

Pore-Space-Partition-Enabled Exceptional Ethane Uptake and Ethane-Selective Ethane-Ethylene Separation

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Supporting Information Placeholder

ABSTRACT: An ideal material for C₂H₆/C₂H₄ separation would simultaneously have the highest C₂H₆ uptake capacity and the highest C₂H₆/C₂H₄ selectivity. But such material is elusive. A benchmark material for ethane-selective C₂H₆/C₂H₄ separation is peroxo-functionalized MOF-74-Fe that exhibits the best known separation performance due to its high C₂H₆/C₂H₄ selectivity (4.4), although its C₂H₆ uptake capacity is modest (74.3 cm³/g). Here, we report a family of pore-space-partitioned crystalline porous materials (CPM) with exceptional C₂H₆ uptake capacity and C₂H₆/C₂H₄ separation potential (i.e., C₂H₄ recovered from the mixture) despite their modest C₂H₆/C₂H₄ selectivity (up to 1.75). The ethane uptake capacity as high as 166.8 cm³/g at 1 atm and 298 K, more than twice that of peroxo-MOF-74-Fe, has been achieved even though the isosteric heat of adsorption (21.9-30.4 kJ/mol) for these CPMs is as low as about 1/3 of that for peroxo-MOF-74-Fe (66.8 kJ/mol). While the overall C₂H₆/C₂H₄ separation potentials have not yet surpassed peroxo-MOF-74-Fe, these robust CPMs exhibit outstanding properties including high thermal stability (up to 450°C) and aqueous stability, low regeneration energy, and a high degree of chemical and geometrical tunability within the same isorecticular framework.

The separation of ethane from ethylene is a vital process in chemical industry and is also energy-intensive.¹ Compared with commonly used cryogenic distillation, adsorptive separation using porous materials would be more energy-efficient.^{2,3} Such separation can be performed with either ethane- or ethylene-selective materials,⁴⁻⁸ but ethane-selective one enjoys the simplicity of being able to produce ethylene directly at the outlet.⁹⁻¹³ This work seeks to demonstrate a high-performance platform for ethane-selective alkane/alkene separation.

A chemical separation benefits from both uptake capacity and selectivity and can be most efficiently done with a material that excels in both aspects.¹⁴⁻¹⁹ In practice, however, the interplay between capacity and selectivity makes it hard to maximize both for the same material and a trade-off is often observed.²⁰ In the aspect of C₂H₆/C₂H₄ selectivity, a breakthrough was recently reported with the synthesis of a peroxo-functionalized MOF-74-Fe (Fe₂(O₂)dobdc, denoted here peroxo-MOF-74-Fe) with the highest known C₂H₆/C₂H₄ selectivity, leading to the best reported separation performance despite its relatively low ethane uptake (74.3 cm³/g).^{12,21,22} In addition to peroxo-MOF-74-Fe, a few other materials have also been reported to have high C₂H₆/C₂H₄

selectivity (>2),^{10,11} but for these materials, both metrics (selectivity and ethane uptake) are well below that of peroxo-MOF-74-Fe, which significantly widens the gap between their separation performance and that of peroxo-MOF-74-Fe. There are also some ethane-selective materials with C₂H₆ uptakes greater than that of peroxo-MOF-74-Fe (e.g., 116.7 cm³/g for PCN-250), which helps to narrow the gap in separation potential.²³⁻²⁸

While chemical functionalization strategy as shown by peroxo-MOF-74-Fe is effective at tuning host-guest interactions and therefore the C₂H₆/C₂H₄ selectivity, it may at times come with unintended consequences, such as decreased stability. For large-scale gas separation applications, factors such as long-term stability and adsorbent regeneration cost are also important considerations.²⁹⁻³⁷

