacuated at 296 K and 393 K to generate the **UTSA-34a** and **UTSA-34b**, respectively. PXRD studies confirmed that the framework retained intact after such vacuum/thermal activation (Figure S1 in the Supporting Information). The N_2 isotherms show type-I reversible sorption behaviours with Brunauer–Emmett–Teller (BET) surface areas of 605.9 and 991.4 m^2g^{-1} , respectively (Figure S5–S7 in the Supporting Information). Their pore volumes calculated from the maximum amount of N_2 adsorbed are 0.334 and 0.542 cm^3g^{-1} , respectively. The moderately high porosity of **UTSA-34b** was further confirmed by its high-pressure sorption isotherms with excess uptakes of 3.3 wt% H_2 at 77 K and 15 bar, 170 $\text{cm}^3(\text{STP})\text{g}^{-1}$ CH_4 at 290 K and 35 bar, and 260 $\text{cm}^3(\text{STP})\text{g}^{-1}$ CO_2 at 290 K and 28 bar, respectively (Figure S8–S10 in the Supporting Information).

In order to establish their potential for selective separation of C_2s from C_1 , we examined their C_1 and C_2 hydrocarbon sorption isotherms at 273 and 296 K (Figure 2 a and Fig-

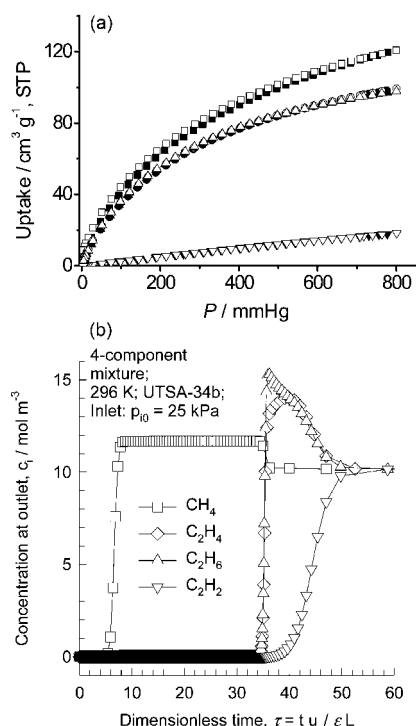


Figure 2. a) The C_2H_2 (squares), C_2H_4 (circles), C_2H_6 (triangles), and CH_4 (inverted triangles) sorption isotherms of **UTSA-34b** at 296 K. Solid symbols: adsorption, open symbols: desorption. b) Transient breakthrough of an equimolar four-component mixture containing C_2H_2 , C_2H_4 , C_2H_6 , and CH_4 in an adsorber packed with **UTSA-34b** operating at isothermal conditions at 296 K. The inlet gas is maintained at partial pressures $p_{i0} = 25$ kPa.

ures S11 and S12 in the Supporting Information). Sorption isotherms are repeatable, which means that the material can be easily regenerated and re-utilised. As expected, the larger accessible pore space in the completely desolvated **UTSA-34b** has enabled it to take much more C_2s than **UTSA-34a**, which will favour the higher separation capacity of **UTSA-34b** for C_2s/C_1 separation. Furthermore, **UTSA-34b** is also expected to exhibit high C_2s/C_1 separation selectivity from their sorption isotherms. The appropriate combination of the selectivity and capacity characteristics is reflected in the breakthrough behaviours in a packed bed adsorber that can be simulated using the established methodology.^[9] Figure 2b shows the transient breakthrough of an equimolar four-component mixture of C_2H_2 , C_2H_4 , C_2H_6 , and CH_4 at 296 K in **UTSA-34b**. We note that CH_4 , the component with the poorest adsorption strength “breaks through” earliest and it is possible to produce pure methane from this four-component mixture during the adsorption cycle. A comparison of breakthrough of C_2s in outlet gas for equimolar four-component mixtures of C_2H_2 , C_2H_4 , C_2H_6 and CH_4 in the **UTSA-33a**,^[6d] **UTSA-34a** and **UTSA-34b** is presented in Figure S13 and S14 in the Supporting Information. From the breakthrough curves, we note that the breakthrough of all C_2s occurs significantly later with **UTSA-34b**, which might be attributed to its both higher separation selectivity and larger adsorption capacity.^[9,10] This longer breakthrough also implies that **UTSA-34b** has higher production capacity, highlighting great promise of **UTSA-34b** for separation of C_2s from methane at room temperature.

We further examined the separation selectivity and capacity of **UTSA-34b** for C_2H_2/CH_4 , C_2H_4/CH_4 , and C_2H_6/CH_4 binary mixtures at 296 K and compared them with those reported MOFs^[6d] in detail, based on the calculation using ideal adsorbed solution theory (IAST).^[11] Apparently, **UTSA-34b** exhibits the highest separation selectivity and capacity for C_2H_2/CH_4 and C_2H_4/CH_4 mixtures (Figure S15 and S16 in the Supporting Information). Even though **UTSA-34b** has lower C_2H_6/CH_4 separation selectivity than **UTSA-34a** (Figure 3a), C_2H_6 elutes much later with **UTSA-34b** (Figure 3b), thus **UTSA-34b** has the highest separation capacity of 3.0 mol kg^{-1} (Figure 3c).

