Efficient separation of 1,3-butadiene from C4 hydrocarbons by flexible metal-organic framework with gate-opening effect

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Abstract

Efficient and economical separation of 1,3-butadiene (C\textsubscript{4}H\textsubscript{6}) from C\textsubscript{4} hydrocarbons is imperative yet challenging in industrial separation processes. Herein, a guest-induced flexible Mn-bpdc MOF has been employed to separate C\textsubscript{4}H\textsubscript{6} from C\textsubscript{4} hydrocarbons, including n-butene (n-C\textsubscript{4}H\textsubscript{8}), iso-butene (iso-C\textsubscript{4}H\textsubscript{8}), n-butane (n-C\textsubscript{4}H\textsubscript{10}) and iso-butane (iso-C\textsubscript{4}H\textsubscript{10}). Significantly, C\textsubscript{4}H\textsubscript{6} can instantaneously induce gate-opening of Mn-bpdc MOF at 0.13 bar and 298 K, thus significant amounts of C\textsubscript{4}H\textsubscript{6} can be adsorbed, while other C\textsubscript{4} hydrocarbons cannot induce the gate-opening even at 1 bar. The uptake selectivities of Mn-bpdc MOF for C\textsubscript{4}H\textsubscript{6}/n-C\textsubscript{4}H\textsubscript{8} and C\textsubscript{4}H\textsubscript{6}/iso-C\textsubscript{4}H\textsubscript{8} are up to 40.0 and 45.0 at 298 K and 1 bar, respectively, both surpassing all the reported adsorbents. In addition, breakthrough experiments verified that C\textsubscript{4}H\textsubscript{6}/n-C\textsubscript{4}H\textsubscript{8}, C\textsubscript{4}H\textsubscript{6}/iso-C\textsubscript{4}H\textsubscript{8}, C\textsubscript{4}H\textsubscript{6}/n-C\textsubscript{4}H\textsubscript{10} and C\textsubscript{4}H\textsubscript{6}/iso-C\textsubscript{4}H\textsubscript{10} mixture can be efficiently separated. More importantly, Mn-bpdc possesses excellent water stability and outstanding regeneration ability for C\textsubscript{4}H\textsubscript{6} separation, making it a new benchmark for C\textsubscript{4}H\textsubscript{6} purification.
all the reported adsorbents. In addition, breakthrough experiments verify that C₄H₆/n-C₄H₈, C₄H₆/iso-C₄H₈, C₄H₆/n-C₄H₈ and C₄H₆/iso-C₄H₈ mixture can be efficiently separated. More importantly, Mn-bpdc possesses excellent water stability and outstanding regeneration ability for C₄H₆ separation, making it a new benchmark for C₄H₆ purification.

**Keywords:** metal-organic frameworks, gate-opening, 1,3-butadiene, adsorption/gas, gas purification.

**Introduction**

1,3-Butadiene (C₄H₆) is one of the basic and important raw material for petrochemical industry, which not only can be used in the production of synthetic rubber, but also in the synthesis of synthetic resins and other organic chemical products, such as tetramethylene sulfone, tetrahydrofuran. It is mainly obtained from the by-product of vapour cracking of naphtha. However, this process is usually accompanied by the presence of other C₄ components, such as n-butene (n-C₄H₈), iso-butene (iso-C₄H₈), n-butane (n-C₄H₁₀) and iso-butane (iso-C₄H₁₀), which will cause structure transformation of polybutadiene in the preparation of synthetic rubber and affect product quality and even reduce polymerization activity by interrupting the polymerization reaction. Hence, the separation of C₄H₆ from the other C₄ hydrocarbons is very imperative. In addition, due to the similar boiling point, molecular size and physical properties of C₄ hydrocarbons, especially for diolefin and mono-olefins, the separation of C₄H₆ from other C₄ hydrocarbons is still remain a particular challenge. At present, the separation of C₄H₆ from other C₄ hydrocarbons is mainly carried out by precise controlled extraction distillation in industry. However, the extraction distillation usually needs high operation temperature (323 K to 393 K) with more than 110 trays of high towers, and consume large amounts of organic solvents. In addition, the polymerization of high reactive C₄H₆ is inevitable at above high temperature distillation process. Therefore, the extraction distillation process is energy intensive and environmental unfriendly process, and it is very important to seek for an efficient and low-cost technology to separate C₄H₆ from C₄ hydrocarbons.

