Controlling guest conformation for efficient purification of butadiene

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Conventional adsorbents preferentially adsorb the small, high-polarity, and unsaturated 1,3-butadiene molecule over the other C4 hydrocarbons from which it must be separated. We show from single-crystal x-ray diffraction and computational simulation that a hydrophilic metal-organic framework, \([\text{Zn}_2(\text{btm})_2]\), where H2btm is bis(5-methyl-1,2,4-triazol-3-yl)methane, has quasi-discrete pores that can induce conformational changes in the flexible guest molecules, weakening 1,3-butadiene adsorption through a large bending energy penalty. In a breakthrough operation at ambient temperature and pressure, this guest conformation–controlling adsorbent eluted 1,3-butadiene first, then butane, butene, and isobutene. Thus, 1,3-butadiene can be efficiently purified (≥99.5%) while avoiding high-temperature conditions that can lead to its undesirable polymerization.

As one of the most produced chemical products (1), 1,3-butadiene (C4H6) is widely used in the production of synthetic rubber and generally obtained from C4 hydrocarbon mixtures—primarily consisting of 30 to 60% C4H8, 10 to 20% 1-butene (n-C4H8), 10 to 30% isobutene (i-C4H8), and 3 to 10% butane (C4H10)—produced in petrochemical plants (2). Because of their similar physical properties (table S1), C4H6 must be isolated from other C4 hydrocarbons through extractive distillation at 3 bar and 323 to 393 K with very high towers (more than 110 trays) and organic solvents, a process that is very energy-consuming and environmentally unfriendly (3, 4). Restricting the polymerization of highly reactive C4H6 at evaluated temperatures is also challenging (5, 6).

Porous materials are promising candidates for efficient separation of gas mixtures by distinguishing the differences in molecular sizes (7, 8), shapes (9), polarities (10–12), polarizabilities (13–16), coordination abilities (17, 18), and so on. In the case of flexible porous coordination polymers or metal-organic frameworks (MOFs), the host structures may even be altered to amplify these differences (19–22). However, available adsorptive separation mechanisms are inefficient for purifying C4H6 or separating C4 hydrocarbons into individual compounds. Most adsorbents prefer to adsorb C4H6, but their adsorption selectivities are usually low because the molecular sizes, shapes (fig. S1), and properties (table S1) of C4 hydrocarbons are similar.

Adsorbents functionalized by open metal sites (OMSs) may selectively extract C4H6 (with the strongest coordination ability because it is the most unsaturated) from C4 hydrocarbons, but recovery of the adsorbent and product is difficult because heating is necessary but induces polymerization (23). This adsorption selectivity leads to the unadsorbed C4 hydrocarbons contaminating the desorbed product (fig. S2), so multiple adsorption-desorption cycles are necessary to achieve a satisfactory C4H6 purity (≥99.5%), the lowest limit for the C4H6 polymerization reactor (24), which increases the energy consumption and the chance of C4H6 polymerization.

We demonstrate an adsorptive separation mechanism that exploits the flexibility of guest molecules and leads to an optimum adsorption-separation sequence for C4H6 purification. Flexibility is an overlooked character of guest molecules. C4H6, n-C4H8, and i-C4H8 are all flexible, with rotation freedom along their central C-C single bonds and with the trans and cis conformations as stable and metastable states, respectively. However, only C4H6 incurs a large energy penalty to adopt the metastable cis conformation, because this conformation breaks the planar conjugation of the adjacent π bonds (fig. S3). Because the cis and trans conformations of these molecules have relatively thin, long and thick, short shapes, respectively, adsorbents with suitable pore size, shape, and dimensionality can be used to control the guest conformation and thereby utilize the difference in guest flexibility to lower the adsorption enthalpy for C4H6 compared with that for other C4 hydrocarbons. As shown in Fig. 1A, large channels cannot control the guest conformations, whereas very small channels can accommodate only the trans conformation with the thin, long shape. To restrict the flexible guest in the metastable cis conformation, discrete pores are optimal, but guest diffusion becomes a problem. Therefore, flexible quasi-discrete pores combining conformation controllability and diffusion ability are the best choice.

