

RESEARCH ARTICLE

Polar-Nonpolar Synergistic Incorporation in Metal-Organic Frameworks for Promoting Methane Separation From Natural Gas

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Received: 4 January 2026 | **Revised:** 12 February 2026 | **Accepted:** 24 February 2026

Keywords: adsorption separation | metal-organic frameworks | methane purification | natural gas | polar-nonpolar sites

ABSTRACT

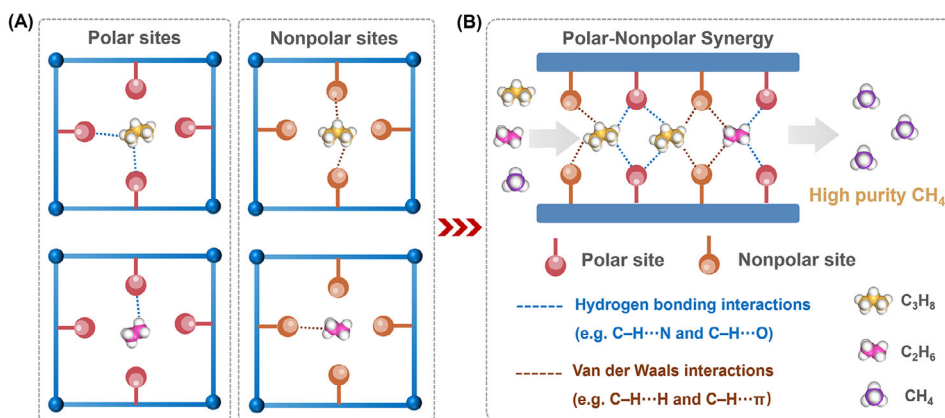
The separation of CH₄ from natural gas is an industrially significant yet challenging task. In this study, we rationally designed metal-organic framework (MOF)-based adsorbents with polar-nonpolar synergistic sites to enhance the efficient separation of CH₄ from natural gas. Our study demonstrates that the adsorbents exhibit superior adsorption capacity for C₃H₈ and C₂H₆ compared to CH₄, as well as high separation selectivity for C₃H₈/CH₄ (1336) and C₂H₆/CH₄ (46), effectively overcoming the trade-off between adsorption capacity and selectivity. Breakthrough experiments further confirm the exceptional dynamic separation performance of the adsorbents for the C₃H₈/C₂H₆/CH₄ ternary mixture under various operating conditions, achieving >99.99% CH₄ purity and a yield of 11.27 mmol·g⁻¹. Molecular simulations and theoretical calculations elucidate that the incorporated polar and nonpolar sites in the adsorbents provide multiple strong interactions, which significantly enhance the separation of CH₄ from the C₃H₈/C₂H₆/CH₄ mixture.

1 | Introduction

Methane (CH₄), the simplest alkane, is widely regarded as an ideal clean energy source to replace traditional fossil fuels, thanks to its high energy density and low carbon emissions [1–3]. Natural gas, primarily composed of CH₄ (70%–90%), typically contains impurities such as ethane (C₂H₆, 0%–20%) and propane (C₃H₈, 1%–5%) [4–6]. These impurities can reduce the combustion efficiency of CH₄ and compromise the storage stability and transportation safety of natural gas in pipeline systems [7, 8]. However, C₂H₆ and C₃H₈ are also valuable chemical feedstocks

with significant commercial potential in low-carbon energy conversion and polyolefin production [9–12]. Therefore, the efficient separation of CH₄ from a ternary mixture of C₃H₈/C₂H₆/CH₄ to obtain high-purity components is critical for achieving hierarchical resource utilization [13–17]. Currently, industrial-scale natural gas purification relies heavily on cryogenic distillation, a process characterized by high capital investment and operational energy costs, which severely constrain its economic feasibility [18–21]. Consequently, there is an urgent need to develop efficient and cost-effective separation technologies for the C₃H₈/C₂H₆/CH₄ mixture.

Kang Wang and Hui Zhang contributed equally to this work.



SCHEME 1 | Schematic illustration of adsorption materials with (A) polar sites, nonpolar sites, and (B) polar-nonpolar synergistic sites for $\text{C}_3\text{H}_8/\text{C}_2\text{H}_6/\text{CH}_4$ separation.

Adsorption separation has emerged as a promising separation technology for natural gas separation because of its high efficiency and mild operational conditions [22–26]. The development of high-performance adsorbents is therefore critical to its success [27, 28]. Metal-organic frameworks (MOFs) are a class of porous crystalline materials formed by coordination bonding between metal ions/clusters and organic ligands [29–32]. They offer remarkable advantages over traditional adsorbents, including ultrahigh specific surface areas, exceptional porosity, structural diversity, and easily functionalized pores [33, 34]. Due to the relatively low concentrations of C_2H_6 and C_3H_8 in natural gas, it is crucial to have adsorbents with high adsorption capacity for C_2H_6 and C_3H_8 under low-pressure (5–10 kPa) conditions for the efficient separation of CH_4 from the $\text{C}_3\text{H}_8/\text{C}_2\text{H}_6/\text{CH}_4$ mixture [35, 36]. Unfortunately, most reported MOF-based adsorbents exhibit low adsorption capacity for C_3H_8 and C_2H_6 at low pressures, which significantly restricts their practical applications [37, 38]. Consequently, research into the MOF-based adsorbents for the efficient separation of $\text{C}_3\text{H}_8/\text{C}_2\text{H}_6/\text{CH}_4$ mixture remains ongoing.

One strategy involves constructing polar sites by introducing functional groups such as F, $-\text{NH}_2$, or $-\text{OH}$ into MOFs [39–41]. This can enhance adsorption selectivity and low-pressure adsorption capacity through strong electrostatic or hydrogen bond interactions with alkane molecules (Scheme 1A). However, strong polar sites can reduce the effective pore channel space or compromise hydrothermal stability, resulting in limited adsorption capacity and compromised reusability [42, 43]. Alternatively, constructing nonpolar sites in MOFs can create hydrophobic pore environments rich in aromatic rings or alkyl chains, which promote separation based on molecular size or polarizability through van der Waals forces [44–46]. While this approach offers higher adsorption capacity, it provides limited improvement in low-pressure selectivity, particularly for $\text{C}_2\text{H}_6/\text{CH}_4$ separation [47, 48]. Therefore, it is not possible to simultaneously achieve high adsorption capacity and selectivity for the separation of CH_4 from $\text{C}_3\text{H}_8/\text{C}_2\text{H}_6/\text{CH}_4$ mixture using a single polar or nonpolar site modification strategy. This challenge highlights the need for innovative adsorbent designs to overcome this critical bottleneck.

