GAS SEPARATION

Ethane/ethylene separation in a metal-organic framework with iron-peroxo sites

Libo Li1,2,6,*, Rui-Biao Lin2,†, Rajamani Krishna3, Hao Li2,4, Shengchang Xiang4, Hui Wu5, Jinping Li1,6†, Wei Zhou5†, Banglin Chen2,†

The separation of ethane from its corresponding ethylene is an important, challenging, and energy-intensive process in the chemical industry. Here we report a microporous metal-organic framework, iron(III) peroxide 2,5-dioxido-1,4-benzenedicarboxylate \(\text{Fe}_2\text{O}_2\text{(dobdc)}\) (dobdc\(^4^-\) : 2,5-dioxido-1,4-benzenedicarboxylate), with iron (Fe)-peroxo sites for the preferential binding of ethane over ethylene and thus highly selective separation of C\(_2\)H\(_6\)/C\(_2\)H\(_4\). Neutron powder diffraction studies and theoretical calculations demonstrate the key role of Fe-peroxo sites for the recognition of ethane. The high performance of Fe\(_2\)O\(_2\) (dobdc) for the ethane/ethylene separation has been validated by gas sorption isotherms, ideal adsorbed solution theory calculations, and simulated and experimental breakthrough curves. Through a fixed-bed column packed with this porous material, polymer-grade ethylene (99.99% pure) can be straightforwardly produced from ethane/ethylene mixtures during the first adsorption cycle, demonstrating the potential of Fe\(_2\)O\(_2\)(dobdc) for this important industrial separation with a low energy cost under ambient conditions.

Ethylene (C\(_2\)H\(_4\)) is the largest feedstock in petrochemical industries, with a global production capacity of more than 170 million tons in 2016. It is usually produced by steam cracking or thermal decomposition of ethane (C\(_2\)H\(_6\)), in which a certain amount of C\(_2\)H\(_6\) residue coexists in the product and needs to be removed to produce polymer-grade (≥99.95% pure) C\(_2\)H\(_4\) as the starting chemical for many other products, particularly the widely utilized polyethylene. The well-established industrial separation technology of the cryogenic high-pressure distillation process is one of the most energy-intensive processes in the chemical industry, requiring large distillation columns with 120 to 180 trays and high reflux ratios because of the similar sizes and volatilities of C\(_2\)H\(_4\) and C\(_2\)H\(_6\) (1, 2). Realization of cost- and energy-efficient C\(_2\)H\(_6\)/C\(_2\)H\(_4\) separation to obtain polymer-grade C\(_2\)H\(_4\) is highly desired and has been recently highlighted as one of the most important industrial separation tasks for future energy-efficient separation processes (3–5).

Adsorbent-based gas separation, through pressure swing adsorption (PSA), temperature swing adsorption, or membranes, is a promising technology to replace the traditional cryogenic distillation and thus to fulfill the energy-efficient separation economy. Some adsorbents, such as γ-Al\(_2\)O\(_3\) (6), zeolite (7, 8), and metal-organic frameworks (MOFs) (9, 10), have been developed for C\(_2\)H\(_6\)/C\(_2\)H\(_4\) adsorptive separation. These porous materials take up larger amounts of C\(_2\)H\(_4\) than of C\(_2\)H\(_6\), mainly because of the stronger interactions of the immobilized metal sites, such as Ag(I) and Fe(II), on the pore surfaces with unsaturated C\(_2\)H\(_4\) molecules (9, 11). Although these kinds of adsorbents exhibit excellent adsorption

\[\text{Fe}_2\text{O}_2\text{(dobdc)}\]

Fig. 1. Structures determined from NPD studies. Shown are structures of (A) Fe\(_2\)(dobdc), (B) Fe\(_2\)(O\(_2\))(dobdc), and (C) Fe\(_2\)(O\(_2\))(dobdc)-C\(_2\)D\(_6\) at 7 K. Note the change from the open Fe(II) site to the Fe(III)-peroxo site for the preferential binding of ethane. Fe, green; C, dark gray; O, pink; O\(_2\)\(^{2-}\), red; H or D, white; C in C\(_2\)D\(_6\), blue.
and examined the separation performance for C$_2$H$_6$/C$_2$H$_4$ mixtures. We found that Fe$_2$(O$_2$)(dobdc) exhibits preferential binding of C$_2$H$_6$ over C$_2$H$_4$. Fe$_2$(O$_2$)(dobdc) not only takes up moderately high amounts of C$_2$H$_6$ but also displays the highest C$_2$H$_6$/C$_2$H$_4$ separation selectivities in the wide pressure range among the examined porous materials, demonstrating it as the best material reported to date for this important gas separation to produce polymer-grade ethylene (99.99% pure).

