Quasi-Orthogonal Configuration of Propylene within a Scalable Metal-Organic Framework Enables Its Purification from Quinary Propane Dehydrogenation Byproducts


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Quasi-Orthogonal Configuration of Propylene within a Scalable Metal–Organic Framework Enables Its Purification from Quinary Propane Dehydrogenation Byproducts

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ABSTRACT: Propylene production via nonoxidative propane dehydrogenation (PDH) holds great promise in meeting growing global demand for propylene. Effective adsorptive purification of a low concentration of propylene from quinary PDH byproducts comprising methane (CH₄), ethylene (C₂H₄), ethane (C₂H₆), propylene (C₃H₆), and propane (C₃H₈) has been an unsolved academic bottleneck. Herein, we now report an ultramicroporous zinc metal–organic framework (Zn-MOF, termed as 1) underlining a rigid one-dimensional channel, enabling trace C₃H₆ capture and effective separation from quinary PDH byproducts. Adsorption isotherms of 1 suggest a record-high C₃H₆ uptake of 34.0/92.4 cm³ cm⁻³ (0.01/0.1 bar) at 298 K. In situ spectroscopies, crystallographic experiments, and modeling have jointly elucidated that the outstanding propylene uptakes at lower pressure are dominated by multiple binding interactions and swift diffusion behavior, yielding quasi-orthogonal configuration of propylene in adaptive channels. Breakthrough tests demonstrate that 30.8 L of propylene with a serviceable purity of 95.0–99.4% can be accomplished from equimolar C₃H₆/C₃H₈ mixtures for 1 kg of activated 1. Such an excellent property is also validated by the breakthrough tests of quinary mixtures containing CH₄/C₂H₆/C₂H₄/C₃H₆/C₃H₈ (3/5/6/42/44, v/v/v/v/v). Particularly, structurally stable 1 can be easily synthesized on the kilogram scale using cheap materials (only $167 per for kilogram of 1), which is important in industrial applications.

1. INTRODUCTION

Propylene (C₃H₆), as one of the most important chemical products, is widely used in the production of various chemicals, including polymers (e.g., polypropylene) and oxygenates (e.g., acetone and propylene oxide) etc.,¹,² and is expected to grow above 130 million metric tons by 2023.³ In the petrochemical industry, nonoxidative propane dehydrogenation (PDH) is becoming popular and is regarded as a promising way to meet the ever-increasing demand for propylene across the globe.⁴ The resultant byproducts in PDH reactions including methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄), and propane (C₃H₈) impurities doubtlessly reduce the purity and productivity of C₃H₆. Effective C₃H₆ separation from binary C₂H₆/C₃H₈ mixtures (only 0.04 nm in kinetic diameter, Table S1) and even quinary mixtures in PDH byproducts (typically consisting of ca. 1–3% CH₄, 0.5–6% C₂H₆, 0.2–5% C₂H₄, 40–45% C₃H₆, and 42–50% C₃H₈) is a prerequisite for improving the quality of propylene. The separation technologies currently used are based on energy- and capital-intensive distillation operation, certainly contributing to larger energy loss and economic costs. Adsorbent-based separation strategies could theoretically alleviate the above-mentioned energy consumption without a phase change, namely, distinguishing the gas molecules only through molecule size, shape, polarity, and other characteristics.⁵