Herein, we present novel MOF-based adsorbents designed with polar-nonpolar synergistic sites for the efficient separation of CH_4

from natural gas (Scheme 1B). These adsorbents are engineered by systematically incorporating low-polarity methyl groups to optimize the pore environment and enhance the interactions between gas molecules and the adsorbent frameworks. Furthermore, the presence of nitrogen atoms in bipyrazoles and uncoordinated oxygen atoms in carboxylic acids creates dense polar sites that strengthen the affinity for C_3H_8 and C_2H_6 through hydrogen bonding. The polar-nonpolar synergy of the adsorbents enables the selective adsorption of C_3H_8 and C_2H_6 over CH_4 through multiple host–guest interactions, thereby promoting the separation of CH_4 from a $\text{C}_3\text{H}_8/\text{C}_2\text{H}_6/\text{CH}_4$ mixture. Experimental results from adsorption isotherms, separation selectivity, adsorption heats, and dynamic breakthrough curves demonstrate that the adsorbents efficiently separate the $\text{C}_3\text{H}_8/\text{C}_2\text{H}_6/\text{CH}_4$ mixture under various operating conditions. Moreover, molecular simulations and density functional theory (DFT) calculations elucidate the differences in adsorption affinity and separation mechanisms for C_3H_8 , C_2H_6 , and CH_4 on the adsorbents.

2 | Results and Discussion

2.1 | Synthesis and Characterization

Three MOF-based adsorbents were synthesized via a solvothermal reaction using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1H,1'H-4,4'-bipyrazole (BPZ), and either 1,4-benzenedicarboxylic acid (BDC), 2-methyl-1,4-benzenedicarboxylic acid (MBDC), or 2,5-dimethyl-1,4-benzenedicarboxylic acid (DBDC) (Figure 1A; Figure S1). The resulting samples were denoted as Zn-BPZ-BDC, Zn-BPZ-MBDC, and Zn-BPZ-DBDC, respectively. The powder X-ray diffraction (PXRD) patterns of the as-synthesized samples of the three isorecticular MOFs match the simulated patterns, confirming their phase purity (Figure 1B). Infrared (IR) spectroscopy revealed characteristic bands at 1563 and 1326 cm^{-1} , which are attributed to the $\text{C}=\text{N}$ and $\text{C}-\text{N}$ vibrations of BPZ (Figure S2) [49]. Notably, the broad band in the $2859\text{--}2955\text{ cm}^{-1}$ range corresponds to the symmetric and asymmetric stretching of $\text{C}-\text{H}$ due to the $-\text{CH}_3$ groups in the MBDC and DBDC ligands [50]. Thermogravimetric analysis (TGA) showed that the thermal stability of the samples increased with the introduction of methyl groups and that all three samples maintained their structural integrity up to 450°C (Figure S3). Additionally, PXRD analysis confirmed the excellent

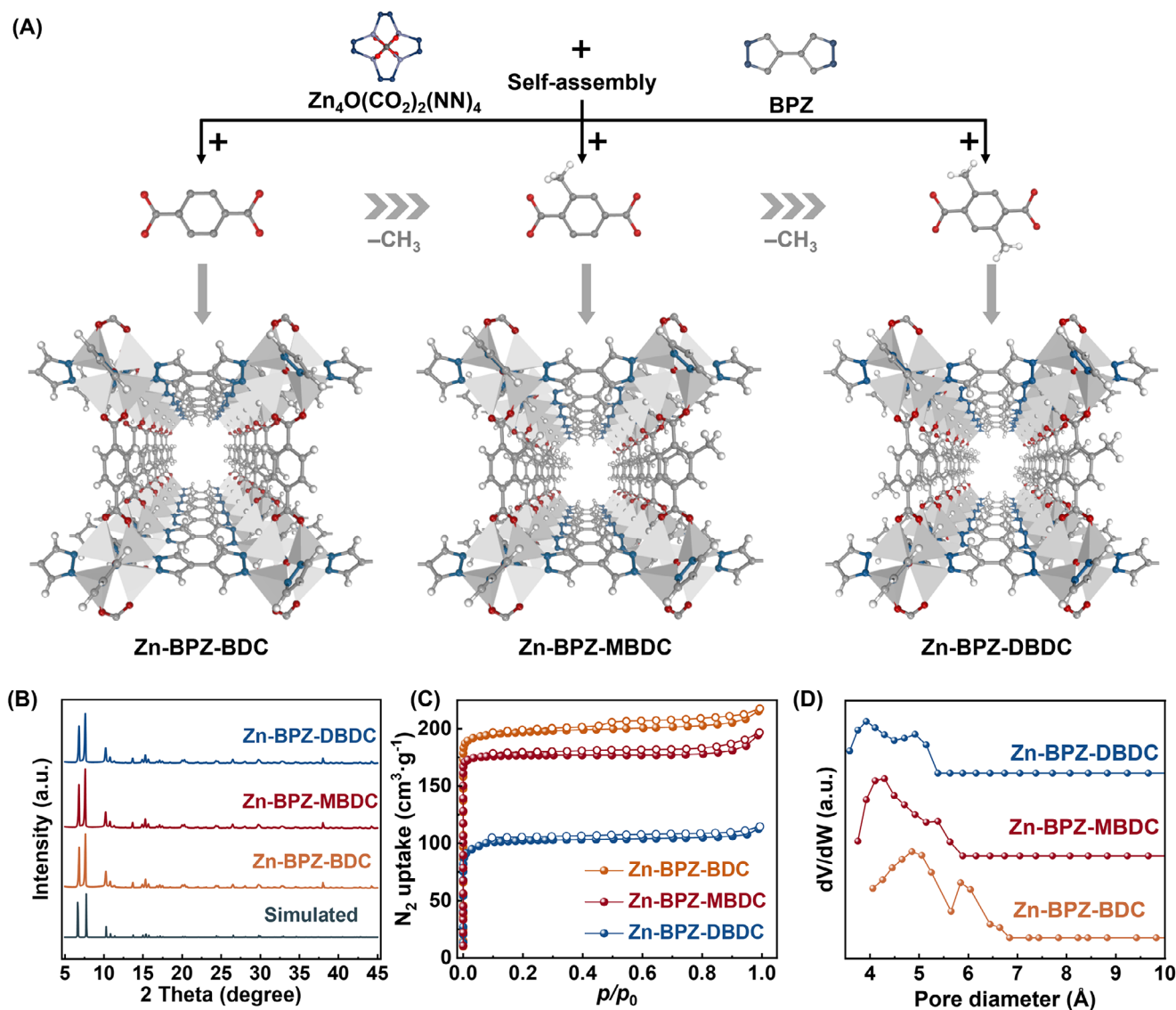


FIGURE 1 | (A) Schematic representation of the assemblies and structures of Zn-BPZ-BDC, Zn-BPZ-MBDC, and Zn-BPZ-DBDC. (B) PXRD patterns, (C) N₂ adsorption–desorption isotherms, and (D) pore size distributions of Zn-BPZ-BDC, Zn-BPZ-MBDC, and Zn-BPZ-DBDC.

stability of the samples under various acid/alkali conditions and organic solvents (Figure S4).