Fe$_2$(O$_2$)(dobdc) was prepared according to the previously reported procedure with a slight modification (28). Both Fe$_2$(dobdc) and Fe$_2$(O$_2$)(dobdc) are air sensitive and need to be handled and stored in a dry box under an N$_2$ atmosphere. As expected, Fe$_2$(O$_2$)(dobdc) maintains the framework structure of Fe$_2$(dobdc) (Fig. 1, A and B, and fig. S1A), with a Brunauer-Emmett-Teller surface area of 1073 m$^2$/g (fig. S1B).

The C$_2$H$_6$ binding affinity in Fe$_2$(O$_2$)(dobdc) was first investigated by single-component sorption isotherms at a temperature of 298 K and pressures up to 1 bar, as shown in Fig. 2A. The C$_2$H$_6$ adsorption capacity on Fe$_2$(O$_2$)(dobdc) is much higher than that of C$_2$H$_4$, implying the distinct binding affinity of Fe$_2$(O$_2$)(dobdc) for C$_2$H$_6$. At 1 bar, the uptake amount of C$_2$H$_6$ in Fe$_2$(O$_2$)(dobdc) is 74.3 cm$^3$/g, corresponding to ~1.1 C$_2$H$_6$ per Fe$_2$(O$_2$)(dobdc) formula. Unlike the pristine Fe$_2$(dobdc), which takes up more C$_2$H$_4$ than C$_2$H$_6$ because of the Fe(II) open sites, Fe$_2$(O$_2$)(dobdc) adsors a larger amount of C$_2$H$_6$ than of C$_2$H$_4$. Therefore, we successfully realized the “reversed C$_2$H$_6$/C$_2$H$_4$ adsorption” in Fe$_2$(O$_2$)(dobdc) (fig. S2). The adsorption heats ($Q_a$) of C$_2$H$_6$ and C$_2$H$_4$ on Fe$_2$(O$_2$)(dobdc) were calculated by using the virial equation (fig. S3). The C$_2$H$_6$ adsorption heat of Fe$_2$(O$_2$)(dobdc) was calculated to be 66.8 kJ/mol at zero coverage, a much higher value than those reported for other MOFs (2), indicating the strong interaction between Fe$_2$(O$_2$)(dobdc) and C$_2$H$_6$ molecules. All of the isotherms are completely reversible and exhibit no hysteresis. Further adsorption cycling tests at 298 K (fig. S4) indicated no loss of C$_2$ uptake capacity over 20 adsorption-desorption cycles.

To structurally elucidate how C$_2$H$_6$ and C$_2$H$_4$ are adsorbed in this MOF, high-resolution neutron powder diffraction (NPD) measurements were carried out on C$_2$D$_6$-loaded and C$_2$D$_4$-loaded samples of Fe$_2$(O$_2$)(dobdc) at 7 K (see supplementary materials and fig. S5). As shown in Fig. 1C, C$_2$D$_6$ molecules exhibit preferential binding with the peroxo sites through C–D···O hydrogen bonds (D···O, ~2.17 to 2.22 Å). The D···O distance is much shorter than the sum of van der Waals radii of oxygen (1.52 Å) and hydrogen (1.20 Å) atoms, indicating a relatively strong interaction, which is consistent with the high C$_2$H$_6$ adsorption heat found in Fe$_2$(O$_2$)(dobdc). In addition, we noticed that, sterically, the nonplanar C$_2$D$_6$ molecule happens to match better to the uneven pore surface in Fe$_2$(O$_2$)(dobdc) than the planar C$_2$D$_4$ molecule (fig. S6), resulting in stronger hydrogen bonds with the Fe-peroxo active site and stronger van der Waals interactions with the ligand surface. To further understand the mechanism of the selective C$_2$H$_6$/C$_2$H$_4$ adsorption in Fe$_2$(O$_2$)(dobdc), we conducted detailed first-principles dispersion-corrected density functional theory calculations (see supplementary materials and table S1). The optimized C$_2$H$_6$ binding configuration on the Fe-peroxo site agrees reasonably well with the C$_2$D$_6$-loaded structures determined from the NPD data, indicating that the reversed C$_2$H$_6$/C$_2$H$_4$ adsorption selectivity originates from the peroxo active sites and the electronegative surface oxygen distribution in Fe$_2$(O$_2$)(dobdc). Similar preferential binding of C$_2$H$_6$ over C$_2$H$_4$ has also been experimentally found in another oxidized MOF, Cr-BTC(O$_2$) (where BTC is 1,3,5-benzenetricarboxylate) (figs. S7 and S8) (30).