We selected 10 MOF materials with three representative structure types and variable pore sizes and shapes for comparison (table S2), including (i) [Cu3(btc)2] (“Cu-BTC”), where H3btc is benzene-1,3,5-tricarboxylic acid (25); (ii) [Co6(dobdc)] (“Co-DOBDC”) and (iii) [Mg9(dobdc)] (“MgDOBDC”) with different OMSs, where H2dobdc is 2,5-dihydroxyl-1,4-benzenedicarboxylic acid (26); (iv) SOD-[Zn(mim)2] (“Zn-MIM”), where Hmim is 2-methylimidazole; (v) ANA-[Zn(eim)2] (“Zn-EIM-ANA”) and (vi) RHO-[Zn(eim)2] (“Zn-EIM-RHO”) with alkyl-lined hydrophobic pore surfaces, where Heim is 2-ethylimidazole (27, 28); (vii) [Zr6O4(OH)4(bdc)6] (“Zr-BDC”), where H2bdc
is 1,4-benzenedicarboxylic acid (29); (vii) [Cu(SiF6)_2(pz)_2] (“Cu-SiF6”), where pz is pyrazine (30); (viii) [Zn_2(btm)_2] (“Zn-BTM”), where H_2btm is bis(5-methyl-1H-1,2,4-triazol-3-yl)methane (31); and (ix) [Zn_2(bta)_2] (“Zn-BTA”) with hydrophilic pore surfaces, where H_2bta is bis(5-amino-1H-1,2,4-triazol-3-yl)methane (32). These MOFs are stable and easy to synthesize with reproducible properties (fig. S4).

The breakthrough sequence of the guest mixture can straightforwardly illustrate the different adsorption tendencies of the involved guests that directly reflect the separation mechanism. Fixed-bed breakthrough experiments using an equimolar mixture of C_4 hydrocarbons (methods and table S3) showed that the breakthrough times for the MOFs with OMSs followed the sequence C_4H_{10} < n-C_4H_8 < i-C_4H_8 < C_4H_6, consistent with the coordination abilities of the gases (fig. S5, A to C). The slight adsorption differences between C_4H_6 and n- and i-C_4H_8 arose because each C_4 hydrocarbon molecule can only coordinate with one OMS, regardless of its number of double bonds. For the hydrophobic MOFs, the breakthrough time decreased with the increase in unsaturated degree or hydrophobicity of the gas, which is useful for the direct purification of C_4H_6.

**Fig. 2. Mixture breakthrough curves for C_4 hydrocarbons.** (A) Zr-BDC, (B) Cu-SiF6, (C) Zn-BTA, and (D) Zn-BTM curves for a 1:1:1:1 C_4H_{10}/n-C_4H_8/i-C_4H_8/C_4H_6 mixture. (E) Zn-BTM and (F) Zn-EIM-RHO curves for a 5:2:2:1 C_4H_{10}/n-C_4H_8/i-C_4H_8/C_4H_6 mixture. C_i and C_o are the concentrations of each gas at the inlet and outlet, respectively. Lines are drawn to guide the eye. Dashed lines highlight the gas composition at 0.5%, corresponding to the composition of other gases at 99.5%. The insets show framework and pore surface structures of the adsorbent.
The four hydrophilic MOFs showed diversified separation sequences that were closely related to their pore sizes, shapes, and dimensionalities. A fast screening using grand canonical Monte Carlo (GCMC) simulation showed that these MOFs represent the large channel, small channel, discrete pore, and quasi-discrete pore situations (tables S4 to S7). Zr-BDC, which has large channels, exhibited the same elution sequence as the OMS-functionalized MOFs, because the hydrophilic pore surface can form stronger dipole–dipole interactions—i.e., weak C–H···O hydrogen bonds with the more unsaturated hydrocarbons (Fig. 2A). CuSiF$_4$, which has very small channels, rejected the relatively large molecule i-C$_4$H$_8$. For the other three C$_4$ hydrocarbons, the elution sequence of CuSiF$_4$ was the same as those of Zr-BDC and the OMS-functionalized MOFs, although it could hardly distinguish C$_4$H$_6$ and n-C$_4$H$_8$ (Fig. 2B).