2.2 | Gas Adsorption Performances

N₂ adsorption–desorption isotherms at 77 K exhibited a typical type-I pattern for all three samples (Figure 1C), which indicates their microporous structures. The Brunauer–Emmett–Teller (BET) surface areas, calculated from the adsorption branches, were 814, 741, and 404 m²·g⁻¹ for Zn-BPZ-BDC, Zn-BPZ-MBDC, and Zn-BPZ-DBDC, respectively. Notably, the gradual introduction of –CH₃ groups results in a noticeable reduction of pore sizes of the samples, as these substituents occupy the void space and limit the accessible surface area (Figure 1D). Pore size distributions, derived using the non-local density functional theory (NLDFT) model, reveal the presence of two predominant pore types across all samples. For Zn-BPZ-BDC, Zn-BPZ-MBDC, and Zn-BPZ-DBDC, the smaller pores are centered at 4.9, 4.3,

and 3.9 Å, respectively, and correspond to channels along the *a/b*-axis. Conversely, the larger pores, centered at 5.9, 5.4, and 5.0 Å for the same respective samples, originate from pores extending along the *c*-axis. Scanning electron microscopy (SEM) revealed uniform octahedral morphologies for all samples, with the C, N, O, and Zn elements distributed homogeneously across their surfaces (Figures S5–S8). X-ray photoelectron spectroscopy (XPS) analysis confirmed the elemental composition of the samples, consistent with SEM-based elemental mapping and energy dispersive spectroscopy (EDS) results (Figures S9–S11).

Adsorption isotherms for C₃H₈, C₂H₆, and CH₄ on different samples were conducted to evaluate the gas separation performance (Figure 2A–C; Figure S12). The results showed that the adsorption isotherms for C₃H₈ across the three samples exhibited a type-I pattern, characterized by steep adsorption curves at low pressures, indicating strong interactions between C₃H₈ and the adsorbents. At 298 K and 1 bar, the adsorption capacities of C₃H₈ and C₂H₆ on Zn-BPZ-MBDC and Zn-BPZ-DBDC are 71 and

