LETTER

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Separation of ethane and ethylene by a robust ethane-selective calcium-based metal–organic framework†

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We report here the selective adsorption of ethane over ethylene by a robust microporous metal–organic framework (MOF) material, $Ca(H_2tcpb)$ (H_4tcpb = 1,2,4,5-tetrakis(4-carboxyphenyl)-benzene). This compound exhibits higher adsorption capacity and stronger affinity toward ethane over ethylene. Multicomponent column breakthrough measurements confirm that it can selectively adsorb ethane from a binary mixture of ethane and ethylene.

As one of the most important feedstocks in the petrochemical industry, ethylene is widely used for the production of poly-ethylene, the world's mostly produced synthetic plastic, as well as various other chemicals.[1] Ethylene streams, produced from steam cracking reactions, contain various light gases besides ethylene, with ethane as the major contaminant. Thus ethylene needs to be purified before its further use. The separation of ethylene and ethane represents the most challenging and energy-intensive processes in industry because of their similar physicochemical properties.[2] Adsorptive separation by porous solids, which could potentially reduce the energy penalty associated with the conventional processes such as heat-driven distillations, represents a promising alternative separation technology. Among the various adsorbent materials investigated for the adsorptive separation of ethane and ethylene, MOFs have shown great promise in light of their structural diversity and highly tunable pore structure and functionality.[3] Several recently reported MOF materials have outperformed traditional adsorbents with respect to adsorption capacity and selectivity.[3–12]

Numerous porous materials, including zeolites, activated carbons, and MOFs, have been studied for the adsorptive separation of ethane and ethylene. Most of them exhibit prefer-ential adsorption of ethylene over ethane, due to the existence of carbon–carbon double bonds in ethylene, which leads to π-complexation interactions with the immobilized metal centers in MOFs.[13] In contrast, ethane-selective materials are rare, but are potentially advantageous as they are capable of removing ethane from ethylene and producing pure ethylene directly. Compared to the reverse process associated with ethylene-selective adsorbents which requires an additional desorption step, ethane-selective adsorbents will be more energy and cost effective. A number of ethane-selective MOFs have been developed in the past few years.[2,5–7,9–12] A notable example is the recently reported $Fe_2O_2(dobdc)$.[2] The iron-peroxo sites in $Fe_2O_2(dobdc)$ provide preferential interaction to ethane over ethylene, leading to high ethane/ethylene selectivity. However, the material is air-sensitive and must be handled in a glove-box with an inert atmosphere. Thus material stability would be a concern when it comes to industrial implementation. In this work we report the selective adsorption of ethane over ethylene by a robust microporous metal–organic framework (MOF) material, $Ca(H_2tcpb)$.[14] Its adsorption and separation perfromance have been evaluated by single-component adsorption isotherms, IAST selectivity calculation and multicomponent column breakthrough, and the underlying mechnism has been explored through analyzing the ethane/ethylene loaded MOF crystal structures.

$Ca(H_2tcpb)$ was synthesized according to reported procedures with modifications, by solvothermal reactions of $CaCl_2$ and H_4tcpb in absolute ethanol at 100 °C for 3 days.[15] Block-shaped crystals were obtained and were subject to characterizations by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) (Fig. S1 and S2, ESI†). The compound features a three dimensional (3D) structure with ∼5.5 Å 1D open channels (Fig. 1). In its crystal structure, Ca^{2+} ions are octahedrally coordinated to six carboxylate oxygen atoms to form primary building units CaO_6, which are further connected through H_2tcpb^{2-} to form the resulting 3D network. $Ca(H_2tcpb)$ possesses moderate porosity,

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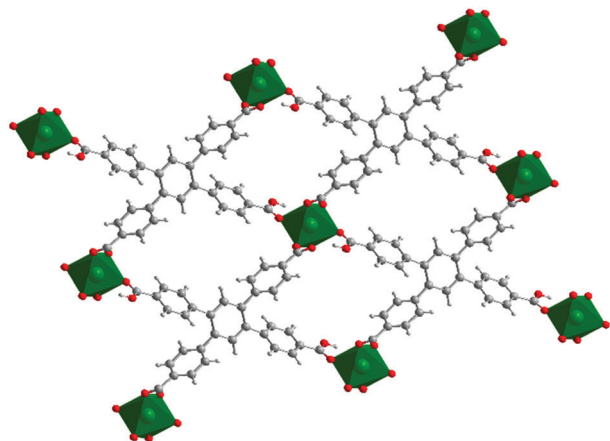† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0nj02655g

Fig. 1 Perspective view of the 3D structure of Ca(H$_2$tcpb). Ca: green, O: red, C: grey, H: light grey.

with a BET surface area of $\sim$200 m^2 g^{-1}. Importantly, the material exhibits high thermal and moisture stability (Fig. S6, ESI†). Its crystallinity and gas adsorption capacity were well-retained after being heated in open air at 180 °C (Fig. S1 and S5, ESI†).