Fig. 2. C$_2$H$_6$ and C$_2$H$_4$ adsorption isotherms of Fe$_2$(O$_2$)(dobdc). IAST calculations, and separation potential simulations on C$_2$H$_6$-selective MOFs. (A) Adsorption (solid) and desorption (open) isotherms of C$_2$H$_6$ (red circles) and C$_2$H$_4$ (blue circles) in Fe$_2$(O$_2$)(dobdc) at 298 K. (B and C) Comparison of the IAST selectivities of Fe$_2$(O$_2$)(dobdc) with those of previously reported best-performing materials for C$_2$H$_6$/C$_2$H$_4$ (50/50 and 10/90) mixtures. (D) Predicted productivity of 99.95% pure C$_2$H$_4$ from C$_2$H$_6$/C$_2$H$_4$ (50/50 and 10/90) mixtures in fixed-bed adsorbers at 298 K. (E and F) Separation potential of Fe$_2$(O$_2$)(dobdc) for C$_2$H$_6$/C$_2$H$_4$ [50/50 (E) and 10/90 (F)] mixtures versus those of best-performing MOFs.
Ideal adsorbed solution theory (IAST) calculations were performed to estimate the adsorption selectivities of C$_2$H$_6$/C$_2$H$_4$ (50/50 and 10/90) for Fe$_2$(O$_2$)(dobdc) and other C$_2$H$_6$-selective materials (Fig. 2B). The fitting details are provided in the supplementary materials (figs. S9 to S17 and tables S2 to S11). Compared with other top-performing MOFs [MAF-49, IRMOF-8, ZIF-8, ZIF-7, PCN-250, Ni(bdc)(ted)$_2$H$_2$, UTSA-33a, and UTSA-35a], Fe$_2$(O$_2$)(dobdc) exhibits a new benchmark for C$_2$H$_6$/C$_2$H$_4$ (50/50) adsorption selectivity (4.4) at 1 bar and 298 K, greater than the selectivity of the previously reported best-performing MOF, MAF-49 (2.7) (2). This value is also higher than the highest value (2.9) among 30,000 all-silica zeolite structures that were investigated by Kim et al. through computational screening (31).

For a C$_2$H$_6$/C$_2$H$_4$ (10/90) mixture, under the same conditions, Fe$_2$(O$_2$)(dobdc) also exhibits the highest adsorption selectivity among these MOFs (Fig. 2C).

Next, transient breakthrough simulations were conducted to validate the feasibility of using Fe$_2$(O$_2$)(dobdc) in a fixed bed for separation of C$_2$H$_6$/C$_2$H$_4$ mixtures (fig. S18). Two C$_2$H$_6$/C$_2$H$_4$ mixtures (50/50 and 10/90) were used as feeds to mimic the industrial process conditions. The simulated breakthrough curves show that C$_2$H$_6$/C$_2$H$_4$ (50/50) mixtures were completely separated by Fe$_2$(O$_2$)(dobdc), whereby C$_2$H$_6$ breakthrough occurred first within seconds to yield the polymer-grade gas and then C$_2$H$_4$ passed through the fixed bed after a certain time ($t_{break}$). To evaluate the C$_2$H$_6$/C$_2$H$_4$ separation ability of these MOFs, the separation potential $\Delta Q$ was calculated to quantify the mixture separations in fixed-bed adsorbers (table S12). Attributed to the record-high C$_2$H$_6$/C$_2$H$_4$ selectivity and relatively high C$_2$H$_6$ uptakes, the amount of 99.95% pure C$_2$H$_6$ recovered by Fe$_2$(O$_2$)(dobdc) reached up to 2172 mmol/liter (C$_2$H$_6$/C$_2$H$_4$, 50/50) and 6855 mmol/liter (C$_2$H$_6$/C$_2$H$_4$, 10/90) (Fig. 2D), values which are almost two times higher than those for the other benchmark materials. Fe$_2$(O$_2$)(dobdc) has the highest separation potential for recovering the pure C$_2$H$_6$ from (50/50) C$_2$H$_6$/C$_2$H$_4$ mixtures during the adsorption process (Fig. 2E). Even when the concentration of C$_2$H$_4$ decreases to 10% (Fig. 2F), Fe$_2$(O$_2$)(dobdc) maintains the highest separation potential (table S13), which makes it the most promising material for the separation of C$_2$H$_6$ from C$_2$H$_6$/C$_2$H$_4$ mixtures.