Among the existing separation technologies, adsorption separation featuring simple operating conditions, energy saving, and high adsorption accuracy has been proved to be a potential separation technology with broad prospects for gas separation. As an emerging advanced adsorbent, metal-organic frameworks (MOFs) are attracting more and more attention by virtue of their multifarious structural topologies, precise structural determination and tunability of pore surface functionalities. In recent years, MOFs have been widely applied to various separation applications, including CO₂ capture, propane-propylene separation, hydrogen storage and so on. From the point of view of the adsorption mechanism, the efficient separation of gas mixtures by MOFs adsorbents usually depends on the thermodynamic separation based on interaction force, kinetic separation determined by adsorption rate and molecular sieving separation and gate-opening flexible separation. Owing to the similarities of molecular sizes, shapes and properties between C₄H₆ and other C₄ hydrocarbons, the potential separation of C₄H₆ from other C₄ hydrocarbons by MOFs adsorbents is still a challenge. The information about physical and chemical properties of C₄ hydrocarbons are illustrated in Table S1. Nowadays, most reported MOF adsorbents used for C₄H₆ separation from other C₄ hydrocarbons mainly based on the reinforcing interactions between C₄H₆ and MOF over other C₄ hydrocarbons, however the other C₄ hydrocarbons could be simultaneously adsorbed to a certain extent, especially for the separation of mono-olefins and diolefin. The co-adsorption separations will cause the low adsorption selectivity and low separation efficiency. As well known, molecular sieving is an ideal efficient separation model and has been well achieved on some olefin/alkane separations. However, since the very similar molecular size of C₄H₆ with other C₄ hydrocarbons, the adsorbent that can separate C₄H₆ with other C₄ hydrocarbons by complete molecular sieving effect have not been reported up to now. Ingeniously, considering the difference that C₄H₆ has two C=C double bonds, whereas the other C₄ hydrocarbons either have one or none C=C double bond, gate-opening flexible MOF hopefully can be deemed as the prospective candidate for the separation of C₄H₆ to achieve the molecular sieving effect. As a very rare example, Kitagawa et al. reported a flexible SD-65 MOF that can selectively capture C₄H₆ and exclude other C₄ hydrocarbons. However, the gate-opening pressure for C₄H₆ is up to 0.6 bar at 298 K. The high gate-opening pressure is disadvantageous for the actual purification and separation of C₄H₆ and the operating range will
be relatively narrow, especially, it is difficult to achieve efficient separation at practical low partial pressure of \( \text{C}_4\text{H}_6 \).\(^{42}\) Considering this problem, the ideal MOF with gate-opening effect on \( \text{C}_4\text{H}_6 / \text{C}_4 \) hydrocarbons separation should not only can sensitively capture \( \text{C}_4\text{H}_6 \) at very low pressure but also can exclude other \( \text{C}_4 \) hydrocarbons even at 1 bar, to realize efficient separation of \( \text{C}_4\text{H}_6 \) over a wide ranges of operation pressures, especially at low partial pressure of \( \text{C}_4\text{H}_6 \).