Ethane and ethylene adsorption by Ca(H$_2$tcpb) was first evaluated by single-component adsorption isotherms. The Type I adsorption

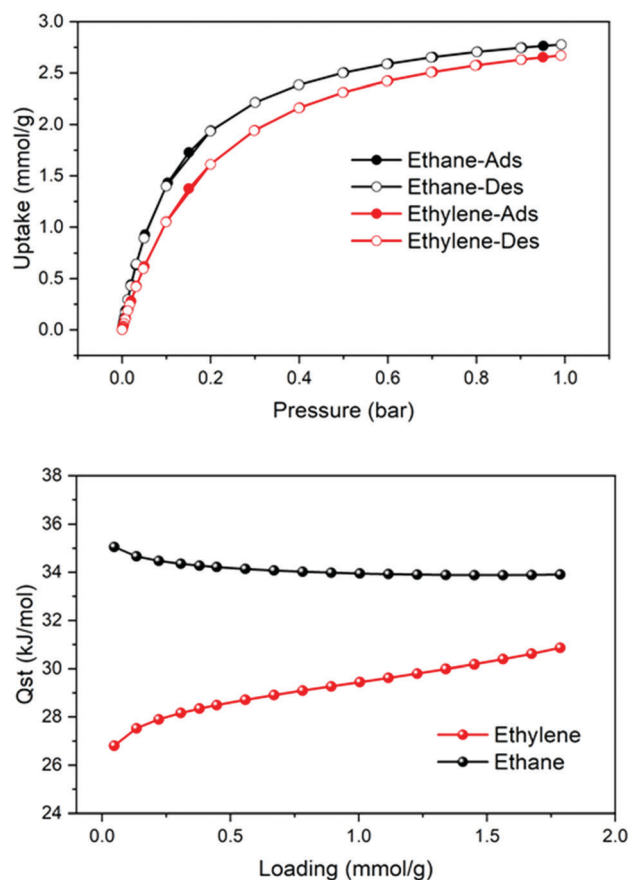Fig. 2 Top: Adsorption–desorption isotherms of ethane and ethylene on Ca(H$_2$tcpb) at 298 K. Bottom: Isosteric heats of adsorption for ethane and ethylene calculated from adsorption isotherms at 278, 288, and 298 K.

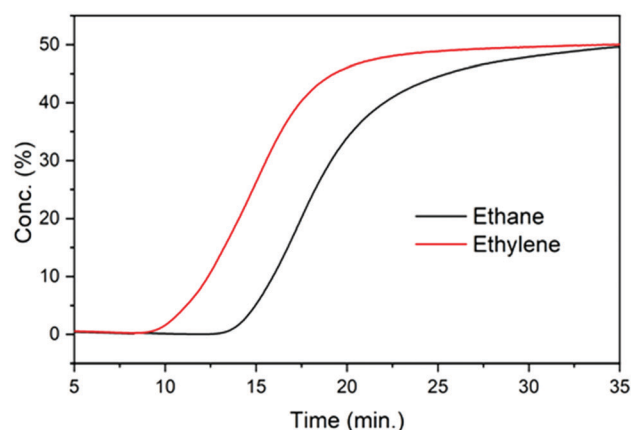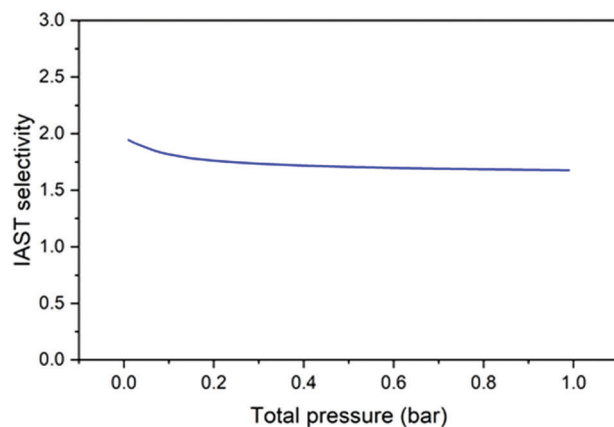Fig. 3 Top: Ethane/ethylene IAST selectivity for Ca(H$_2$tcpb) for an equimolar binary mixture at 298 K. Bottom: Multicomponent column breakthrough curve for an equimolar binary mixture of ethane and ethylene at 298 K.

profiles indicate its physisorption nature. It adsorbs 2.78 and 2.67 mmol g^{-1} of ethane and ethylene respectively at 298 K and 1 bar (Fig. 2). The Henry constants for ethane and ethylene are 2.97 and 2.53 mmol g^{-1} bar^{-1}, respectively. The higher adsorption capacity and Henry constant for ethane over ethylene indicates that the material preferentially adsorbs ethane. Isosteric heats of adsorption (Q_{st}) were calculated based on adsorption isotherms at 278, 288, and 298 K (Fig. S3 and S4, ESI†), and the zero-coverage values for ethane and ethylene are 35.1 and 26.8 kJ mol^{-1}, respectively (Fig. 2). The Q_{st} of ethylene is substantially lower than that for MOFs with open metal sites (OMSs) which show ethylene-selective behavior through π-complexation interactions.[16] The notably higher Q_{st} for ethane than ethylene suggests stronger adsorption affinity between ethane and the MOF framework.