Metal–organic frameworks (MOFs), as well-known porous adsorbents, have been extensively explored for gas separation due to their adjustable pore chemistry and structural diversity etc.⁶–⁹ In terms of separation mechanisms, it can be roughly divided into thermodynamic separation and nonequilibrium separation. Compared with unilateral thermodynamic equilibrium dominated by binding affinities, the strategies that rely on nonequilibrium separation (including sieving separation and kinetic-driven separation) can be more energy-efficient and realistic given the fact that industrial pressure swing adsorption (PSA), vacuum swing adsorption (VSA), and temperature swing adsorption (TSA) processes are actually operating under nonequilibrium operating conditions. For example, Chen et al.¹⁰ covered the Co-gallate for sieving...
separation of C\(_6\)/C\(_8\) mixtures, which suggested a notable adsorption capacity of 66.6 cm\(^3\) cm\(^{-3}\) at 1 bar and 298 K. Breakthrough tests revealed the high purity of propylene (97.7%) with a high dynamic separation productivity of 36.4 cm\(^3\) cm\(^{-3}\) under ambient conditions. Another praiseworthy sieving stage, JNU-3a, designed by Li et al.,\(^\text{11}\) featured one-dimensional channels with embedded molecular pockets and realized the sieving separation of binary C\(_6\)/C\(_8\) mixtures, yielding high-purity C\(_6\) (\(\geq 99.5\%\)) and a C\(_6\) productivity of 53.5 L kg\(^{-1}\). Unfortunately, strong sieving restriction in the pore channels might cause some unavoidable issues associated with the diffusion behavior and regeneration process. From the perspective of structural flexibility, most linkers are flexible in nature; accurately controlling pore size within a critical range to fully sieve C\(_6\) from C\(_6\)/C\(_8\) mixtures is still in its infancy. Conversely, the kinetic effects, a significative diffusion-driven mechanism in the nonequilibrium process, could be dexterously designed to effectively accomplish the nonequilibrium separation. Li et al.,\(^\text{12}\) prepared a MOF (termed as ELM-12), showing an enhanced C\(_6\) uptake of 62.0 mg g\(^{-1}\) at 298 K and 1 bar and higher kinetic C\(_6\)/C\(_8\) selectivity (204 at 298 K and 971 at 308 K). Breakthrough tests also confirmed the separation performance for binary mixtures, yielding a C\(_6\) productivity of 457 mmol per liter. Also, the Li and Eddaoudi groups developed several MOFs having good kinetic selectivity that could be used for binary C\(_6\)/C\(_8\) separation.\(^\text{13,14}\) Of particular note is that, albeit conspicuous achievements have been achieved for kinetic separation of C\(_6\)/C\(_8\) mixtures, these studies have only focused on binary mixtures. Synergistic kinetic-driven separation of C\(_6\) from quinary mixtures, especially from PDH byproducts containing CH\(_3\)OH, C\(_2\)H\(_5\)OH, C\(_3\)H\(_8\), and C\(_4\)H\(_{10}\) impurities, has not been realized yet. Another crucial but easily overlooked fact is that the partial pressure of propylene is usually low (<300 mbar) in quinary mixtures,\(^\text{15}\) which undoubtedly poses a serious challenge for trace C\(_6\) capture and C\(_8\) purification at a low partial pressure (Scheme 1).

Given the concerns mentioned above, we now report the first paradigm of using an ultramicroporous zinc metal–organic framework (Zn-MOF, termed as 1) with rigid one-dimensional channels and decent pore chemistry for trace C\(_6\) capture and its purification from quinary PDH byproducts containing CH\(_3\)OH, C\(_2\)H\(_5\)OH, C\(_3\)H\(_8\), C\(_4\)H\(_{10}\), and C\(_6\)H\(_8\) mixtures. Static adsorption isotherms suggest that 1 possesses the record-high C\(_6\) uptake of 92.4 cm\(^3\) cm\(^{-3}\) at 298 K and 0.1 atm, indicating a great potential for C\(_6\) capture at lower partial pressure. Further, comprehensive analysis including in situ spectroscopies, crystallographic experiments, and modeling analysis have cooperatively demonstrated that the decent pore microenvironment and multiple task-specific groups enabled synergistic equilibrium effects and “sweet spots” of kinetics for trapping C\(_6\) effectively boosting C\(_6\) separation. In particular, two C\(_6\) molecules adsorbed in one unit cell exhibit an unusual quasi-orthorhombic configuration, which favors the intramolecular interaction and multiple binding models with pore pockets. Breakthrough tests demonstrate that 1 is capable of separating high-purity C\(_6\) (95.0—99.4%) from an equimolar C\(_6\)/C\(_8\) mixture under ambient conditions, giving a maximum C\(_6\) productivity of 30.8 L for 1 kg of activated 1 under ambient conditions. The excellent separation property of C\(_6\) on 1 is also validated by the experimental and simulated breakthrough tests of quinary PDH byproducts containing CH\(_3\)OH, C\(_2\)H\(_5\)OH, C\(_3\)H\(_8\), C\(_4\)H\(_{10}\), and C\(_6\)H\(_8\) (3/5/6/42/44, v/v/v/v/v) mixtures, suggesting that 1 could inherit the preferable separation performance for trapping C\(_6\) from PDH byproducts. Notably, 1 possesses good structural stability and can be easily synthesized on the kilogram scale using cheap raw materials (only $167 for per kilogram of 1), awarding 1 the potential benchmark stage to purify C\(_6\) from multiple components.

2. EXPERIMENTAL SECTION

2.1. Materials. All reagents and solvents were purchased commercially and used without further processing. Zinc oxide and 1,2,4-triazole were purchased from Macklin, Shanghai, China. Ethanol (C\(_2\)H\(_5\)OH, 99.5%) and methanol (CH\(_3\)OH, 99.5%) were purchased from Aladdin Industrial Co., Ltd., Shanghai, China.