Herein, we adopt a guest induced flexible Mn-bpdc MOF with neat one-dimensional channels for the separation of \( \text{C}_4\text{H}_6 \) from other four major \( \text{C}_4 \) hydrocarbons, including two mono-olefins and two paraffins. The intrinsic flexibility of Mn-bpdc MOF is confirmed by thermal responded variable temperature X-ray diffraction (VT-XRD) and guest-depended structure transformations, while its gate-opening effects on olefins and paraffins are explored by the adsorption isotherms of \( \text{C}_2\text{H}_4 \), \( \text{C}_3\text{H}_6 \), \( \text{C}_2\text{H}_6 \) and \( \text{C}_3\text{H}_8 \). Surprisingly, the single-component adsorption isotherms of \( \text{C}_4 \) hydrocarbons with Mn-bpdc demonstrates that Mn-bpdc can specifically and sensitively capture \( \text{C}_4\text{H}_6 \) with very low gate-opening pressure and exclude for other \( \text{C}_4 \) components even to 1 bar, including \( \text{n-C}_4\text{H}_8 \), \( \text{iso-C}_4\text{H}_8 \), \( \text{n-C}_4\text{H}_{10} \) and \( \text{iso-C}_4\text{H}_{10} \). At the same time, the uptake selectivities of \( \text{C}_4\text{H}_6 / \text{n-C}_4\text{H}_8 \) and \( \text{C}_4\text{H}_6 / \text{iso-C}_4\text{H}_8 \) in Mn-bpdc exceed the overall reported adsorbents. The four column breakthrough experiments of gas mixtures of \( \text{C}_4\text{H}_6 / \text{n-C}_4\text{H}_8 \), \( \text{C}_4\text{H}_6 / \text{iso-C}_4\text{H}_8 \), \( \text{C}_4\text{H}_6 / \text{n-C}_4\text{H}_{10} \) and \( \text{C}_4\text{H}_6 / \text{iso-C}_4\text{H}_{10} \) furtherly credibly verify that the efficient dynamic separation effect on Mn-bpdc to separate \( \text{C}_4\text{H}_6 \) from other \( \text{C}_4 \) components can be achieved. In addition, the Mn-bpdc MOF possesses outstanding water stability, well regeneration and cyclic utilization performance, which comprehensively affirm the great potential of Mn-bpdc adsorbent for the challenging separation of \( \text{C}_4\text{H}_6 \) from other \( \text{C}_4 \) hydrocarbons.

**Results and Discussion**

![Figure 1](image1.png)

**Figure 1.** a) 2,2'-bipyridyl-4,4'-dicarboxylic acid ligand in Mn-bpdc MOF; b) Local coordination geometry of the central Mn metal atoms; c) The 3D structure and connolly surface of Mn-bpdc MOF front view of the structure along the c axis; d) The one-dimensional channels of Mn-bpdc MOF. The inner and external surfaces are lilac and grey, respectively. Color codes: Grey violet, red, dark blue, and gray nodes represent manganese metal, oxygen, nitrogen and carbon atoms, respectively.

The Mn-bpdc MOF was synthesized by hydrothermal method through the reaction of commercially available 2,2'-bipyridine-4,4'-dicarboxylic acid ligand (H\(_2\)BPDC) and manganese sulfate.\(^{43}\) The experimental PXRD pattern of the as-synthesized Mn-based MOF is accorded with the simulated ones, revealing the successful synthesis of Mn-bpdc MOF (**Figure S1**). The framework of Mn-bpdc consists of infinite chains of corner-sharing Mn(II) centers connected with two nitrogen atoms from bipyridyl and four oxygen atoms from
carboxylic of BPDC ligands, possessing uniform one dimensional channels (Figure 1a-d). The scanning electron microscopy (SEM) of Mn-bpdc MOF is showed in Figure S2, which reveals that the Mn-bpdc MOF has rod-shaped laminated microstructures.

![Figure 2](image_url)

**Figure 2.** a) VT- PXRD patterns of Mn-bpdc MOF at different temperatures under atmospheric environment; b) PXRD patterns of Mn-bpdc MOF after different treatments by immersing in acetone, dichloromethane and water, respectively; c) Adsorption isotherms of Mn-bpdc MOF for single component $C_2H_4$ and $C_2H_6$ at different temperatures; d) Adsorption isotherms of Mn-bpdc MOF for single component $C_3H_6$ and $C_3H_8$ at different temperatures.