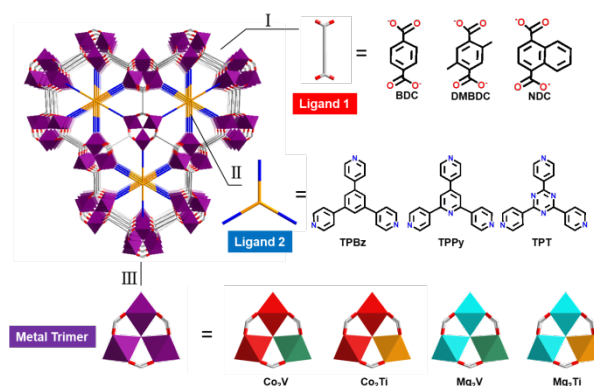


Figure 1. Three modules of *pacs* MOFs studied in this work. Three kinds of Ligand Type 1, three kinds of Ligand Type 2 and four kinds of metal trimers are used (BDC=terephthalate; DMBDC=2,5-dimethylterephthalate; NDC=1,4-naphthalenedicarboxylate; TPBz=1,3,5-tri(4-pyridyl)-benzene, TPPy=2,4,6-tris(4-pyridyl)pyridine, TPT=2,4,6-tri(4-pyridyl)-1,3,5-triazine).

In this work, we report the first application of our pore-space-partition (PSP) strategy,³⁸ a geometry-focused method, for the C₂H₆-selective C₂H₆/C₂H₄ separation. An outstanding feature of this PSP method is that it can dramatically increase the uptake capacity of C₂H₆ to more than 2-fold of the benchmark material peroxo-MOF-74-Fe and yet the binding strength is just a fraction of that of peroxo-MOF-74-Fe. We show that the C₂H₆/C₂H₄ separation performance can be tuned via any one of three

structural modules. Importantly, these materials are highly stable and are capable of excellent ethane-selective C_2H_6/C_2H_4 separation potential due to the ultrahigh C_2H_6 uptake capacity.

The family of materials is built via introduction of pore-partitioning agent into the hexagonal channel of MIL-88/MOF-235-type (the *acs* net) framework,³⁹⁻⁴¹ resulting in the partitioned *acs* net known as the *pacs* net.^{42,43} They have a general framework formula of $[(M1_2M2)(O/OH)L1_3]L2$, where **M1** and **M2** are the metals in trimer, **L1** is the dicarboxylate ligand for the formation of the *acs* framework and **L2** is the pore-partitioning agent. All the structural modules (i.e., **L1**, **L2**, and metal trimers,) are tunable with many possibilities. In this work, we have examined the effects of all three modules. The variation in each module is chosen as following: (Module 1) dicarboxylate ligands - bdc, dmbdc, and ndc; (Module 2) pore-partitioning agent - tpbz, tppy, and tpt; and (Module 3) metal trimers - Co_2V , Co_2Ti , Mg_2V , and Mg_2Ti (Figure 1). While there are 36 permutations by combining these modules, we are able to establish general trends in ethane-selective C_2H_6/C_2H_4 separation properties with nine combinations reported here.

The metal combinations such as Co-V trimers in this study are unusual among MOFs. The heterometallic compositions were established by EDS analysis (Figure S2) and supported by single-crystal X-ray diffraction analysis. It is worth noting that while it is typically difficult to grow large single crystals of vanadium and titanium MOFs for use with conventional-X-ray-source, crystals around 50 μm in size can be made readily in this work,⁴⁴⁻⁴⁷ ENREF 46 and 7 structures reported here were analyzed with in-house single-crystal diffraction data.

The materials in this work are highly stable. They are thermally stable up to 450 $^{\circ}C$ (Figure S3-4). All of them maintain their structural integrity after repeated gas adsorption-desorption experiments (Figure S5). As shown by Figure S6, Co_2Ti -bdc-tpt and Co_2V -bdc-tpt are hydrothermally stable and could retain their high crystallinity even after immersion in water for 24 hours.

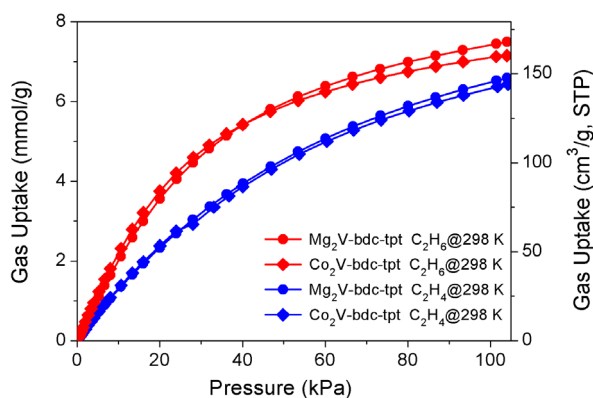


Figure 2. Experimental C_2H_6 and C_2H_4 adsorption isotherms of Mg_2V -bdc-tpt and Co_2V -bdc-tpt at 298 K.