2.2. Scalable Synthesis of Robust Zn-MOF (1). 1 was prepared according to the following method with some modifications.\(^\text{16}\) In detail, zinc oxide and 1,2,4-triazole were mixed at the molar ratio of 1:2.3, then added into aqueous solution containing methanol/ethanol and ultrasonic stirring.
Figure 1. (a) ORTEP plot of the single-crystal X-ray structure of the 1 model with probability ellipsoids drawn at 80%. (b) 3D crystal structure of 1 along the a axis. (c) View orthogonal to b showing the pillaring of the zinc triazolate layers by oxalate anions (the different nets are highlighted in blue, pink, bright blue, and gray-40% for clarity (code mode: C in ligands, gray-40%; Zn, bright blue; O, pink). (d) Accessible Connolly surface representation of one-dimensional pore geometry along the a axis, with an aperture size of 4.27 × 4.60 Å² (excluding van der Waals radii). (e) Diagram of diffusion channels for various guests and (f) the Hirshfeld surface (de) displaying the favorable electrostatic potential for C\(_2\)H\(_6\) capture from PDH byproducts containing CH\(_3\)C\(_2\)H\(_6\), C\(_3\)H\(_6\), C\(_3\)H\(_8\), and C\(_3\)H\(_6\) mixtures, of which C\(_3\)H\(_6\) was drawn in pink and other guests were drawn in green for clarity.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis of Robust 1. In the case of single unit cell, the Zn center was five-coordinated with a distorted trigonal bipyramidal geometry (Figure 1a). In detail, the nitrogen atoms located in the 1,2-positions of the triazolate coordinated with Zn dimers and further connected to the next dimer via the nitrogen atom in the 4-position of the triazolate, as a result, forming into two-dimensional (2D) lattice planes. Interestingly, the layers of 1,2,4-triazolate-bridged zinc(II) were further pillared by oxalate species to construct the three-dimensional (3D) lattice and 3D pore geometry (Figure 1b,c; a detailed list of atomic positions for the Zn-MOF model are available in Table S2). The crystalline phase and purity of as-prepared bulk 1 was verified by combing the comparisons of theoretical and experimental PXRD diffractions. As clearly shown in Figure S1, all of the experimentally measured characteristic peaks agreed well with the simulated data and crystallized in the P2\(_{1}/c\) space group, indicating the isostructural topological structure of 1. Further, the cell volumes derived from refinement analysis between experimental 1 and the theoretical model gave a ΔV/V of 0.005% (Table S3), being much lower than that of reported rigid MOF-5 (0.8%).\(^{17}\) The quas-unchanged cell volume shrinkage revealed the excellent skeleton rigidity of 1, although indirectly. In order to confirm the structural rigidity under variable-temperature conditions, we conducted PXRD tests at 298 and 373 K to investigate the evolution of the unit cell. As shown in Figure S2a,b, it is suggested that there are no apparent shifts in the positions of all peaks for 1, revealing a higher framework lattice rigidity and structure stability without phase changes observed. In addition, the cell volumes of 1 at 298 (Figure S2a) and 373 K (Figure S2b) afforded a ΔV/V of 0.02% (Table S3). Intuitively, the cell structures of 1 underwent quasi-unchanged conformation deformations (Figure S2c,d) compared with that of theoretical topology, suggesting a credible structure stability. The excellent structure stability was
also demonstrated by TGA analysis (Figure S3), yielding a higher decomposition temperature exceeding 600 K.

Intuitive visualization of pore conformation, the simulated Connolly pore surface exhibited a zigzag shaped one-dimensional pore geometry along the crystallographic a axis, with a cross-sectional size of ca. 4.27 × 4.60 Å² (Figure 1d,e; excluding the distances of the van der Waals radii), which would be favorable for distinguishing the gas diffusion behaviors. Especially for C₃H₈ and C₄H₁₀ guests with highly similar molecular attributes, the decent pore window seemed to be unfulfillable for both C₃H₈ (with the kinetic diameter of 5.1 Å) and C₄H₁₀ (4.7 Å) to diffusion into the pore channels from the kinetic diameter point of view. Nevertheless, the suitable pore space and the van der Waals molecular dimension differentiation could be expected to realize the separation of C₃H₈ (4.20 × 4.80 × 6.80 Å³) and C₄H₁₀ (4.16 × 4.65 × 6.45 Å³; Table S1). Thus, the propylene molecule with a minimum cross-section size of 4.16 × 4.65 Å² or 19.34 Å² could theoretically diffuse into the channel of I with a contended cross-section size (4.27 × 4.60 Å² or 19.64 Å²), while propane with a minimum cross-section size of 4.20 × 4.80 Å² or 20.16 Å² would be excluded from the pore channels due to the limited cross-section size of I. Note that this slight shape sieving may not achieve an ideal sieving effect, but it is important to influence the diffusion behavior of molecules. A deep insight into the Hirshfeld surface (Figure 1f) is that it can be observed that a highly attractive negative electrostatic potential mapped with −0.05 au (red) was clearly distributed in the pore channel, suggesting the enriched pore polarity, which favored the binding interaction with the molecule that had a larger dipole moment.¹⁸,¹⁹ In brief, due to decent molecule dimensions and the large dipole moment of C₃H₈, it is expected to form strong interactions with the polar pore surface and will effortlessly diffuse into the adaptive pore channel.