To investigate the flexible structure of Mn-bpdc, firstly, the VT-PXRD measurements at different temperatures under atmospheric environment were measured, as drawn in Figure 2a. At the temperatures of 303 K and 323 K, the PXRD patterns are consistent with the simulated ones. When the temperature raises from 373 K to 473 K, the diffraction peak at around 11.3° slightly shifts to the high angle, while new diffraction peak appears at 26.3° and the pristine diffraction peaks at 24.1° of Mn-bpdc at 303 K and 323 K completely disappear, which illustrate temperature responded structural transformation of Mn-bpdc. It is worth noting that when the temperature drops from 473 K to 303 K, the PXRD patterns were restored to the original state at 303 K, which indicates that the reversible structure transformation of Mn-bpdc upon thermal stimulation.

To explore the guest molecule induced structural transformation of Mn-bpdc, we measured the PXRD of the Mn-bpdc MOF samples by immersing in water, dichloromethane and acetone, respectively. The PXRD pattern of Mn-bpdc under water environment is consistent with that simulated one (Figure 2b). However, the PXRD patterns change obviously when the MOF immersed in acetone or dichloromethane, and the diffraction peaks at 24.1° disappear while new diffraction peaks appear at 26.3°, which indicates that guest molecules can also induce the structure transformation of Mn-bpdc. In addition, when the dichloromethane treated Mn-bpdc MOF was exchanged by water, the consistent PXRD pattern of water exchanged Mn-bpdc MOF (Figure S4) with simulated ones credibly verifies the structural reversibility of Mn-bpdc MOF. In a word, it illustrates that both thermal stimulation and guest molecule induction can trigger the structural transformation of the Mn-bpdc MOF.
Taking into account the peculiarity of both temperature and guest molecular can induce structural transformation, gas molecules with different polarity might also be able to regulate the structural transformation of the Mn-bpdc MOF at proper temperature. To study the stimulus-response behavior of Mn-bpdc towards gas molecules, the single-component gas adsorption isotherms of C$_2$H$_4$ and C$_3$H$_6$ were collected at 273 K, 288 K, 298 K and 323 K, respectively, as shown in Figure 2c. For the C$_2$H$_4$ adsorption at 323 K, there is almost no observed adsorption even up to 1 bar, indicating that C$_2$H$_4$ cannot open the door of Mn-bpdc at 323 K. However, when the temperature reduces, obvious adsorption begins to be observed at 273 K, which shows typical S-typed curves and implies structural transformation in the adsorption process. In particular, the lower adsorption temperatures, the lower gate-opening pressures can be achieved, illustrating that low temperature is more conducive for C$_2$H$_4$ to open the door of Mn-bpdc. Similar results also can be observed for C$_3$H$_6$ adsorption (Figure 2d). We can obviously find that it fails to open the door at both 298 K and 323 K for C$_3$H$_6$ adsorption, but the gate-opening effects are appeared at 273 K and 288 K, corresponding to the gate-opening pressure points at 0.35 bar and 0.80 bar, respectively. These results mean that the gate-opening pressure points of adsorption can be well regulated by different temperatures and object gas molecule. In addition, the single component gas sorption isotherms of Mn-bpdc MOF for C$_2$H$_6$ (Figure 2c) and C$_3$H$_8$ (Figure 2d) were measured both at 273 K and 298 K. Obviously, no matter at 273 K or 298 K, they have no ability to open the door of Mn-bpdc MOF, which suggests that the occurrence of gate-opening can be induced by the C=C double bond of olefins. Furtherly, compared the adsorption curves of C$_2$H$_4$ and C$_3$H$_6$ at 273 K, it should be noticed that the gate-opening points of C$_2$H$_4$ (0.2 bar) is lower than that of C$_3$H$_6$ (0.35 bar). Similar changes of gate-opening pressure can also be observed for C$_2$H$_4$ and C$_3$H$_6$ adsorption at 298 K. It verifies that C$_2$H$_4$ has higher capability to induce the gate-opening behavior of Mn-bpdc than that of C$_3$H$_6$, and gate-opening pressure of Mn-bpdc will increase when the number of carbon atoms increased in mono-olefines.