In addition to partitioning the pore space, pore-partitioning agents deactivate all open-metal sites (OMS) of the parent 6-connected *acs* framework. While OMSs can be beneficial for ethylene-selective C_2H_4/C_2H_6 separation,⁴ the total annihilation of OMS in this family of materials could be helpful for ethane-selective C_2H_4/C_2H_6 separation. In fact, all the MOFs in this work show ethane-selective C_2H_4/C_2H_6 separation according to the single-component adsorption isotherms (Figure S7-S15). Moreover, the ethane uptakes of these MOFs are remarkably high. Six of nine MOFs have the uptake capacity from 154.2 to 166.8 cm^3/g at 298 K and 1 atm (Table S2), all of which by far exceed

116.7 cm^3/g for PCN-250, a benchmark material for ethane uptake among ethane-selective MOFs. This corresponds to about 6-7 C_2H_6 molecules per formula unit. In particular, the uptake by Mg_2V -bdc-tpt is 166.8 cm^3/g (7.45 mmol/g), which is likely the highest among MOFs reported to date (Figure 2 & Table S3-4).

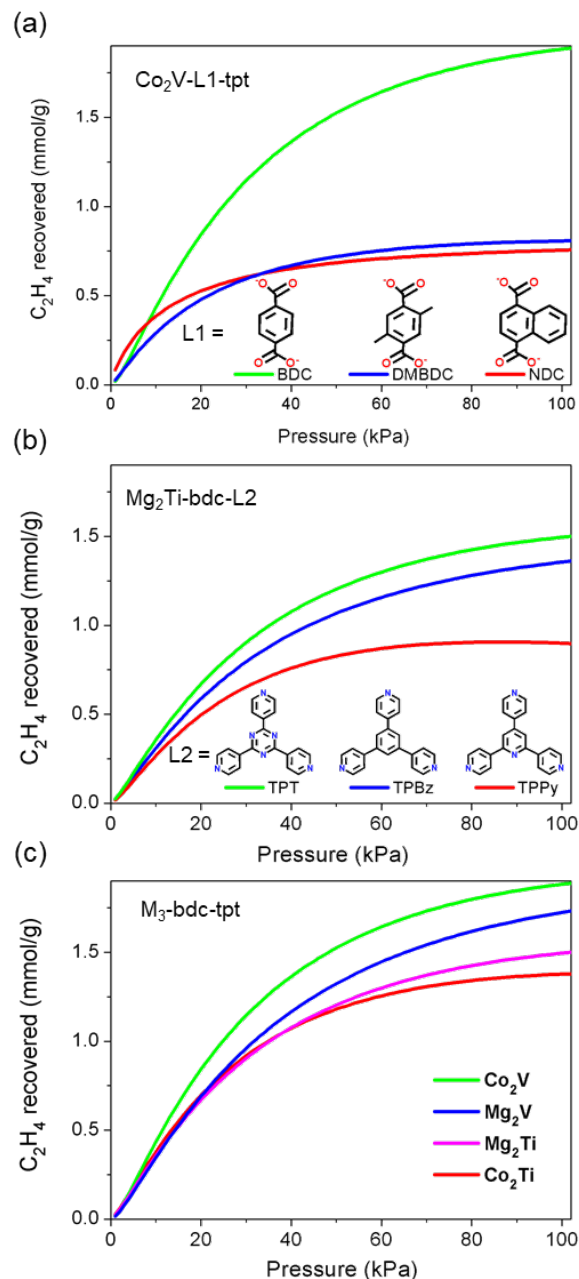


Figure 3. Comparisons of separation potential for C_2H_6/C_2H_4 (50/50) mixture: (a) Co_2V -L1-tpt with different dicarboxylate ligands; (b) Mg_2Ti -bdc-L2 with different pore-partitioning agents; (c) M_3 -bdc-tpt with different metal trimers.