3.2. Isothermal Adsorption and Selectivity Analysis.

The eternal pore attributes of I were determined at 77 K through using N₂ as the probe molecule. As clearly seen in Figure 2a, I exhibited a representative I-type profile, yielding a N₂ capacity of 127.4 cm³ g⁻¹ at 1 atm. The Brunauer–Emmett–Teller (BET) surface area and pore volume were evaluated to be 526.1 m² g⁻¹ and 0.35 cm³ g⁻¹ by adopting the ASAP 2020 physisorption analyzer, being nearly identical to the theoretical values of 510.8 m² g⁻¹ and 0.29 cm³ g⁻¹ (calculated from the optimized crystal structure). The pore size distribution (PSD) according to the Horvath–Kawazoe model revealed the ultramicropore with a peak centered at ca. 4.62 Å (inset in Figure 2a). The permanent ultraporosity and the decent pore dimensions motivated us to explore the potential adsorption performance of propane dehydrogenation byproducts including CH₄, C₂H₂, C₂H₆, C₃H₆, and C₄H₁₀ on activated I. We collected the single-component adsorption isotherms of various guests on I at 298 K up to 1 atm. Here, volumetric uptake is adopted to evaluate the adsorption performance of the adsorbents in industry as that would determine the footprint of the gas separation units.²⁰ As clearly depicted in Figure 2b, I exhibited a distinguished C₃H₆ adsorption steepness at lower concentrations of 0.01–0.1 bar, giving the ultrahigh volumetric C₃H₆ uptakes of 34.0/92.4 cm³ cm⁻³ (0.01/0.1 bar) at 298 K, as revealed by the steepness of the C₃H₆ adsorption isotherms. Conversely, it indicated eclipsed adsorption capacity for other guest molecules under identical conditions (Figure 2b). Further increasing pressure to 1 bar, I suggested quasi-saturated capacity of 97.4 cm³ cm⁻³, corresponding to 9.4 wt % or 1.94 C₃H₆ molecule per cell unit. In addition, the differences of statical adsorption capacity (denoted as ΔQ) for C₂H₂ and C₂H₆ at a lower pressure of 0.01/0.1 bar afforded ΔQ₁ and ΔQ₂ values of 20.2 and 32.0 cm³ cm⁻³ at 298 K (Figure 2b), confirming the preference for trapping trace C₂H₂ under lower partial pressure. Such differences could be visually observed at 273 K (Figure 2c).
Figure 3. (a) Density distribution of C\textsubscript{3}H\textsubscript{6} molecules within 1 topology obtained from GCMC simulations. (b) Side views of the packing diagram of the C\textsubscript{3}H\textsubscript{6} adsorbed in the framework of 1. (c) Visualized planes of guest molecule yielded from 1 (1 and 2, marked with red color) and created by three C atoms on a molecule (the atoms in guest molecules are highlighted with orange and other atoms in MOF structure are highlighted with light turquoise for clarity). (d) DFT calculated adsorption conformation of C\textsubscript{3}H\textsubscript{6}-loaded 1 in site I and (e) DFT calculated adsorption conformation of C\textsubscript{3}H\textsubscript{6}-loaded 1 in site II (note that the binding types are colored in gray, red, and turquoise, corresponding to van der Waals interaction, hydrogen-bonding, and intramolecular forces; color modes: H in ligands, white; H in guest molecule, light blue; Zn, bright green; O, pink; N, blue; C, sea green). (f) Hirshfeld surface (de) displaying host–guest interactions of C\textsubscript{3}H\textsubscript{6}-loaded 1 in site I.

Apparantly, 1 revealed the enhanced C\textsubscript{3}H\textsubscript{6} uptake, with values of 45.3/125.4/133.4 cm\textsuperscript{3} cm\textsuperscript{-3} (0.01/0.1/1 bar), and the \Delta Q values between C\textsubscript{3}H\textsubscript{6} and C\textsubscript{4}H\textsubscript{8} were up to 28.4/49.2/40.0 cm\textsuperscript{3} cm\textsuperscript{-3} for 0.01/0.1/1 bar, respectively. In addition, according to the saturated C\textsubscript{3}H\textsubscript{6} capacity, the density of gaseous C\textsubscript{3}H\textsubscript{6} in 1 was determined to be 281.3 g L\textsuperscript{-1} at 298 K and 0.1 bar. To our knowledge, the storage density of confined C\textsubscript{3}H\textsubscript{6} in the channel far surpassed that of other benchmark materials including Zn\textsubscript{2}(5-aip)\textsubscript{2}(bpy) (135.9 g L\textsuperscript{-1}),\textsuperscript{20} SIFSIX-2-Cu-i (135.5 g L\textsuperscript{-1}),\textsuperscript{22} and CPL-1 (43.7 g L\textsuperscript{-1})\textsuperscript{25} etc. Such a higher storage density of C\textsubscript{3}H\textsubscript{6} at 0.1 atm was more than 164-fold higher than that of gaseous C\textsubscript{3}H\textsubscript{6} (1.707 g L\textsuperscript{-1}) under similar conditions, suggesting that cooperative stacking models or intramolecular binding affinities may be responsible for C\textsubscript{3}H\textsubscript{6} capture under lower pressure. Such an unusual adsorption configuration for trace C\textsubscript{3}H\textsubscript{6} capture on 1 was mainly attributed to the larger polarizability/dipole moment of C\textsubscript{3}H\textsubscript{6} (Table S1), which exerted a crucial effect on the purification of propylene at lower concentrations, especially for propane cracking-gas mixtures containing multiple components.