Enlightened by the above experimental results, it implies that Mn-bpdc depending on its structural response to different types olefins can achieve the separation of C$_4$H$_6$ from other C$_4$ at room temperature. In detail, since C$_4$H$_6$ has two C=C double bonds, it could be more easily to open the door of Mn-bpdc MOF with lower gate-opening pressure. On the contrary, for other C$_4$ components, the gate-opening ability will be weaker due to the increases of carbon atoms numbers. Since C$_5$H$_6$ cannot open the door of Mn-bpdc even up to 1 bar at 298 K, we can infer that n-C$_4$H$_8$ and iso-C$_4$H$_8$ will fail to open the door at 298 K although they have one C=C double bond. On the other hand, n-C$_4$H$_{10}$ and iso-C$_4$H$_{10}$ also certainly cannot open the gate of Mn-bpdc at 298 K owning to the absence of C=C double bond. Hence, theoretically, the Mn-MOF can efficiently separate C$_4$H$_6$ from other C$_4$ hydrocarbons by recognizing C$_4$H$_6$ and rejecting other C$_4$ hydrocarbons to enter the framework of Mn-bpdc MOF at room temperature.
Figure 3. a) Adsorption isotherms of Mn-bpdc MOF for single component C$_4$H$_6$ at different temperatures; b) Adsorption isotherms of Mn-bpdc MOF for single component C$_4$H$_6$, n-C$_4$H$_8$, iso-C$_4$H$_8$, n-C$_4$H$_{10}$, and iso-C$_4$H$_{10}$ at 273 K; c) Adsorption isotherms of Mn-bpdc MOF for single component C$_4$H$_6$, n-C$_4$H$_8$, iso-C$_4$H$_8$, n-C$_4$H$_{10}$ and iso-C$_4$H$_{10}$ at 298 K, respectively; d) The comparison of uptake selectivity of C$_4$H$_6$/n-C$_4$H$_8$ and C$_4$H$_6$/iso-C$_4$H$_8$ with reported adsorbents at 298 K and 1 bar.

Figure 4. (a) Adsorption isotherms of Mn-bpdc marked with four adsorption positions for C$_4$H$_6$ at 298 K; (b) In situ PXRD experiments collected under different gas pressures corresponding to the four adsorption positions as shown in (a), point A (0 bar), point B (0.11 bar), point C (0.17 bar), point D (1 bar).

To confirm our hypothesis, firstly, the adsorption isotherms of C$_4$H$_6$ at different temperatures were collected. As shown in Figure 3a, the Mn-bpdc MOF exhibits abrupt adsorption phenomenon for C$_4$H$_6$ at all temperatures, including 273 K, 288 K, 298 K, 308 K, 318 K and 323 K. As expected, the gate-opening pressure for C$_4$H$_6$ is found to be as low as 0.13 bar at 298 K by virtue of the presence of two C=C double bonds. In addition, the C$_4$H$_6$ uptake at 0.20 bar is about 30 cm$^3$g$^{-1}$, 93% of that at 1 bar (32.12 cm$^3$g$^{-1}$),
which both demonstrates that C₄H₆ with double C=C bonds has strong ability to open the doors of Mn-bpdc MOF.⁴⁶ Besides, the gate-opening pressure is observed to be increased with the increasing of adsorption temperature. In detail, at 273 K, 288 K, 308 K, 318 K and 323 K, the abrupt gate-opening pressures are 0.02 bar, 0.06 bar, 0.26 bar, 0.50 bar, 0.92 bar (Figure S5), corresponding to the uptake of 33.57 cm³ g⁻¹, 32.81 cm³ g⁻¹, 31.40 cm³ g⁻¹, 30.51 cm³ g⁻¹ and 26.04 cm³ g⁻¹ at 1 bar, respectively. Consistent with the observations of C₂H₄ and C₃H₆ adsorptions, it can be found that lower temperatures are more conducive to opening the door of Mn-bpdc for C₄H₆, which due to the gas molecules slow down at low temperatures and are more likely to be bound by MOF, thus providing adequate gate-opening capacity per unit time.⁴⁷,⁴⁸ In addition, compared with the gate-opening pressures of C₂H₄ (nearly 1 bar) and C₃H₆ (cannot open the gate even at 1 bar) at 298 K, C₄H₆ can open the flexible door of Mn-bpdc MOF at very low pressure (0.13 bar) (Figure S5), which is consistent with the previous inferences. It should be noticed that although the SD-65 MOF with gate-opening effect has been reported for C₄H₆ separation from other C₄ mono-olefines and paraffins, the gate-opening pressure of SD-65 reaches up to 0.6 bar at 298 K.⁴¹ Obviously, the very low gate-opening pressure of Mn-bpdc for C₄H₆ is a huge advantageous to achieve efficient separation of C₄H₆ from other C₄ hydrocarbons at lower partial pressure of C₄H₆.