Zn-BTA and Zn-BTM both possess discrete or quasi-discrete cavities interconnected by very small apertures, but they differ in the shapes and sizes of their cavities and apertures (fig. S6 and table S2). Zn-BTA showed no adsorption of any of the four C$_4$ hydrocarbons (Fig. 2C and fig. S7), because its aperture size is too small (fig. S6). Zn-BTM showed a distinctive elution sequence with quite different breakthrough times in the sequence C$_4$H$_8$ < C$_4$H$_6$ < n-C$_4$H$_8$ < i-C$_4$H$_8$ (Fig. 2D), which is beneficial for not only directly producing highly pure C$_4$H$_8$ from C$_4$ hydrocarbons, but also for efficiently separating the four components (fig. S2).

To emphasize the different C$_4$H$_8$ purification performances of Zn-BTM and the hydrophobic MOFs, we carried out further breakthrough experiments using a 5:2:2:1 C$_4$H$_8$/n-C$_4$H$_8$/i-C$_4$H$_8$/C$_4$H$_{10}$ mixture, the typical composition of C$_4$ hydrocarbon mixtures (2). Compared with the equilibrium input, Zn-BTM showed much improved separation performance because the reduced C$_4$H$_{10}$/C$_4$H$_8$ ratio increased the differences in the breakthrough times of the two gases. The lowest impurity concentration (n-C$_4$H$_8$ + i-C$_4$H$_8$ + C$_4$H$_{10}$) or the highest C$_4$H$_8$ purity was determined as 0.1 or 99.9%, respectively. For the required purity threshold of ≥99.5%, 0.89 mmol of C$_4$H$_8$ per gram of Zn-BTM (or 1.27 mol liter$^{-1}$) could be purified by a single breakthrough operation (Fig. 2E and table S8). In contrast, the separation performance of Zn-EIM-RHO remained very poor for the 5:2:2:1 mixture, with negligible productivity even for a C$_4$H$_8$ purity of 90% (Fig. 2F and table S6), because of the low adsorption selectivity of hydrophobic adsorbents (15). Unlike hydrophobic adsorbents, the stronger adsorption affinities of Zn-BTM for the unsaturated n-C$_4$H$_8$ and i-C$_4$H$_8$ molecules can further improve the C$_4$H$_8$ purification performance (table S9).

To verify the thermodynamic nature of the unusual C$_4$ hydrocarbon adsorption of Zn-BTM, single-component adsorption isotherms for C$_4$H$_6$, n-C$_4$H$_8$, i-C$_4$H$_8$, and C$_4$H$_{10}$ were measured at 288, 298, and 308 K (Fig. 3A and fig. S8). All displayed the type-I characteristic and reached saturation uptake of 45 cm$^3$ g$^{-1}$, corresponding to 1.0 molecule per cavity. Nevertheless, their isotherm slopes at low pressure followed the sequence C$_4$H$_6$ < C$_4$H$_8$ < n-C$_4$H$_8$ < i-C$_4$H$_8$, which can be quantitatively demonstrated by the substantially different adsorption enthalpies of −72, −79, −87, and −101 kJ mol$^{-1}$, respectively (Fig. 3B and fig. S9), and which is consistent with the breakthrough sequence (Fig. 2, D and E). We also carried out adsorption-separation studies for Zn-BTM by using other adsorbate systems. For a pair of flexible C$_4$ hydrocarbons, namely, trans-1,3-pentadiene and 1-pentene, Zn-BTM showed higher affinity for the less-saturated trans-1,3-pentadiene, conversely from other hydrophilic adsorbents (figs. S10 and S11 and table S10). In contrast, single-component adsorption isotherms of C$_4$H$_6$, C$_4$H$_8$, and C$_4$H$_{10}$ showed that Zn-BTM behaves as a normal hydrophilic adsorbent for smaller and rigid guest molecules (fig. S12). Zn-BTM exhibits a special adsorption mechanism for flexible guests, as compared with other adsorbents, including the hydrophobic ones.