In order to further highlight the advantages of 1 at low pressure, detailed comparisons with other advanced materials were integrated at 298 K and 0.1 bar. Results evidenced that 1 remained the record-high volumetric capacity of C\textsubscript{3}H\textsubscript{6} (92.4 cm\textsuperscript{3} cm\textsuperscript{-3}), surpassing that of most state-of-the-art competitors, including the newly reported MOF platforms ZU-36-Co (41.4 cm\textsuperscript{3} cm\textsuperscript{-3}),\textsuperscript{24} Zn\textsubscript{2}(5-aip)\textsubscript{2}(bpy) (36.2 cm\textsuperscript{3} cm\textsuperscript{-3}),\textsuperscript{25} and JNU-3a (14.4 cm\textsuperscript{3} cm\textsuperscript{-3}),\textsuperscript{26} etc. (Figure 2d). To quantitatively evaluate the separation potential of 1 for binary C\textsubscript{3}H\textsubscript{6}/C\textsubscript{4}H\textsubscript{8} mixtures, the ideal adsorbed solution theory (IAST) selectivity was evaluated using the double site Langmuir–Freundlich (DSLF) model (Figure S4a,b and Table S5).\textsuperscript{20,27} Obviously, 1 indicated a remarkable C\textsubscript{3}H\textsubscript{6}/C\textsubscript{4}H\textsubscript{8} IAST selectivity, with a value of 63 at 0.1 bar (Table S4), far ascendant to many C\textsubscript{3}H\textsubscript{6} selective prototypes covered, including MAF-23-O (8.9),\textsuperscript{28} Zn\textsubscript{2}(5-aip)\textsubscript{2}(bpy) (14.2),\textsuperscript{21} and MIL-100(Fe) (3.8).\textsuperscript{29} In addition, the comprehensive comparisons between C\textsubscript{3}H\textsubscript{6} uptake and the selectivity of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{4}H\textsubscript{8} at 0.1 bar suggested that 1 ranked in the “ceiling” level (Figure 2e), uncovering that 1 can effectively overcome the obstacles in balancing insurmountable “trade-off” effects. The unwonted breakthrough in trapping trace C\textsubscript{3}H\textsubscript{6} is of the utmost importance, especially from multiple components with lower partial pressures of propylene. Note that IAST methods are often subject to uncertainties and limited requirements, and large errors can arise from narrow pores (nonideal gas solution), framework flexibility, a large binding difference, etc. So, the IAST selectivites were calculated here just for qualitative comparison.\textsuperscript{20} The coverage-dependent isosteric adsorption heats (Q\textsubscript{s}) were calculated using the virial method (Figure 2f and Table S6) to explore the interaction energies between various molecules and the host framework. Apparently, the Q\textsubscript{s} of 1 at zero coverage followed the hierarchy of C\textsubscript{3}H\textsubscript{6} (38.3 kJ mol\textsuperscript{-1}) > C\textsubscript{4}H\textsubscript{8} (28.9 kJ mol\textsuperscript{-1}) > C\textsubscript{2}H\textsubscript{4} (22.4 kJ mol\textsuperscript{-1}) > C\textsubscript{3}H\textsubscript{4} (20.7 kJ mol\textsuperscript{-1}) > CH\textsubscript{4} (8.2 kJ mol\textsuperscript{-1}) (Figure 2f), conferring 1 with the obvious potential stage to capture C\textsubscript{3}H\textsubscript{6} from propane dehydrogenation byproducts. To be noted, the Q\textsubscript{s} of C\textsubscript{3}H\textsubscript{6} at zero coverage was much lower than that of known Zn\textsubscript{2}(5-aip)\textsubscript{2}(bpy) (46 kJ mol\textsuperscript{-1})\textsuperscript{21} and MAF-23-O (54 kJ mol\textsuperscript{-1}),\textsuperscript{28} being comparable to SIFSIX-2-Cu-i (35.8 kJ mol\textsuperscript{-1})\textsuperscript{22} and ZU-36-Co (38.0 kJ mol\textsuperscript{-1}).\textsuperscript{31} The desorption activation energy of C\textsubscript{3}H\textsubscript{6} obtained from the TPD profiles was calculated to be 41.5 kJ mol\textsuperscript{-1} (Figure S5a,b), also evidently confirming the strong binding affinity between C\textsubscript{3}H\textsubscript{6} and the framework. Such a low adsorption enthalpy not only awarded the 1 platform a lower regeneration energy to yield higher C\textsubscript{3}H\textsubscript{6} productivity but also avoided C\textsubscript{3}H\textsubscript{6} oligomerization/polymerization that may damage the binding sites.