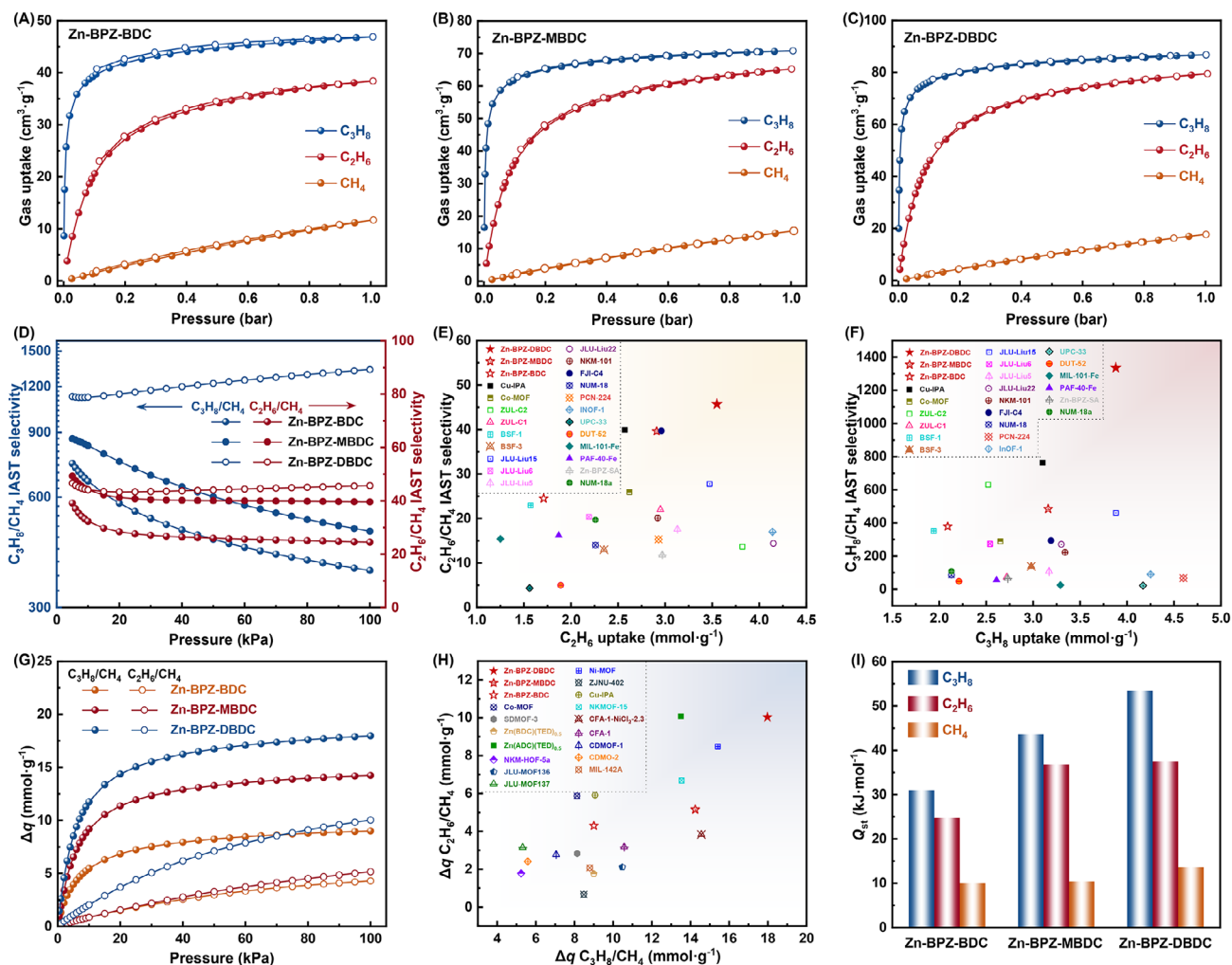


FIGURE 2 | Adsorption isotherms for C_3H_8 , C_2H_6 , and CH_4 on (A) Zn-BPZ-BDC, (B) Zn-BPZ-MBDC, and (C) Zn-BPZ-DBDC at 298 K. (D) IAST selectivity curves for C_3H_8/CH_4 (5/85, v/v) and C_2H_6/CH_4 (10/85, v/v) on different samples at 298 K. Comparison of IAST selectivity values for (E) C_2H_6/CH_4 with C_2H_6 uptake and (F) C_3H_8/CH_4 with C_3H_8 uptake on various MOF-based materials. (G) Separation potential (Δq) curves for C_3H_8/CH_4 (5/85, v/v) and C_2H_6/CH_4 (10/85, v/v) on different samples at 298 K. (H) Comparison of Δq values for C_3H_8/CH_4 and C_2H_6/CH_4 on various MOF-based materials. (I) Adsorption heat (Q_{st}) values for C_3H_8 , C_2H_6 , and CH_4 on different samples.

$65 \text{ cm}^3 \cdot \text{g}^{-1}$ and 87 and $80 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively. These values are significantly higher than those of Zn-BPZ-BDC under the same conditions. It is also notable that the C_3H_8 adsorption capacities of Zn-BPZ-MBDC and Zn-BPZ-DBDC in the low-pressure (0–10 kPa) regions surpass those of well-known MOFs such as Zn-BPZ-SA [22], DUT-52 [47], and Co-MOF [23] (Tables S1 and S2).

To further evaluate the performance of the adsorbents in separating gas mixtures, the adsorption selectivity predicted by the ideal adsorbed solution theory (IAST) was calculated by fitting the adsorption isotherms to the dual-site Langmuir–Freundlich model (Figures S13–S19 and Table S3). Figure 2D shows that the IAST selectivities of the C_3H_8/CH_4 (5/85) and C_2H_6/CH_4 (10/85) mixtures were calculated to be 1336 and 46 for Zn-BPZ-DBDC. These values are significantly higher than those for Zn-BPZ-MBDC (484 and 40) and Zn-BPZ-BDC (379 and 24) (Figure 2E,F). As a comprehensive indicator of adsorption selectivity and capacity, the separation potential (Δq) was calculated for the three adsorbents (Figure 2G; Figure S20). At 298

K and 100 kPa, the Δq values for C_3H_8/CH_4 and C_2H_6/CH_4 are 9.0 and 4.3 for Zn-BPZ-BDC, 14.2 and 5.2 for Zn-BPZ-MBDC, and 18.0 and 10.0 $mmol \cdot g^{-1}$ for Zn-BPZ-DBDC, respectively. Notably, Zn-BPZ-DBDC exhibited superior Δq values compared to some reported MOF-based adsorbents (Figure 2H), highlighting its effectiveness in selectively separating CH_4 from natural gas.

To understand the adsorption affinity between the gas molecules and the adsorbents, the adsorption heats (Q_{st}) for C_3H_8 , C_2H_6 , and CH_4 were predicted from the adsorption isotherms fitted using the Virial equation at 273 and 298 K (Figures S21–S24 and Table S4). The results indicated that C_3H_8 has a higher adsorption affinity than C_2H_6 and CH_4 with all three adsorbents (Figure 2I). The introduction of methyl groups appears to enhance the interactions between the gas molecules and the adsorbents, particularly for C_3H_8 and C_2H_6 . It is worth noting that the moderate Q_{st} values ensure the preferential adsorption of C_3H_8 and C_2H_6 while facilitating the mild regeneration of the adsorbents.