The structural origins of the abnormal C$_4$ hydrocarbon adsorption in Zn-BTM were visualized by single-crystal x-ray diffraction (SCXRD) analyses of the host-guest structures and interactions. Because of the degraded single crystallinity of the samples, as commonly encountered in similar systems (32), the SCXRD data are not of sufficient quality to determine the precise positions of the hydrogen atoms, especially for the labile guest molecules. Nevertheless, the adsorbed C$_4$ hydrocarbon molecules could be observed inside the cavities of Zn-BTM, with clearly distinguishable molecular conformations (fig. 4 and table S11). Specifically, C$_4$H$_6$ and C$_4$H$_8$ adopted the more stable trans conformation, whereas n-C$_4$H$_8$ adopted the metastable cis conformation. Except for the rigid i-C$_4$H$_8$ molecule, both the host framework and guest molecules showed small distortions, indicating a non-negligible role of framework and guest flexibility.

To elucidate the structure-energy relationships for adsorption of C$_4$ hydrocarbons in Zn-BTM and to understand why this host does not prefer cis-C$_4$H$_6$, trans-n-C$_4$H$_8$, and cis-C$_4$H$_{10}$, we carried out multilevel computational simulations. First, the SCXRD host-guest structures were subjected to periodic density functional theory (PDFT) calculations (14). The PDFT-optimized structures changed little from the starting SCXRD models (fig. S13). Unlike conventional host-guest systems, the energy balances of C$_4$ hydrocarbon adsorption in Zn-BTM need to consider the flexibilities of both the host and the guest, and they can be expressed by

$$\Delta E_{\text{binding}} = E_{\text{host+guest}} - E_{\text{host}} - E_{\text{guest}}$$

$$\Delta E_{\text{ads}} = E_{\text{host+guest}} - E_{\text{apohost}} - E_{\text{apoguest}}$$

$$\Delta E_{\text{host}} = \Delta E_{\text{binding}} + \Delta E_{\text{host+transf}} + \Delta E_{\text{guest+transf}}$$

$$\Delta E_{\text{host+transf}} = E_{\text{host}} - E_{\text{apohost}}$$

$$\Delta E_{\text{guest+transf}} = E_{\text{guest}} - E_{\text{apoguest}}$$

where $\Delta E_{\text{binding}}$ is the host-guest binding energy; $\Delta E_{\text{ads}}$ is the adsorption enthalpy; $E_{\text{host+guest}}$, $E_{\text{apohost}}$, and $E_{\text{apoguest}}$ are the energies of the final host-guest system, the pristine host (guest) before adsorption, and the transformed host (guest) after adsorption, respectively; and $\Delta E_{\text{host+transf}}$ and $\Delta E_{\text{guest+transf}}$ are the energy consumed for the structural transformation of the host (guest). The obtained adsorption enthalpies for trans-C$_4$H$_6$, trans-n-C$_4$H$_8$, cis-n-C$_4$H$_8$, and i-C$_4$H$_8$ were −70.4, −78.4, −88.1, and −95.3 kJ mol$^{-1}$, respectively (table S12), which are consistent with the experimental trends (Figs. 2 and 3) and can be ascribed to the different numbers and strengths of C–H···N hydrogen bonds (Fig. 4 and table S13).

For cis-C$_4$H$_6$, trans-n-C$_4$H$_8$, and cis-C$_4$H$_{10}$, we simulated their adsorption using the molecular dynamics (MM) method by loading a guest molecule with the conformation of interest into the

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**Fig. 3. Single-component gas adsorption properties of Zn-BTM.** (A) Adsorption isotherms for C$_4$H$_6$, n-C$_4$H$_8$, i-C$_4$H$_8$, and C$_4$H$_{10}$ in Zn-BTM at 298 K. Lines are drawn to guide the eye. (B) The coverage-dependent C$_4$H$_6$, n-C$_4$H$_8$, i-C$_4$H$_8$, and C$_4$H$_{10}$ adsorption enthalpies were calculated by the Clausius-Clapeyron equation using original data without fitting (points) or using data fitted by the Langmuir-Freundlich equation (lines). Q$_{ui}$, adsorption enthalpy; n, guest loading.