3.3. Adsorption Conformation and Binding Mechanism. To deeply elucidate the binding sites, we adopted Grand Canonical Monte Carlo (GCMC) simulations to investigate the binding models and adsorption mechanism between guest molecules and 1. As obviously observed, the simulated adsorption isotherms on 1 agreed well with the experimental
results on the overall trend at 298 K, although some points at ultralow pressure and higher pressure were not particularly intimate (Figure S6). The inconsistent paces may derive from the strong binding affinity between guest molecules and the framework, which were intractable to construct the topology models using simple force fields. Additionally, the visualized density distribution contours of C\textsubscript{3}H\textsubscript{6}-loaded 1 (Figure 3a) suggested that the adsorbed C\textsubscript{3}H\textsubscript{6} was concentrated and arranged in the pore space one by one in a straight line along the zigzag shaped open channels. The optimized C\textsubscript{3}H\textsubscript{6} configurations obtained from GCMC-simulated saturated capacity also indicated 2-fold disordering over two binding sites (detailed adsorption configurations are available in Figure S9a,b). The theoretical binding energies between the host and guest showed an expected Q\textsubscript{st} order of C\textsubscript{3}H\textsubscript{6} (1 (38.9 kJ mol\textsuperscript{-1}) > C\textsubscript{3}H\textsubscript{6} (1 (26.4 kJ mol\textsuperscript{-1})), which was consistent with that obtained from experimental results (38.3 kJ mol\textsuperscript{-1} for C\textsubscript{3}H\textsubscript{6} and 28.9 kJ mol\textsuperscript{-1} for C\textsubscript{3}H\textsubscript{6} Figure 2f). Notably, the binding interactions between the gas molecules and framework were modest (van der Waals interaction, hydrogen bonding, and electrostatic interaction in nature), indicating that enriched C\textsubscript{3}H\textsubscript{6} can then be recovered with high purity during the regeneration step.

To further elucidate the unwanted geometrical conformation and adsorption mechanism of C\textsubscript{3}H\textsubscript{6} in the I skeleton, an in situ PXRD test and Rietveld structural refinements of C\textsubscript{3}H\textsubscript{6}-loaded 1 were carefully analyzed. As shown in Figure S10a, the refined lattice parameters (a = 8.9427 Å, b = 9.7210 Å, c = 9.5827 Å) of C\textsubscript{3}H\textsubscript{6}-loaded 1 seemed to be somewhat larger than that of pristine 1 (a = 8.9139 Å, b = 9.6932 Å, c = 9.4836 Å; Table S3), attributed to C\textsubscript{3}H\textsubscript{6} occupation in the unit cell of 1. An intuitional binding scenario (Figure S10b,c) yielded from structural refinements demonstrated that the geometry configurations derived from in situ crystallographic experiments were quasi-consistent with those calculated by theoretical DFT calculations (Figure 3d,e). By comparing the binding distances of the same binding types obtained from experimental and theoretical results, the low relative errors are between 0.0 and 3.1% (Table S8). Such lower relative errors further reveal that the adsorption conformation yielded from crystallographic tests were convincing. In addition, the geometrical planes of two C\textsubscript{3}H\textsubscript{6} molecules also exhibited an approximate orthogonal adsorption configuration from a static view, with a dihedral angle of ca. 93.1° (Figure S10d), being consistent with that obtained from theoretical values.