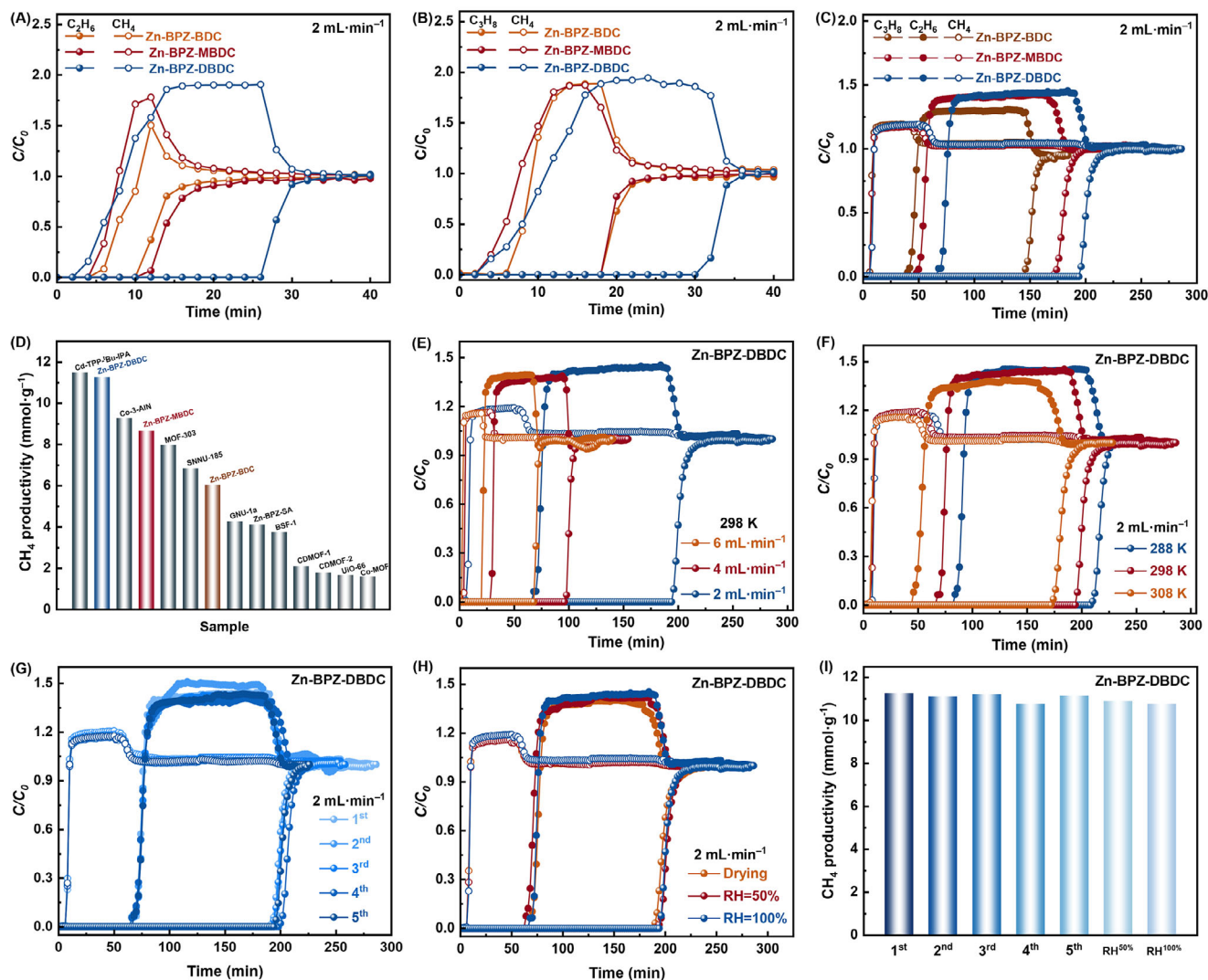


FIGURE 3 | Dynamic breakthrough curves for (A) C_2H_6/CH_4 (50/50, v/v), (B) C_3H_8/CH_4 (50/50, v/v), and (C) $C_3H_8/C_2H_6/CH_4$ (5/10/85, v/v/v) on different samples at a flow rate of $2 \text{ mL} \cdot \text{min}^{-1}$. (D) Comparison of the CH_4 productivity among various MOF-based materials. Breakthrough curves for $C_3H_8/C_2H_6/CH_4$ (5/10/85, v/v/v) on Zn-BPZ-DBDC under different (E) flow rates and (F) temperatures. (G) Cyclic breakthrough curves for $C_3H_8/C_2H_6/CH_4$ (5/10/85, v/v/v) on Zn-BPZ-DBDC. (H) Breakthrough curves for $C_3H_8/C_2H_6/CH_4$ (5/10/85, v/v/v) on Zn-BPZ-DBDC under dry and humid conditions. (I) CH_4 productivity of Zn-BPZ-DBDC after cyclic breakthrough experiments and under wet conditions.

2.3 | Dynamic Breakthrough Performances

Dynamic breakthrough experiments were conducted using gas mixtures at a flow rate of $2 \text{ mL} \cdot \text{min}^{-1}$ through packed columns of different adsorbents under ambient conditions to evaluate their practical separation capabilities. As illustrated in Figure 3A, in the case of a binary C_3H_8/CH_4 mixture (50/50, v/v), CH_4 was first detected in the Zn-BPZ-DBDC column after 2 min. In contrast, C_3H_8 exhibited a significant adsorption delay, being detected after 30 min and reaching adsorption saturation after 40 min. The breakthrough time interval between the two gases on Zn-BPZ-DBDC was 28 min, which is substantially longer than the 12 min observed on Zn-BPZ-BDC and the 16 min observed on Zn-BPZ-MBDC. A similar trend was observed for the separation of a C_2H_6/CH_4 binary mixture (50/50, v/v), as the retention times of C_2H_6 on Zn-BPZ-BDC, Zn-BPZ-MBDC, and Zn-BPZ-DBDC were 8, 8, and 24 min, respectively (Figure 3B). Notably, Zn-BPZ-DBDC exhibited high CH_4 productivity, achieving $5.36 \text{ mmol} \cdot \text{g}^{-1}$

from a C_2H_6/CH_4 mixture and $5.88 \text{ mmol} \cdot \text{g}^{-1}$ from a C_3H_8/CH_4 mixture in a single separation cycle (Figure S25). In addition, the C_2H_6 productivity values were determined to be 0.77, 1.01, and $2.0 \text{ mmol} \cdot \text{g}^{-1}$ for Zn-BPZ-BDC, Zn-BPZ-MBDC, and Zn-BPZ-DBDC, respectively (Figure S26). These results indicate that the adsorbents have a significantly higher affinity for C_3H_8 and C_2H_6 than for CH_4 during the separation of binary mixtures.

In addition, the separation of a ternary mixture of $C_3H_8/C_2H_6/CH_4$ (5/10/85, v/v/v) on different adsorbents was further performed. As shown in Figure 3C, CH_4 eluted first and rapidly reached a high purity level across the three adsorbents, while C_3H_8 and C_2H_6 were retained within the adsorbent bed. The respective retention times for C_3H_8 were 144, 177, and 196 min for Zn-BPZ-BDC, Zn-BPZ-MBDC, and Zn-BPZ-DBDC. Further analysis revealed that Zn-BPZ-DBDC demonstrated significantly higher CH_4 productivity, with a purity of $>99.99\%$ and a yield of $11.27 \text{ mmol} \cdot \text{g}^{-1}$, compared to $8.56 \text{ mmol} \cdot \text{g}^{-1}$ for

Zn-BPZ-MBDC and $6.03 \text{ mmol}\cdot\text{g}^{-1}$ for Zn-BPZ-BDC. Notably, the higher CH_4 productivity of Zn-BPZ-DBDC surpassed that of some well-known MOFs, such as MOF-303 [13], SNU-185 [24], and GNU-1a (Figure 3D) [51]. Moreover, desorption experiments revealed that CH_4 and C_2H_6 were rapidly eluted from the packed column, while exhibited a significantly slower desorption rate. This sharp kinetic contrast enabled C_3H_8 to be recovered with a purity of over 99.5% (Figure S27). The C_3H_8 productivity for Zn-BPZ-BDC, Zn-BPZ-MBDC, and Zn-BPZ-DBDC was determined from the desorption curves to be 0.18, 0.26, and $0.36 \text{ mmol}\cdot\text{g}^{-1}$, respectively.

The influence of gas flow rates and temperatures on the dynamic separation performance of the adsorbents was further investigated, as these factors are critical for practical industrial applications. As can be observed in Figure 3E,F, the experimental breakthrough curves showed that all three adsorbents consistently exhibited high separation efficiency under different operating conditions, highlighting their potential for effectively recovering high-purity CH_4 from $\text{C}_3\text{H}_8/\text{C}_2\text{H}_6/\text{CH}_4$ mixtures (Figures S28–S31). In addition, reusability is a critical consideration in industrial adsorption processes. Figure 3G–I illustrated the cyclic breakthrough experiments of C_3H_8 , C_2H_6 , and CH_4 on different samples under drying and wet conditions with relative humidities of 50% and 100%. The results showed that all samples retained almost all of their initial retention times, adsorption capacities, and CH_4 productivities (Figures S32–S37). Furthermore, no detectable loss of adsorption capacity was observed for C_3H_8 , C_2H_6 , and CH_4 after five adsorption isothermal cycles (Figure S38). Moreover, PXRD analysis revealed that they demonstrated excellent stability after multiple adsorption–desorption cycles and dynamic breakthrough experiments (Figure S39). These results strongly suggest that the adsorbents are highly reusable for the purification of CH_4 from natural gas.