The high ethane uptakes are accomplished with low adsorption enthalpies ranging from 21.9 to 30.4 kJ/mol at zero coverage (Figure S16). In contrast, $Fe_2(O_2)(dobdc)$ has a high ethane adsorption enthalpy (66.8 kJ/mol).¹² The low Q_{st} of CPMs could be advantageous for adsorbent regeneration due to the reduced energy consumption. The low adsorption enthalpy was further validated by GCMC simulations. The density distribution of C_2H_6

molecules within Co₂V-bdc-tpt was analyzed at different pressures (Figure S17). No strong adsorption sites were observed on the framework. Also, the density distribution of C₂H₆ molecules was found to be quite dispersive in all the pore space, indicative of the widespread weak adsorption sites that are responsible for the ultrahigh C₂H₆ uptake.

The IAST selectivity has been calculated to evaluate the separation performance (Figure S18). The best selectivity is 1.75 for Co₂V-bdc-tpt, which is comparable to ZIF-7 (1.5), IRMOF-8 (1.6), PCN-250 (1.9), and MUF-15 (1.96), but significantly lower than Fe₂(O₂)(dobdc) (4.4), Cu(Qc)₂ (3.4), and MAF-49 (2.7) (Table S3).

In addition to uptake capacity and selectivity, separation potential, which is a metric incorporating of the influence of both factors, is also used to evaluate the separation performance.^{48,49} It represents the maximum amount of pure C₂H₄ that could be recovered from the mixture in a fixed bed adsorber; the separation potentials are calculable from IAST using eq S3 of the SI. Separation potentials, together with uptake capacity and selectivity of 9 materials are discussed below when we systematically vary one structural module while keeping two other modules unchanged.

As shown in Figure 3a, the BDC ligand was determined to have the best separation potential. We explored the possibility of boosting C₂H₆ uptake by incorporating nonpolar groups which was considered helpful in some structure types studied previously.^{50,51} It was observed here that nonpolar functionalization on dicarboxylate ligands does not improve separation performance. An increase in C₂H₆ adsorption enthalpy was indeed observed with the installation of nonpolar groups in the Co₂V compositions from 23.4 for Co₂V-bdc-tpt to 27.9 for Co₂V-dmbdc-tpt and to 30.4 kJ/mol for Co₂V-ndc-tpt (Figure S15). However, the extra group also led to a significant decrease in surface area (Figure S19), which likely resulted in a significant decrease in C₂H₆ uptake capacity. The BET surface areas decreased from 1328.5 m²/g for Co₂V-bdc-tpt, to 1161.5 m²/g for Co₂V-dmbdc-tpt and to 472.5 m²/g for Co₂V-ndc-tpt. Following the same trend, the C₂H₆ uptake decreased from 159.6 cm³/g for Co₂V-bdc-tpt to 104.6 cm³/g for Co₂V-dmbdc-tpt and to 90.2 cm³/g for Co₂V-ndc-tpt (Table S2). Furthermore, the Co₂V-bdc-tpt also has the highest C₂H₆/C₂H₄ selectivity among all the phases reported here (Figure S18). For the Mg₂V system, Mg₂V-bdc-tpt also outperforms Mg₂V-dmbdc-tpt in terms of uptake capacity and selectivity (Figure S21).

In comparison with the module 1 (dicarboxylates) that exhibits a large impact on C₂H₆/C₂H₄ uptake capacity, the module 2 (pore-partitioning agent) exerts a significant impact on C₂H₆/C₂H₄ selectivity. Overall, the separation potential for this family of MOFs with different pore-partitioning agent follows the order of tpt > tpbz > tppy (Figure 3b). These materials (Mg₂Ti-bdc-tpbz, Mg₂Ti-bdc-tpy, and Mg₂Ti-bdc-tpt) have similar surface areas and ethane uptakes, but their selectivity differs obviously. The lowest selectivity for ethane was found in Mg₂Ti-bdc-tpy (Figure S18), which led to its lowest separation potential. This may be due to the more basic feature of pyridine core in the partitioning agent (as compared to the cores in tpt and tpbz), which enables a relatively stronger interaction with ethylene.

With bdc and tpt as the best choices for C₂H₆/C₂H₄ separation, the effects of metal trimers on the separation potential were subsequently evaluated. The order was found to be Co₂V > Mg₂V > Mg₂Ti > Co₂Ti (Figure 3c). The best performance of Co₂V-bdc-tpt among this family is due to the combined effect from uptake capacity and selectivity (Table S2). Also, vanadium MOFs show higher separation performance than titanium MOFs with the same M1(Co or Mg).

