High Separation Capacity and Selectivity of C_2 Hydrocarbons over Methane within a Microporous Metal–Organic Framework at Room Temperature


Separation of C_2 hydrocarbons (C_2s) from methane (C_1) is a very important industrial process.[1] This is because the recovery of C_2 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 C_2s for further chemical processing and transformation. Furthermore, C_2s 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 C_2s from C_1 over the past two decades.[2]

ExxonMobil started to search for porous metal–organic frameworks (MOFs) [3,4] for such a C_2s/C_1 separation back in 2006.[5] The examined porous ZIF-8 (Zn(MeIM)_2, MeIM = 2-methylimidazolate) 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 C_2s/C_1 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 C_2s. Herein we report a novel copper–organic framework [Cu_3(H_8L)(H_2O)_3]·3DEF·2.5H_2O (which we termed as UTSA-34, UTSA = University of Texas at San Antonio; H_8L = 1,2,4,5-tetra(5-isophthalate)benzene; DEF = N,N'-diethylformamide) constructed from the paddle-wheel Cu_2(CO_2)_4 secondary building units (SBUs) and the expanded octacarboxylate organic linkers H_8L. The resulting desolvated UTSA-34b, which has cage sizes of about 12.8 Å, BET surface area of 991.4 m^2 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 C_2 hydrocarbons from methane at room temperature.

The organic linker H_8L was readily synthesised by cross-coupling between 1,2,4,5-tetrabromobenzene and dimethyl 5-(pinacolboryl)isophthalate followed by hydrolysis. UTSA-34 was obtained as small rod-like crystals from the solvothermal reaction of H_8L and Cu(NO_3)_2·2.5H_2O in DEF/H_2O 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...
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 Cu₂(COO)₄ SBUs (Figure S3 in the Supporting Information) to form a topologically novel non-interpenetrated binodal (4,6)-connected ybh network (topologically, each binuclear Cu₂(COO)₄ unit and each organic linker can be considered as the four-coordinate and six-coordinate nodes, respectively, Figure 1a). 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 (Figure 1b). PLATON calculations indicate that UTSA-34 contains 64.7% void space that is accessible to the solvent molecules after removal of the terminal H₂O molecules from the Cu centres.[8]

The permanent microporosities were established with N₂ 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 N₂ isotherms show type-I reversible sorption behaviours with Brunauer–Emmett–Teller (BET) surface areas of 605.9 and 991.4 m² g⁻¹, respectively (Figure S5–S7 in the Supporting Information). Their pore volumes calculated from the maximum amount of N₂ adsorbed are 0.334 and 0.542 cm³ g⁻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% H₂ at 77 K and 15 bar, 170 cm³ (STP) g⁻¹ CH₄ at 290 K and 35 bar, and 260 cm³ (STP) g⁻¹ CO₂ at 290 K and 28 bar, respectively (Figure S8–S10 in the Supporting Information).

In order to establish their potential for selective separation of C₂s from C₁, we examined their C₁ and C₂ hydrocarbon sorption isotherms at 273 and 296 K (Figure 2a and Figure 1b).
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$_2$s than UTSA-34a, which will favour the higher separation capacity of UTSA-34b for C$_2$s/C$_1$ separation. Furthermore, UTSA-34b is also expected to exhibit high C$_2$s/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$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, 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$_2$s in outlet gas for equimolar four-component mixtures of C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, 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$_2$s 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$_2$s from methane at room temperature.

We further examined the separation selectivity and capacity of UTSA-34b for C$_2$H$_2$/CH$_4$, C$_2$H$_4$/CH$_4$, and C$_2$H$_6$/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$_2$H$_2$/CH$_4$ and C$_2$H$_4$/CH$_4$ mixtures (Figure S15 and S16 in the Supporting Information). Even though UTSA-34b has lower C$_2$H$_6$/CH$_4$ separation selectivity than UTSA-34a (Figure 3a), C$_2$H$_6$ 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$_2$H$_2$ in the outlet gas. For a specified purity of 1 mol% C$_2$H$_2$ in outlet gas, the dimensionless breakthrough time ($\tau_{break}$) and the amount of C$_2$H$_2$ adsorbed during the time interval 0–$\tau_{break}$, can be determined. A comparison of the amount of C$_2$H$_2$ adsorbed during the time interval 0–$\tau_{break}$ as a function of $\tau_{break}$ 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$_2$H$_2$/CH$_4$. Similarly, UTSA-34b is far superior to other porous MOFs for their PSA separation of C$_2$H$_2$/CH$_4$ (Figure S16c in the Supporting Information) and C$_2$H$_6$/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 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 CH$_4$ will be significantly higher with UTSA-34b, underlining the potency of UTSA-34b for the efficient and high-capacity separation of C$_8$/C$_1$ 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 C$_2$ hydrocarbons from C$_1$ 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 C$_2$H$_6$ and C$_2$H$_4$. The higher C$_2$H$_6$ uptake in the completely desolvated UTSA-34b also exhibits significantly higher separation capacity and selectivity for C$_8$/C$_1$ 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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