Subsequently, the adsorption isotherms for n-C₄H₈, iso-C₄H₈, n-C₄H₁₀ and iso-C₄H₁₀ were measured at 273 K (Figure 3b) and 298 K (Figure 3c), respectively. At 273 K and 1 bar, there are almost no uptakes for n-C₄H₈ (1.78 cm³ g⁻¹), iso-C₄H₈ (1.48 cm³ g⁻¹), n-C₄H₁₀ (0.61 cm³ g⁻¹) and iso-C₄H₁₀ (0.05 cm³ g⁻¹), but high uptake for C₄H₆ (34.12 cm³ g⁻¹) is retained. Additionally, the uptake of C₄H₆ at the gate-opening pressure of 0.02 bar is closed to the maximum adsorption capacity. The distinct difference between adsorption isotherms of C₄H₆ and other C₄ hydrocarbons means great theoretical selectivity could be achieved and this MOF has huge potential for actual separation of C₄H₆ over other C₄ hydrocarbons. Importantly, the very low uptakes of n-C₄H₈ (0.80 cm³ g⁻¹), iso-C₄H₈ (0.74 cm³ g⁻¹), n-C₄H₁₀ (0.29 cm³ g⁻¹) and iso-C₄H₁₀ (0.02 cm³ g⁻¹) can be also observed at 298 K and 1 bar. The extreme low uptakes illustrate that the Mn-bpdc MOF is very negative to capture n-C₄H₈, iso-C₄H₈, n-C₄H₁₀ and iso-C₄H₁₀. On the contrary, by virtue of much stronger polarity of C₄H₆, it can actively push open the molecular door of Mn-bpdc MOF, which is definitely verified by the very low gate-opening pressure (0.13 bar) and close saturation adsorption capacity of C₄H₆ (32.2 cm³ g⁻¹) at the low pressure. As we known, the adsorption selectivity is a critical factor to evaluate the separation performance for adsorbent materials.⁴⁹ Notably, the calculated uptake selectivities of Mn-bpdc MOF for C₄H₆/n-C₄H₈ and C₄H₆/iso-C₄H₈ are 40.0 and 45.0 at 298 K and 1 bar, respectively, both of which are much higher than that all previous porous materials. (Mg-gallate: 1.3, 15.1,⁵⁰ Ni-gallate: 2.4, 15.4,⁵⁰ GeFSIX-14-Cu-i: 4.7, 6.4,³⁷ NbFSIX-2-Cu-i: 1.2, 5.7,³⁷ GeFSIX-2-Cu-i: 1.1, 2.9,³⁷ ZJNU-30a: 1.0, 1.2,⁵⁶ and SD-65: 22.3, 25.4,⁴¹ Figure 3d and Table S2). Those results powerfully indicate the potential utility of Mn-bpdc MOF for the separation of C₄H₆ from other C₄ hydrocarbons under ambient conditions.