2.4 | Molecular Simulations and Theory Calculations

Molecular simulations were conducted to analyze the density distributions and identify the adsorption sites of gas molecules within the frameworks of the three adsorbents under different pressures (Figure S40). The density distributions of C_3H_8 , C_2H_6 , and CH_4 revealed two primary adsorption regions: a polar region formed by the oxygen atoms of carboxylic acids and the nitrogen atoms of pyrazoles, and a nonpolar region formed by methyl groups and benzene rings. The results suggest the potential occurrence of polar-nonpolar interactions between the adsorbents and the gas molecules. In addition, DFT calculations were performed to determine the preferential binding sites and elucidate the binding affinities of C_3H_8 , C_2H_6 , and CH_4 on the different adsorbents. As illustrated in Figure 4, all gas molecules predominantly occupy the corner positions in square channels, forming multiple polar-nonpolar interactions with the adsorbent frameworks. The calculated binding energies (ΔE) for the three adsorbents are in order $\text{C}_3\text{H}_8 > \text{C}_2\text{H}_6 > \text{CH}_4$, which indicates that the interactions between the adsorbents and C_3H_8 and C_2H_6 are significantly stronger than those with CH_4 . For the same gas molecule on different adsorbents, the binding energies of the three adsorbents follow the order of Zn-BPZ-DBDC > Zn-BPZ-MBDC > Zn-BPZ-BDC. These results suggest that introducing

methyl groups can enhance the binding affinities of C_3H_8 and C_2H_6 to the adsorbent frameworks through increased nonpolar interactions.

As displayed in Figure 4A, C_3H_8 and C_2H_6 form numerous $\text{C}\cdots\text{H}\cdots\text{N}$ and $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonding interactions with Zn-BPZ-BDC, whereas fewer such interactions are observed between CH_4 and Zn-BPZ-BDC. Differential charge density analysis of Zn-BPZ-MBDC and Zn-BPZ-DBDC revealed that the introduction of methyl groups can alter the adsorption configuration, with significant charge transfer occurring between gas molecules and both polar and nonpolar sites on their frameworks (Figure 4B,C). Specifically, C_3H_8 forms two $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds and four $\text{C}\cdots\text{H}\cdots\text{N}$ hydrogen bonds with the polar oxygen and nitrogen atoms of the carboxylic acids and bipyrazoles in Zn-BPZ-MBDC, along with four $\text{C}\cdots\text{H}\cdots\text{H}$ and one $\text{C}\cdots\text{H}\cdots\pi$ interactions with the nonpolar methyl groups and aromatic rings. Similarly, C_2H_6 exhibits strong binding modes with Zn-BPZ-MBDC, involving multiple $\text{C}\cdots\text{H}\cdots\text{O}$, $\text{C}\cdots\text{H}\cdots\text{N}$, $\text{C}\cdots\text{H}\cdots\text{H}$, and $\text{C}\cdots\text{H}\cdots\pi$ interactions, while CH_4 interacts weakly through $\text{C}\cdots\text{H}\cdots\text{O}$, $\text{C}\cdots\text{H}\cdots\text{N}$, and $\text{C}\cdots\text{H}\cdots\text{H}$ interactions. With the further addition of methyl groups, the larger C_3H_8 and C_2H_6 molecules tilt slightly within the pores of Zn-BPZ-DBDC to minimize steric hindrance and optimize surface interactions. Consequently, Zn-BPZ-DBDC provides more favorable binding regions for C_2H_6 and C_3H_8 , resulting in more effective interactions and stronger affinities for these gas molecules. Notably, C_3H_8 forms two $\text{C}\cdots\text{H}\cdots\text{O}$ and two $\text{C}\cdots\text{H}\cdots\text{N}$ interactions with polar sites, as well as three $\text{C}\cdots\text{H}\cdots\text{H}$ and two $\text{C}\cdots\text{H}\cdots\pi$ interactions with nonpolar sites. C_2H_6 also shows relatively strong interactions with both polar and nonpolar sites. In contrast, CH_4 forms only a few weak $\text{C}\cdots\text{H}\cdots\text{O}$ and $\text{C}\cdots\text{H}\cdots\text{H}$ interactions within the framework. As a result, the synergistic effect of the polar and nonpolar sites enables the C_3H_8 and C_2H_6 molecules to be firmly anchored within the pores, significantly enhancing the separation efficiency of CH_4 .

Hirshfeld surface analysis and 2D fingerprint plots were performed to visualize the interactions between the adsorbates and the adsorbents (Figure 5; Figures S41 and S42) [52, 53]. The results showed that the bright red spots on the Hirshfeld surfaces of the C_3H_8 and C_2H_6 -loaded adsorbents corresponded to strong close contacts. In contrast, the CH_4 -loaded adsorbents exhibited fewer red spot regions, indicating weaker interactions. Further analysis revealed distinct synergistic polar and nonpolar interactions between C_3H_8 , C_2H_6 , and the Zn-BPZ-DBDC framework. Nonpolar van der Waals interactions were evident through $\text{H}\cdots\text{C}$ and $\text{H}\cdots\text{H}$ contacts, while polar hydrogen bonding interactions were reflected in $\text{H}\cdots\text{N}$ and $\text{H}\cdots\text{O}$ contacts. Notably, the coexistence of multiple interactions, such as nonpolar $\text{C}\cdots\text{H}\cdots\text{H}/\text{C}\cdots\text{H}\cdots\pi$ and polar $\text{C}\cdots\text{H}\cdots\text{N}/\text{C}\cdots\text{H}\cdots\text{O}$, demonstrates the synergistic effect between polar and nonpolar sites during the adsorption process. The expansion of the color region in the fingerprint plots and the significant increase in the interaction ranges on the Hirshfeld surface indicate that the interaction intensity and spatial extent increase with the number of alkane carbons, from CH_4 to C_3H_8 . Of the alkanes, C_3H_8 formed the most extensive binding sites with the adsorbent frameworks, exhibiting the strongest host–guest interactions. These results clearly show that the adsorption selectivity follows the order $\text{C}_3\text{H}_8 > \text{C}_2\text{H}_6 > \text{CH}_4$, driven primarily by the synergistic effect of polar and nonpolar sites within the adsorbents. Moreover, the increase in the molecular size and