These excellent breakthrough results from simulation encouraged us to further evaluate the separation performance of Fe$_2$(O$_2$)(dobdc) in the actual separation process. Several breakthrough experiments were performed on an in-house–constructed apparatus, which was described in our previous work (32). The breakthrough experiments were performed on several selected MOFs, including Fe$_2$(O$_2$)(dobdc), with C$_2$H$_6$/C$_2$H$_4$ (50/50) mixtures flowed over a packed bed at a total flow rate of 5 ml/min at 298 K (fig. S19 and table S14). For Fe$_2$(O$_2$)(dobdc), a clean and sharp separation of C$_2$H$_6$/C$_2$H$_4$ was observed (Fig. 3A). C$_2$H$_4$ was first to elute through the bed, before it was contaminated with undetectable amounts of C$_2$H$_6$, resulting in a high concentration of C$_2$H$_6$ feed that was ≥99.99% pure (the detection limit of the instrument is 0.01%). After some period, the adsorbent got saturated, C$_2$H$_4$ broke through, and then the outlet gas stream quickly reached equimolar concentrations. To make the systematic comparison for the C$_2$H$_6$ separation performance in the selected MOFs, C$_2$H$_6$ purity and productivity were calculated from their breakthrough curves (table S15). For Fe$_2$(O$_2$)(dobdc), 0.79 mmol/g of C$_2$H$_6$ with ≥99.99% purity can be recovered from the C$_2$H$_6$/C$_2$H$_4$ (50/50) mixture in a single breakthrough operation; this value is nearly three times that for the benchmark material MAF-49 (0.28 mmol/g). In addition, the cycle and regeneration capabilities of Fe$_2$(O$_2$)(dobdc) were further studied by breakthrough cycle experiments (Fig. 3B), with no noticeable decrease in the mean residence times for both C$_2$H$_6$ and C$_2$H$_4$ within five continuous cycles under ambient conditions. Moreover, Fe$_2$(O$_2$)(dobdc) material retained its stability after the breakthrough cycling test (fig. S20).

In the real production of high-purity C$_2$H$_6$, the C$_2$H$_6$ concentration in C$_2$H$_6$/C$_2$H$_4$ mixtures produced by naphtha cracking is about 6 to 10% (21), C$_2$H$_4$ concentrations were also contaminated by low levels of impurities such as CH$_4$, H$_2$, and C$_2$H$_2$ (33). Therefore, breakthrough experiments on C$_2$H$_6$/C$_2$H$_4$ (10/90) mixtures and C$_2$H$_6$/CH$_4$/C$_2$H$_4$ (10/87/1/1) mixtures were also performed for Fe$_2$(O$_2$)(dobdc). As shown in Fig. 3, C and D, highly efficient separations for both mixtures were realized, which further demonstrates that Fe$_2$(O$_2$)(dobdc) can be used to purify C$_2$H$_6$ with low concentrations of C$_2$H$_4$ even in the presence of CH$_4$, H$_2$, and C$_2$H$_2$ impurities.

In summary, we discovered that a distinctive MOF with Fe-peroxo sites can induce strong interactions with C$_2$H$_6$ than with C$_2$H$_4$, leading to the unusual reversed C$_2$H$_6$/C$_2$H$_4$ adsorption. The fundamental binding mechanism of Fe$_2$(O$_2$)(dobdc) for the recognition of C$_2$H$_6$ has been demonstrated through neutron diffraction studies and theoretical calculations, indicating the important role of the Fe-peroxo sites for the preferential interactions with C$_2$H$_6$. This material can readily produce high-purity C$_2$H$_6$ (≥99.99% pure) from C$_2$H$_6$/C$_2$H$_4$ mixtures during the first breakthrough cycle with moderately high productivity and a low energy cost. The strategy we developed in this work may be broadly applicable, which will facilitate extensive research on the immobilization of different sites into porous MOFs for stronger interactions with C$_2$H$_6$ than with C$_2$H$_4$, thus targeting some practically useful porous materials with low material costs and high productivity for the practical industrial realization of this very challenging and important separation.

**REFERENCES AND NOTES**


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SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S20

Tables S1 to S15

References (34–40)

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Ethane/ethylene separation in a metal-organic framework with iron-peroxo sites
Libo Li, Rui-Biao Lin, Rajamani Krishna, Hao Li, Shengchang Xiang, Hui Wu, Jinping Li, Wei Zhou and Banglin Chen

A preference for ethane
Industrial production of ethylene requires its separation from ethane in a cryogenic process that consumes large amounts of energy. An alternative would be differential sorption in microporous materials. Most of these materials bind ethylene more strongly that ethane, but adsorption of ethane would be more efficient. Li et al. found that a metal-organic framework containing iron-peroxo sites bound ethane more strongly than ethylene and could be used to separate the gases at ambient conditions.

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