guest-free host, during which both the host and guest were allowed to deform to fit each other. The MM-derived host-guest structures were then subjected to PDFT optimization for accurate structures and energies (methods). The accuracy of this MM-PDFT simulation method was first shown by applying it to the adsorption of trans-C$_4$H$_6$, cis-n-C$_4$H$_8$, f-C$_4$H$_6$, and trans-C$_4$H$_6$ for which the obtained host-guest structures and energies showed the same trends as for the above-mentioned experimental and SCXRD-PDFT results (figs. S14 and S15 and tables S12 and S14). Comparison of the MM-PDFT energies of the seven host-guest structures (for all guests and all conformations) showed that Zn-BTM exhibited higher binding energy and affinity for the cis conformation of all three flexible C$_4$ hydrocarbons (table S12 and Fig. 1B), meaning that its pore characteristics are suitable for controlling the guest conformations. However, after consideration of the energy consumption of the guest distortion, especially 14 kJ mol$^{-1}$ for cis-C$_4$H$_6$, the hypothetical host-guest structures for cis-C$_4$H$_8$ and cis-C$_4$H$_10$ became less energy-favorable (adsorption enthalpy), consistent with the SCXRD observations. More importantly, if all C$_4$ hydrocarbon molecules were rigid and had the same conformation, both the cis and trans cases exhibited adsorption-separation sequences that differed from the experimental ones (fig. S16 and table S12), which highlights the crucial roles of the conformation controllability of the pores and the different flexibilities of the guests.

As demonstrated by GCMC simulation, Zn-BTA has a higher cis conformation preference and lower C$_4$H$_6$ adsorption preference (tables S6 and S7), which can be understood by the more spherical shape of its cavities compared with those in Zn-BTM (fig. S6 and table S2). The inability of Zn-BTA to adsorb C$_4$ hydrocarbons can be attributed to its relatively small aperture size and/or lower framework flexibility. The aperture sizes between the cavities are 3.6 and 3.0 Å for Zn-BTM and Zn-BTA, respectively, which are both smaller than the smallest cross sections of all C$_4$ hydrocarbons and may hinder the guest diffusion (fig. S1). We carried out molecular dynamics simulations to investigate the diffusion behaviors of the C$_4$ hydrocarbons in Zn-BTM and Zn-BTA (figs. S10 and S11 and tables S15 and S16). For Zn-BTM, the self-diffusion coefficients of all four C$_4$ guests were $<$1 × 10$^{-13}$ or $>$1 × 10$^{-10}$ m$^2$ s$^{-1}$ when the host frameworks were set as rigid or flexible during the simulations, respectively. However, all of the self-diffusion coefficients in Zn-BTA were $<$1 × 10$^{-11}$ m$^2$ s$^{-1}$, regardless of the rigid versus flexible setting of the host, which can be ascribed to the smaller apertures and/or lower flexibility of this adsorbent.

Isolated cavities with suitable sizes, shapes, and surface functionalities are useful for controlling guest conformation and achieving abnormal adsorption selectivity, but continuous channels are necessary for guest diffusion. Our results show that it is possible to combine the advantages of isolated cavities and continuous channels in the same porous material to achieve on-demand gas adsorption and separation.

REFERENCES AND NOTES

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SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/356/6343/1193/suppl/DC1
Materials and Methods
Figs. S1 to S18
Tables S1 to S16
References (33, 34)
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Selecting against cis conformers

Before 1,3-butadiene can be used to make polymers, it must be separated from similar hydrocarbons in an energy-intensive distillation process. Liao et al. show that a zinc metal–organic framework can accommodate the cis isomer of 1,3-butadiene. It binds less tightly than butane and butene because its π-bond conjugation is broken. They used this preferential desorption to separate 1,3-butadiene with ≥99.5% purity under ambient conditions.

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