Furthermore, to explore the structure variations upon the adsorption of C₄H₆ and directly observe the guest-induced structural transformations, we measured the in situ PXRD of Mn-bpdc under C₄H₆ environment with different pressures (0 bar, 0.11 bar, 0.17 bar and 1 bar) at 298 K (Figure 4b). The four different pressures points at in situ PXRD data are corresponded to the detailed adsorption points in the adsorption curves of C₄H₆ at 298 K (Figure 4a). As shown in Figure 4b, compared with the PXRD pattern of Mn-bpdc under vacuum environment (point A), obvious new diffraction peak at 25.4° appears and slight peak at 24.4° begins to appear when the pressure increases to 0.11 bar (point B), which means small amount adsorption of C₄H₆ before isotherm obviously jumping can lead to the initial transformation of the structure of Mn-bpdc MOF and proves the sensitivity of the structure for C₄H₆. Subsequently, the diffraction peak at 26.5° completely disappears and the peak at 24.4° gradually increases when the pressure raises to 0.17 bar (point C), which corresponds to a large amount of C₄H₆ (28.4 cm³ g⁻¹) enter the pore structure and furtherly facilitate the structural changes. Then, when the pressure reaches 1 bar and the amount adsorption of C₄H₆ reaches the saturated state, the diffraction peak at 25.4° disappears and the intensity of diffraction peak at 24.4° reaches its maximum value (point D). These results together reveal gradual transformation of the structure of Mn-bpdc in the adsorption process of C₄H₆. In addition, it is found that the strong peaks at around 11.6° under vacuum transforms into several unidentifiable weaker diffraction peaks when
the pressures increased to 0.11 bar and 0.17 bar, then, furtherly splits into two strong peaks at around 11° at 1 bar, which due to the formation of metastable distorted structure of Mn-bpdc at the adsorption process of C₄H₆ and also verifies the huge structure transformation of Mn-bpdc induced by C₄H₆.41,51 Furtherly, the PXRD pattern of Mn-bpdc after C₄H₆ desorption is highly consistent with that of initial vacuum state, which means the well reversibility of structure transformation for C₄H₆ adsorption (Figure S6).

Figure 5. Column breakthrough experiment for C₄H₆/n-C₄H₈(1/1 (v/v)) (a); C₄H₆/iso-C₄H₈(1/1 (v/v)) (b); C₄H₆/n-C₄H₁₀(1/1 (v/v)) (c); C₄H₆/iso-C₄H₁₀(1/1 (v/v)) (d) at 298 K, respectively.

To explore the actual separation performance, dynamic fixed-bed column breakthrough experiments were conducted by using binary gas mixtures of C₄H₆/n-C₄H₈(1:1 v/v), C₄H₆/iso-C₄H₈(1:1 v/v), C₄H₆/n-C₄H₁₀(1:1 v/v) and C₄H₆/iso-C₄H₁₀(1:1 v/v) at 298 K, respectively. As shown in Figure 5(a-d), the n-C₄H₈, iso-C₄H₈, n-C₄H₁₀ and iso-C₄H₁₀ all begin to break through the bed gradually as soon as the feeding of target gas mixture, meanwhile, C₄H₆ keeps continuous adsorption with breakthrough retention times of 167.1 s, 171.8 s, 175.7 s, 177.4 s, respectively, which attributes to its super sensitive gate-opening effect on C₄H₆ and unrecognized responses for n-C₄H₈, iso-C₄H₈, n-C₄H₁₀ and iso-C₄H₁₀. In consequence, the excellent dynamic separation performance toward C₄H₆ for all the binary C₄H₆/n-C₄H₈, C₄H₆/iso-C₄H₈, C₄H₆/n-C₄H₁₀ and C₄H₆/iso-C₄H₁₀ gas mixtures furtherly verifies that this MOF is a very promising soft MOF adsorbent for C₄H₆ purification.