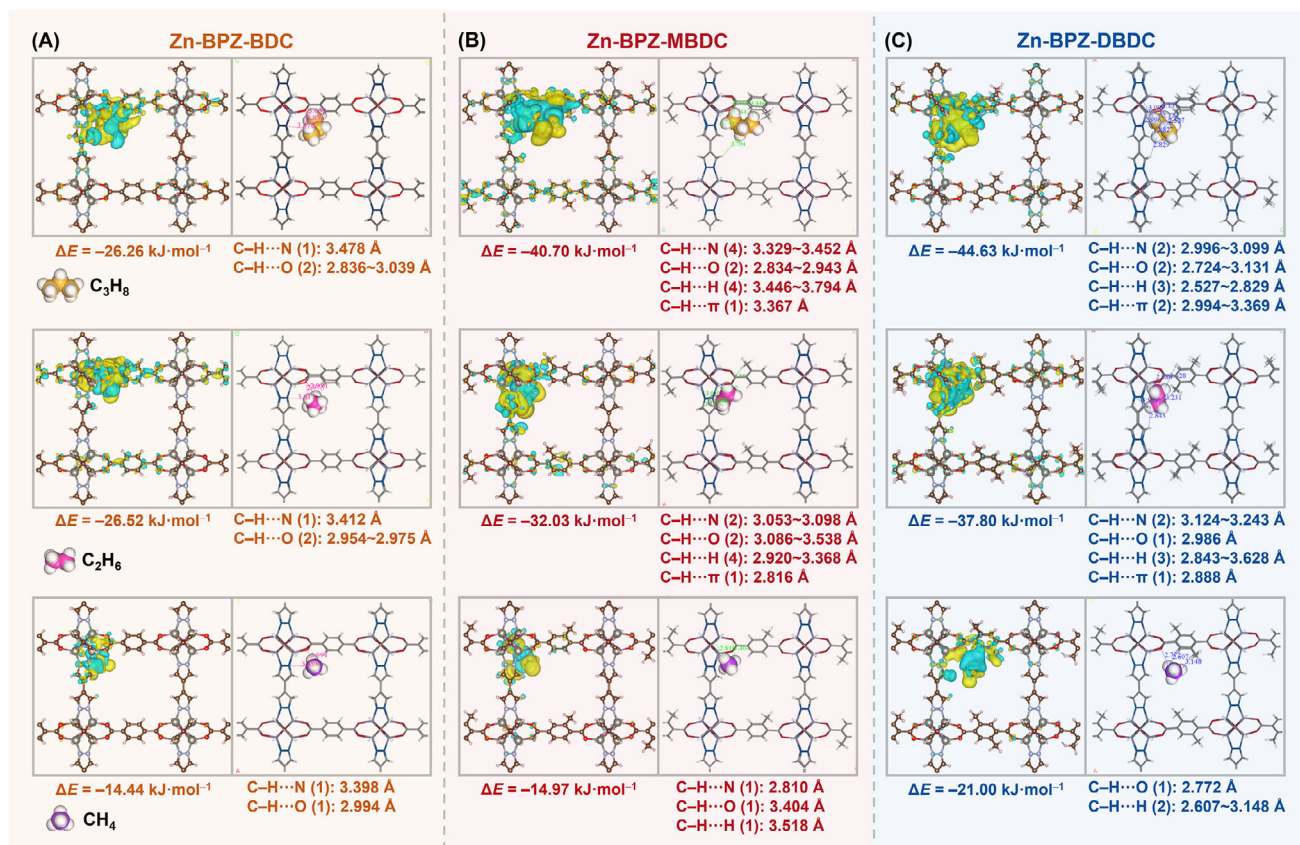


FIGURE 4 | Calculated preferential binding sites and differential charge densities of C_3H_8 , C_2H_6 , and CH_4 on (A) Zn-BPZ-BDC, (B) Zn-BPZ-MBDC, and (C) Zn-BPZ-DBDC (iso-level of 0.0015 electrons per $\text{\AA}^3$).

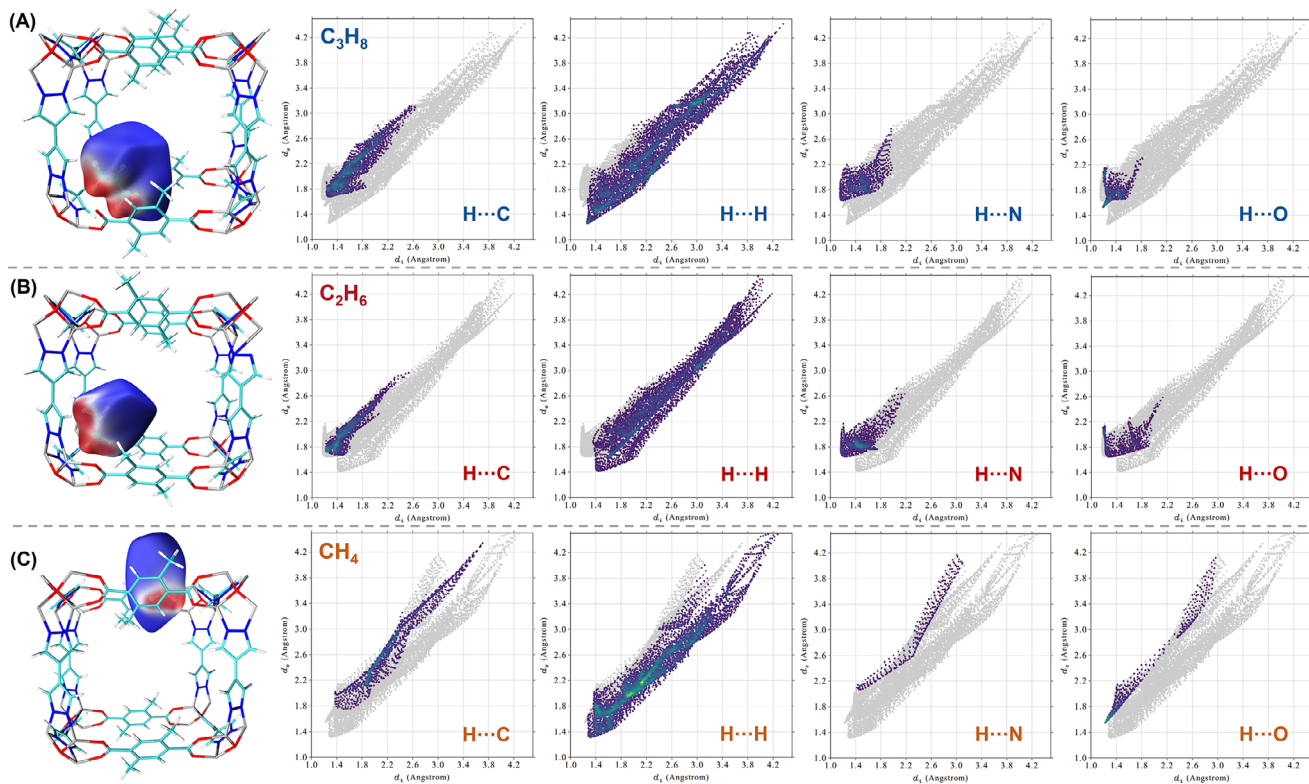


FIGURE 5 | Hirshfeld surface and 2D-fingerprint plots mapped with d_{norm} for (A) C_3H_8 , (B) C_2H_6 , and (C) CH_4 within Zn-BPZ-DBDC.