Further, in situ Fourier transform infrared (FT-IR) tests were recorded to reveal the potential host–guest interaction between C\textsubscript{3}H\textsubscript{6} and 1. As clearly shown in Figure S11a, the peaks located in 1630, 1320, and 1171 cm\textsuperscript{-1} in both activated 1 and C\textsubscript{3}H\textsubscript{6}-loaded 1 were assigned to the C≡N adsorption band, symmetric carbonyl stretching, and C–O stretching vibrations in 1 structure.\textsuperscript{32–34} While for C\textsubscript{3}H\textsubscript{6}-loaded 1, some characteristic peaks associated with the propylene molecule were clearly observed. For example, the emerging peaks located at about 2924 and 1436 cm\textsuperscript{-1} could be attributed to symmetric C–H bending of terminal methyl and methylene motifs in propylene.\textsuperscript{35,36} Also, the peak at around 996 cm\textsuperscript{-1} was the C–C stretching mode in propylene.\textsuperscript{37} Such spectral changes evidently confirmed the fact that propylene molecules could be adsorbed in the 1 structure. We investigated in situ Raman spectra of C\textsubscript{3}H\textsubscript{6}-loaded 1 to carefully analyze the host–guest interaction. As explicated in Figure S11b, the peak concentrated at 3147 cm\textsuperscript{-1} was the stretching mode of the C–H bond in the triazole ring of the 1 structure,\textsuperscript{32,33} and the other Raman vibration of the triazole ring (i.e., heterocyclic methyl C–H bending) could be observed at 1477 cm\textsuperscript{-1}.\textsuperscript{34} In addition, it was also found that there was an emerging peak that appeared at 1624 cm\textsuperscript{-1}, corresponding to the C≡C stretching vibrations in the propylene molecule. This value was downsifted in
comparison with that for gaseous propylene, which was 1640 cm$^{-1}$, mainly ascribed to the formed binding interaction between propylene and the framework, as demonstrated by Yaghi. The negative shift to lower frequency could also be visualized for the Zn$-$N peak (Figure S11b). Obviously, the Zn$-$N peak of I also experienced a downshift behavior upon propylene adsorption on I, suggestive of potential adsorption sites between propylene and I.

In addition, Hirshfeld surface analysis was used for probing the host–guest interactions and quantifying the binding interaction types. Hirshfeld surface was a novel partitioning of crystal space, affording a unique 3D $d_{norm}$ surface which could further be resolved into a 2D fingerprint plot. As shown in Figure 3f, it revealed the Hirshfeld surfaces of adsorbed C$_3$H$_8$ in site I mapped over $d_{norm}$, where the larger red spots in the map indicated strong short-range interactions with close contact effects (i.e., hydrogen-bonding) and a negative $d_{norm}$ value. White spots corresponded to contacts around the van der Waals separation and with a $d_{norm}$ value of zero, and blue spots reflected the long-range binding contact with a positive $d_{norm}$ value. Clearly, for C$_3$H$_8$-loaded I at site I, hydrogen-bonding interactions (red spots) and van der Waals effects (white spots) reflected in the map (Figure 3f) were basically consistent with the results obtained by DFT calculations (Figure 3d). Further, the binding types could be quantified by plotting two-dimensional (2D) fingerprint plots. Results showed that van der Waals interaction occupied 48.6% of the total Hirshfeld surface, while hydrogen bonding and intramolecular interaction occupied 33.0 and 18.4%, albeit not being particularly precise. Such consistence also could be found for the C$_3$H$_8$ molecule adsorbed at site II (Figure S12).

**3.4. Molecular Dynamics and Diffusion Analysis.** Diffusion-driven adsorption behavior, a realistic and signifivative separation metric in industrial PSA, VSA, and TSA-based nonequilibrium working conditions, needed to be given enough attention. We hereby adopted a molecular dynamics (MD) method to probe the diffusion behavior of guest molecules in channels. During the simulations, the initial configurations for the MD simulations were produced by GCMC simulation; the host framework and the gas molecule were both regarded as rigid. As shown in Figure S13 and Table S9, MD-derived diffusion coefficients of CH$_4$/C$_3$H$_8$/C$_2$H$_6$/$C_6$H$_6$/C$_3$H$_8$ for I were calculated as 0.217/0.717/0.517/13.3/258 $\times 10^{-11}$ m$^2$ s$^{-1}$. Therefore, the obtained diffusion coefficient of C$_3$H$_8$ (258 $\times 10^{-11}$ m$^2$ s$^{-1}$) on I was much higher than that of the covered UiO-66 analogue (97.8 $\times 10^{-12}$ m$^2$ s$^{-1}$) and MAF-23-O (0.82 $\times 10^{-16}$ m$^2$ s$^{-1}$), confirming the fast diffusion rate. The obtained diffusion selectivity of C$_3$H$_8$/C$_2$H$_6$ was calculated to be 19.4, which was eclipsed compared with that of MAF-23-O (112.3). Intuional snapshots of the MD results with both the host and guests as rigid suggested that two C$_3$H$_8$ molecules can be adaptively located in the confined channel of I after being steadily confined in the pore pocket (Figure S14b), yet that in I seemed to be escaping from the host when entering the aperture of the host framework (Figure S14a). Such transient diffusion trajectories further confirmed the favorable diffusion intensity for trapping C$_3$H$_8$ molecule.