Figure 6. a) PXRD patterns of Mn-bpdc MOF after different treatments by immersing in water (RT) for 60 days, boiled water (100°C) for 24 hours and air for 60 days, respectively; b) Adsorption isotherms of single component C₄H₆ at 298 K for Mn-bpdc samples after different treatments; c) Adsorption isotherms of single component C₄H₆ for 10 cycles at 298 K. Adsorption and desorption profiles are shown in closed and open symbols, respectively; d) Cycling breakthrough tests for C₄H₆/n-C₄H₈(1/1 (v/v)) separation with Mn-bpdc MOF at 298 K for five times. The column was reactivated with a helium flow at 100 after each breakthrough test.
The excellent stability and regeneration of absorbents are prerequisites for the practical applications in the adsorptive separation of C₄H₆ from C₄ hydrocarbons. In order to examine the water stability of Mn-bpdc MOF, we carried out stability tests of Mn-bpdc at water (RT) for 60 days, air for 60 days and boiled water (100 °C) for 24 h. As shown in Figure 6a, the PXRD patterns verifies that the framework of Mn-bpdc MOF can well maintain even in those harsh conditions. Furthermore, the C₄H₆ sorption isotherms of Mn-bpdc MOF after different stability tests are shown in Figure 6b. The almost identical adsorption isotherms with original simple demonstrate that it can still preserve its intact structure without phase transition and framework collapse after stability treatments. In addition, thermogravimetric analysis (TGA) was performed on the Mn-bpdc MOF to survey its thermal stability. As shown in Figure S3, Mn-bpdc MOF can undergo a sustaining 4% loss of weight up to 360 °C, which dues to the loss of all free molecules. Then, the weight remains constant until the framework begins to collapse at 480 °C. The excellent water and thermal stability of Mn-bpdc MOF can be attributed to the strong coordinate bonds with high coordination numbers formed between central hard acids (Mn²⁺) and connected four hard bases (CH₃COO⁻) and two hard-medial bases (C₅H₅N). The regeneration ability of Mn-bpdc MOF was firstly evaluated by cycling single component adsorption of C₄H₆ at 298 K for ten times. As shown in Figure 6c, all the adsorption curves at each cycle are almost consistent and the uptake capacities do not have any loss. Notably, the sample only needs regenerate by vacuum treatment at room temperature instead of degassing by high temperature before each cycle. Furtherly, the PXRD pattern of Mn-bpdc MOF after ten times cycles was measured (Figure S7), which is consistent with activated MOF. In addition, the recycling breakthrough test of Mn-bpdc for C₄H₆/n-C₄H₄ separation is shown in Figure 6d and the breakthrough times for C₄H₆ remain nearly unchanged after five cycles. Those results comprehensively reveal that the integrality of frameworks can be retained after repeated uses and the Mn-bpdc MOF possesses outstanding recyclability for C₄H₆ adsorption and separation. Importantly, it is a scarce report that confirms Mn-bpdc can be well recycled many times by easily regenerating under vacuum with room temperature and the cost of regeneration will be relatively low. Hence, the excellent water-stability and cycling tests furtherly manifest that it is a great valuable adsorbent for industrial C₄H₆ purification.

Conclusions

In this work, we have employed a flexible Mn-bpdc MOF featuring distinct gate-opening and reversible switch behavior for C₄H₆ purification. The intrinsic flexibility is confirmed by VT-XRD with gradient temperature control. In addition, the different polarity guest-depended molecule can lead to structure transformation with different gate-opening pressure points at different temperatures, such as C₂H₄ and C₃H₆. Importantly, it exhibits prominent gate-opening and abrupt adsorption for C₄H₆ at very low pressure (0.13 bar) but no stimulus-response behavior for all n-C₄H₈, iso-C₄H₈, n-C₅H₁₀ and iso-C₅H₁₀ even at 1 bar and ambient conditions. Notably, the uptake selectivities of Mn-bpdc MOF for both C₄H₆/n-C₄H₈ and C₄H₆/iso-C₄H₈ surpass the reported adsorbents. Furtherly, four dynamic breakthrough experiment results of C₄H₆/n-C₄H₈, C₄H₆/iso-C₄H₈, C₅H₁₀/n-C₅H₁₀ and C₅H₁₀/iso-C₅H₁₀ mixtures verifies that this Mn-bpdc MOF can practically separate C₄H₆ from other C₄paraffins and mono-olefins. In addition, the unexpected water stability, benign regeneration ability, signifies that this MOF has great potentiality for industrial C₄H₆ purification and makes it a new benchmark of flexible adsorbent for the separation of C₄H₆ over other C₄ hydrocarbons.

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References