The above-mentioned single-component adsorption results suggest that Ca(H$_2$tcpb) could potentially separate ethane and ethylene through selective adsorption of ethane over ethylene, which motivated us to explore its separation performance under mixed gas conditions. Adsorption selectivity was evaluated by the Ideal Adsorbed Solution Theory (IAST). The ethane/ethylene selectivity was calculated to be 2.0 for an equimolar binary mixture (Fig. 3). The value is lower than that for Fe$_2$O$_2$(dobdc),[2] but is comparable to most reported ethane-selective MOFs.[5]
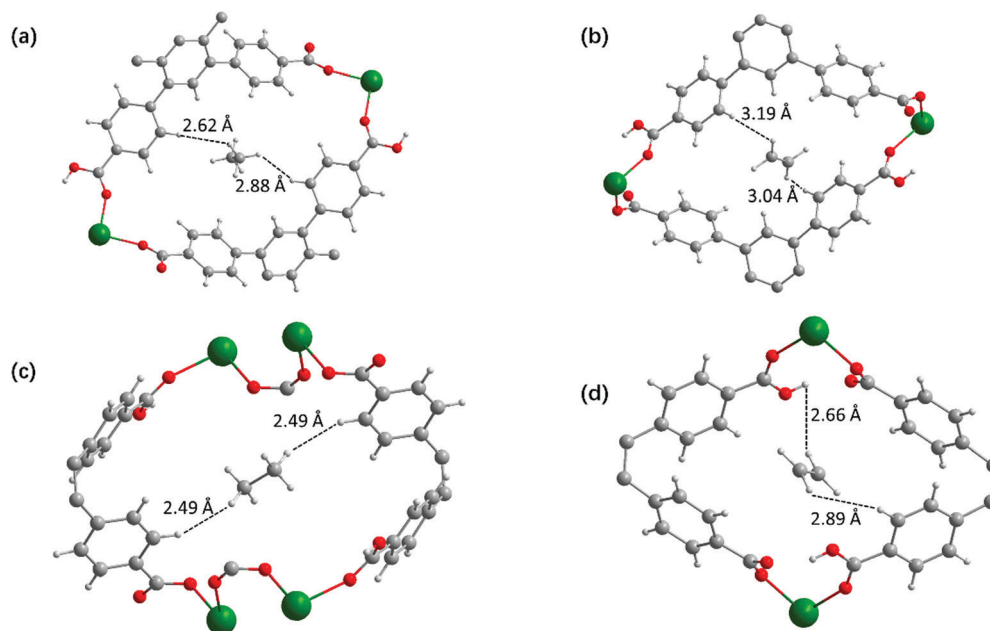
Fig. 4 Crystal structure of ethane (a and c) and ethylene (b and d) loaded Ca(H$_2$tcpb). Ca: green, O: red, C: grey, H: light grey.

We further performed experimental multi-component column breakthrough measurements to evaluate its separation performance. The breakthrough curve for an ethane–ethylene binary mixture revealed that ethylene broke at the 8th minute while ethane was retained in the column for a longer time ($\sim$13 min), indicating that ethane was preferentially adsorbed under mixed gases conditions, consistent with results from single-component adsorption experiments. The column breakthrough measurements confirmed that the material is capable of selectively removing ethane from ethylene. The material exhibited good cycling performance for the separation process (Fig. S8, ESI†). In addition, its separation capability was maintained under low concentration ethane conditions (ethane : ethylene = 1 : 9, Fig. S7, ESI†).[17]

We looked into the crystal structures of Ca(H$_2$tcpb) with ethane and ethylene loaded inside its channels to explore possible reasons why ethane is preferentially adsorbed over ethylene.[14] The compound has two different types of channels and in both channels ethane (or ethylene) molecules were identified. As shown in Fig. 4a and c, the closest H$\cdots$H distances for adsorbed ethane and the frameworks are 2.62 and 2.49 Å in the two channels, respectively. In comparison, the distances are 3.04 and 2.66 Å for ethylene (Fig. 4b and d), longer than those for ethane. In addition, the closest H$\cdots$O and H$\cdots$benzene ring distances are 2.78 and 3.38 Å for ethane, and the values are 2.47 and 3.35 Å for ethylene. The smaller H$\cdots$H distance for an ethane loaded structure may contribute to its stronger adsorption affinity due to better matching with the channels and more sufficient contacts.

Conclusions

In summary, we have presented the adsorption and separation of ethane and ethylene by a robust microporous metal–organic framework Ca(H$_2$tcpb). The compound is highly resistant

toward heat and moisture. It exhibits ethane-selective behavior, and its preferential adsorption toward ethane over ethylene was studied by single-component adsorption experiments, and confirmed by multicomponent column breakthrough measurements. The adsorption mechanisms were explored by analysing ethane and ethylene loaded crystal structures of the MOF.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

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