Co₂V-bdc-tpt and Mg₂V-bdc-tpt could produce 1.88 and 1.73 mmol/g C₂H₄ from C₂H₆/C₂H₄ (50/50) mixture, respectively.

These values are lower than that of Fe₂O₂(dobdc) (1.93), but higher than other prominent MOFs (Figure 4a). Other materials reported here such as Mg₂Ti-bdc-tpt and Co₂Ti-bdc-tpt also show strong separation performance.

To validate the excellent separation performance, transient breakthrough simulations were also performed using Co₂V-bdc-tpt and Mg₂V-bdc-tpt. C₂H₆/C₂H₄ mixtures with two ratios (50/50 and 10/90) were used as feeding gases in the simulation to mimic the industrial separation process. The results clearly show that both materials are capable of separating these two gases. In the simulated breakthrough curves, C₂H₄ breakthrough occurred first and subsequently reached a plateau, which could thereby produce polymer-grade C₂H₄ before C₂H₆ breakthrough occurred (Figure 4b). The productivities were also calculated based on the breakthrough curves. For 50/50 C₂H₆/C₂H₄ mixture, Co₂V-bdc-tpt and Mg₂V-bdc-tpt can produce 0.88 and 0.60 mmol/g C₂H₄ (purity > 99.95%), respectively. These values are higher than some benchmark MOFs including MAF-49 (0.52 mmol/g), and Cu(Qc)₂ (0.49 mmol/g). Similarly, excellent separation performances were also found in Co₂V-bdc-tpt and Mg₂V-bdc-tpt with 10/90 C₂H₆/C₂H₄ mixture (Figure S22).

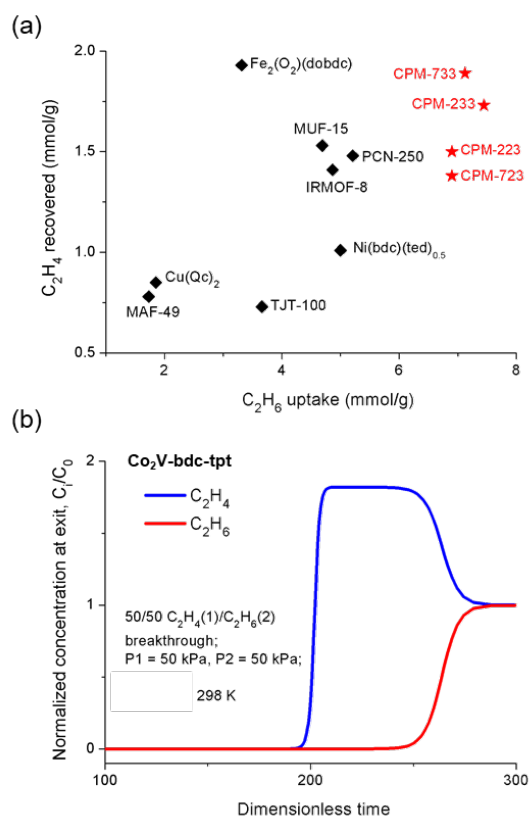


Figure 4. (a) Separation potential (calculated using eq S3 of the SI) versus single-component ethane uptake for the select high-performance ethane-selective materials reported to date (CPM-733: Co₂V-bdc-tpt; CPM-233: Mg₂V-bdc-tpt; CPM-223: Mg₂Ti-bdc-tpt; CPM-723: Co₂Ti-bdc-tpt). (b) Simulated breakthrough curve for CPM-733. Binary equimolar C₂H₆/C₂H₄ mixtures were used in all calculations and simulations.

In conclusion, we have made 9 heterometallic vanadium and titanium MOFs and systematically investigated the effects of three separate modules on the C₂H₆/C₂H₄ separation performance. Compared with Fe₂O₂(dobdc) with very high selectivity, this family of materials have exceptional high uptake and provide an

alternative way to achieve excellent separation performance. Some advantages of this family of materials include high stability, easy adsorbent regeneration, and broad chemical tunability. The correlations between the structure and the C₂H₆/C₂H₄ separation performance revealed in this work could be useful for designing novel high-performance C₂H₆-selective MOFs. Finally, novel metal combinations in this work highlight new possibilities for the construction of trimer-based MOFs.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental Procedures and compound characterization data (PDF), Crystallographic data with CCDC No. 1967756-1967761 (CIF)

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Notes

The authors declare no competing financial interests.

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