**3.5. Dynamic Column Breakthrough Experiments.** To further explore separation natures of propylene on I from imitated propane dehydrogenation byproducts, transient breakthrough simulations were first probed for C$_3$H$_8$/C$_3$H$_6$/He (30/30/40, v/v/v) mixtures in a column adsorption–desorption cycle. Simulation results suggested that C$_3$H$_8$/C$_3$H$_6$ mixtures with distinct breakthrough time could be effectively separated (Figure 4a), yielding a higher C$_3$H$_8$ capture capacity of 51.5 L kg$^{-1}$. These excellent breakthrough results from simulation motivated us to evaluate the separation performance of I in the actual separation process. As shown in Figure 4b, C$_3$H$_8$ first broke through the adsorption bed, while targeted C$_3$H$_6$ was still captured over a flow gas volume of 100 mL. To be noted, the simulated breakthroughs are sharper than those observed experimentally, mainly attributed to the fact that, in the simulations, intracrystalline diffusional influences...
confirmed that 1 could effectively purify C₃H₆ from initiative propane dehydrogenation byproducts.

3.6. Structural Stability Tests and Costs Evaluation. It is well perceived that structural stability is the first and necessary prerequisite for MOFs to develop from laboratory research to the pilot scale and industry applications. We herein carried out multifaceted investigations on 1, which had experienced cycling breakthrough experiments, including N₂ adsorption, single-gas adsorption, and crystallographic tests under variable-temperature conditions etc., to systematically analyze the structural stability of 1. We first probed the pore geometry changes through N₂ adsorption at 77 K. As shown in Figure S17a, the N₂ uptake of 1 still inherited the quasi-unchanged adsorption capacity after cycling breakthrough tests, and the aperture distribution was concentrated at 4.67 Å (inset in Figure S17a), suggesting the unfading ultramicropore nature. In addition, single-gas adsorption isotherms of C₃H₆ on 1 yielded a higher capacity of 31.1–35.0/88.5–94.1 cm³ g⁻¹ at 0.01/0.1 atm and 298 K after 10 cycles (Figure S17b). Further, the variable-temperature PXRDs of 1 after cycling tests were recorded. As observed in Figure S17c, all of the diffractions all exhibited extremely consistent patterns compared with the theoretical diffractions, indicative of intact structural integrity. The derived top contour plots of variable-temperature PXRD (Figure S17d) evidenced that a main peak shift could hardly be observed, confirming a higher structural rigidity and thermal stability.

Of particular note was that the costs of raw materials should also be taken into account for laboratory-scale synthesis. As visualized in Figure S18 and Table S10, the total costs of raw materials were just $167 for per kilogram of 1 adsorbent, which were much cheaper than other materials, including ZU-36-Ni ($17 399), Fe₄(dobdc) ($4527), and MCF-57 ($10 073) etc. (Table S10), further reinforcing its potential application for C₃H₆ purification. Therefore, the excellent separation performance, steam stability, scalability of production, and cheap costs etc. awarded 1 the prominent potential to purify C₃H₆ from PDH byproducts.

4. CONCLUSIONS

To sum up, an ultramicroporous Zn-MOF with scaled-up production could be easily synthesized using the cost-effective raw materials. An optimized geometry model revealed the ultramicroporous pore conformation for 1, with a cross-sectional size of 4.27 × 4.60 Å² (19.64 Å²). The decent pore aperture was slightly larger than that of the propylene molecule with a minimum cross-section size of 4.16 × 4.65 Å² (19.34 Å²) but less than that of propane molecule with minimum cross-section size of 4.20 × 4.80 Å² (20.16 Å²), anticipating a diffusion barrier for the highly similar molecules. Static isotherm adsorption suggested that 1 possessed a record-high C₃H₆ uptake of 92.4 cm³ g⁻¹ at 298 and 0.1 bar, yielding an IAST selectivity of up to 63 among the reported benchmark MOFs. In situ spectroscopies, crystallographic experiments, and modeling demonstrated that two C₃H₆ molecules confined in one unit cell were grasped through multiple binding interaction including van der Waals effects, hydrogen bonding, and intramolecular interaction. Molecular dynamics showed that 1 possessed a higher diffusion selectivity of 19.4 for C₃H₆/C₂H₆. Column breakthrough tests demonstrated that about 30.8 L of C₃H₆ product with a purity of 95.0–99.4% could be accomplished from the equimolar C₃H₆/C₂H₆ mixtures for 1 kg of activated 1 in a single breakthrough operation.
operation. Such an excellent separation property of propylene on 1 is also validated by the experimental and simulated breakthrough tests of quinary PDH byproducts containing $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8/\text{C}_4\text{H}_{10}$ (3/5/6/42/44, v/v/v/v/v). Particularly, structurally stable 1 can be easily synthesized on the kilogram scale using cheap raw materials (only $167$ for per kilogram of 1). The excellent separation performance, steam stability, scalability of production, and cheap costs etc. awarded 1 the prominent potential to purify $\text{C}_3\text{H}_8$ from PDH byproducts.

■ ASSOCIATED CONTENT

◆ Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.2c00554.

Structural characterizations, spectroscopy tests, modeling details, calculation of separation potential, transient breakthrough simulations, supporting figures and tables (PDF)

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