For natural gas purification applications, there will be a limit on the purity of C_2H_2 in the outlet gas. For a specified purity of 1 mol% C_2H_2 in outlet gas, the dimensionless breakthrough time (τ_{break}) and the amount of C_2H_2 adsorbed during the time interval $0-\tau_{\text{break}}$, can be determined. A comparison of the amount of C_2H_2 adsorbed during the time interval $0-\tau_{\text{break}}$ as a function of τ_{break} is provided in Figure S15c in the Supporting Information. Clearly, **UTSA-34b** has the best performance for the pressure swing adsorption (PSA) separation of C_2H_2/CH_4 . Similarly, **UTSA-34b** is far superior to other porous MOFs for their PSA separation of C_2H_4/CH_4 (Figure S16c in the Supporting Information) and C_2H_6/CH_4 (Figure 3c). In view of the fact that ExxonMobil Research has patented zeolitic imidazolate frameworks (ZIFs) for separation of methane from higher hydrocarbons, we attempted to compare the performance of **UTSA-34b**

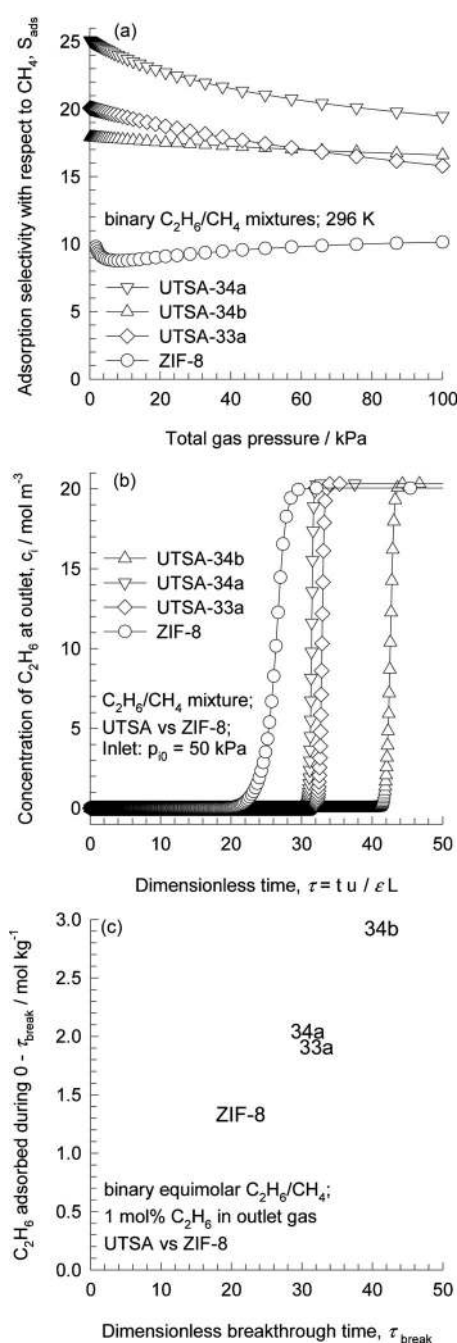


Figure 3. a) Comparison of the adsorption selectivity, S_{ads} , for equimolar C_2H_6/CH_4 mixtures at 296 K in **UTSA-34b** with the corresponding values for **UTSA-34a**, **UTSA-33a**, and **ZIF-8**. b) Comparison of breakthrough of C_2H_6 in outlet gas for an equimolar binary C_2H_6/CH_4 mixture in adsorbers packed with **ZIF-8**, **UTSA-33a**, **UTSA-34a**, and **UTSA-34b** operating at isothermal conditions at 296 K. The inlet gas is maintained at partial pressures $p_{i0} = 50 \text{ kPa}$. c) Comparison of the total amount of C_2H_6 adsorbed during the time interval $0-\tau_{\text{break}}$. τ_{break} is the dimensionless breakthrough time corresponding to outlet gas containing 1 mol% C_2H_6 .

with **ZIF-8**.^[5,12] From Figure 3, we note that **UTSA-34b** yields much higher separation selectivity and capacity than **ZIF-8**. This is an important finding, because recent Exxon patent claims ZIFs are good for separation of ethane from

methane. Our study implies that the production capacity of pure CH₄ will be significantly higher with **UTSA-34b**, underlining the potency of **UTSA-34b** for the efficient and high-capacity separation of C₂/C₁ at room temperature.

In summary, we report a new microporous metal–organic framework **UTSA-34b** with high separation capacity and selectivity for the separation of C₂ hydrocarbons from C₁ methane at room temperature. Such high separation capacity and selectivity are attributed to the moderately high pore spaces within the framework to take up a large amount of hydrocarbons and open copper metal sites on the pore surfaces for their stronger interactions with C₂H₂ and C₂H₄. The higher C₂H₆ uptake in the completely desolvated **UTSA-34b** has also lead to a higher breakthrough separation capacity than the partially desolvated **UTSA-34a**. The fact that **UTSA-34b** exhibits significantly higher separation capacity and selectivity for C₂/C₁ than the well-examined **ZIF-8** gives great promise of the emerging microporous MOFs for such a very important industrial separation. It is expected that this work will initiate more extensive studies on tuning the pore structures and immobilising functional sites on pore surfaces within porous MOFs to target some more industrially useful porous MOF materials for these important industrial tasks.

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Keywords: gas separation • hydrocarbons • metal–organic frameworks • natural gas

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