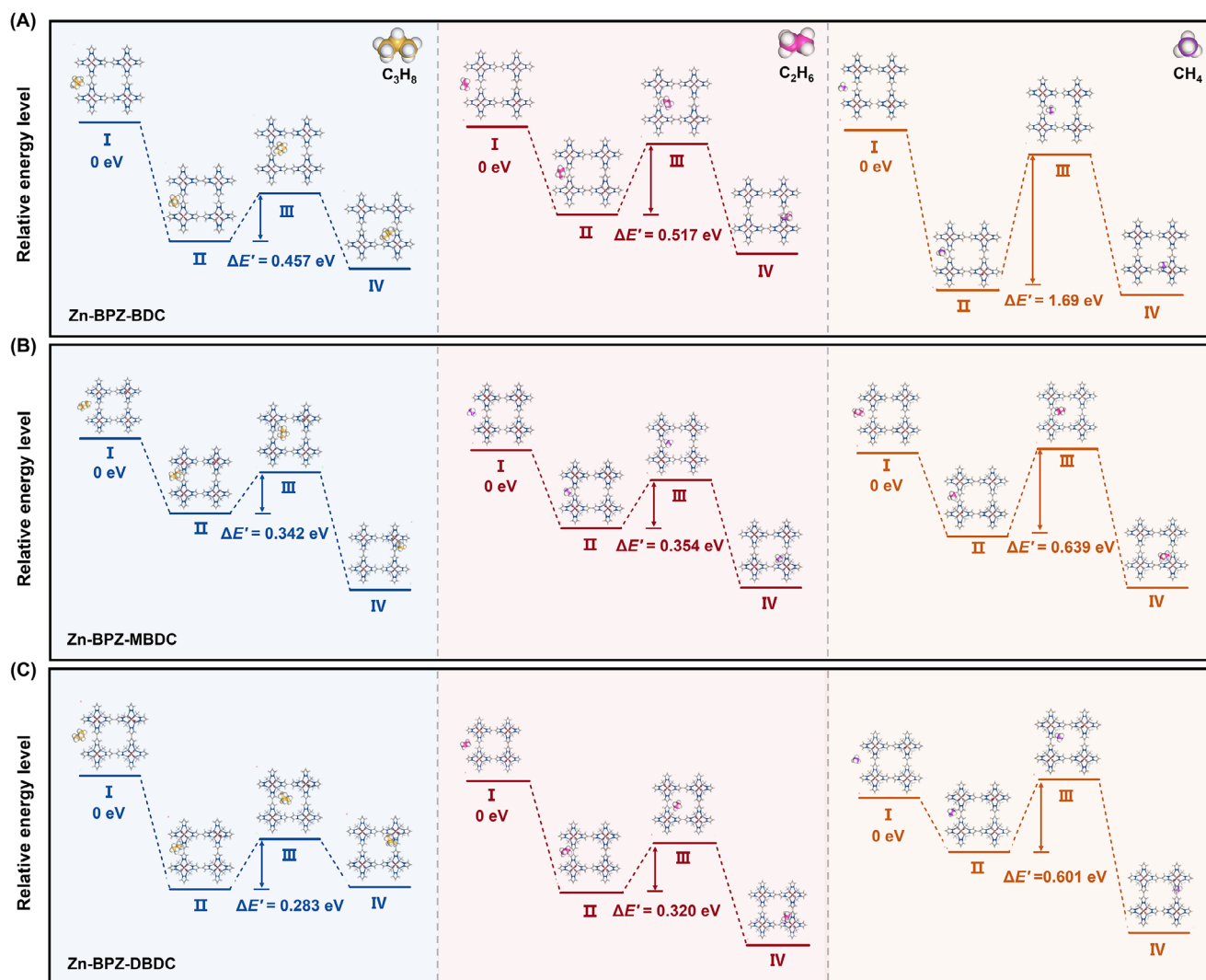


FIGURE 6 | DFT calculated diffusion pathways and corresponding energy levels of C₃H₈, C₂H₆, and CH₄ on (A) Zn-BPZ-BDC, (B) Zn-BPZ-MBDC, and (C) Zn-BPZ-DBDC (along the *a/b*-axis).

polarizability in alkanes can further enhance these synergistic interactions.

DFT calculations were performed to analyze the energy profiles associated with the adsorption and diffusion of C₃H₈, C₂H₆, and CH₄ into different adsorbents (Figure 6). The rate-determining step in these processes is governed by the highest energy barrier encountered during the transition state (TS) from surface adsorption TS(II) to pore diffusion TS(III). The results showed that CH₄ has the highest pore-entry barrier of the three adsorbents along the *a/b*-axis, which is significantly higher than those of C₂H₆ and C₃H₈. This high barrier explains the extremely low uptake of CH₄, as the molecules lack the kinetic energy required to overcome it under standard conditions. In contrast, C₃H₈ and C₂H₆ can efficiently diffuse into the pores due to their lower energy barriers and form strong interactions with the binding sites within the pores. These interactions stabilize the transition state configuration, thereby reducing the diffusion energy barrier. Notably, C₃H₈ has the lowest energy barriers, particularly in Zn-BPZ-DBDC, where it is as low as 0.283 eV. This can be attributed to its stronger interactions with both polar and nonpolar sites in Zn-BPZ-DBDC. Furthermore, DFT calculations of diffusion

pathways along the *c*-axis indicated that the energy barriers in this direction are considerably lower than those associated with the functionalized *a/b*-axis channels for all gas molecules (Figure S43). This reduced resistance allows gas molecules to be transported rapidly throughout the adsorbent framework.

3 | Conclusion

In summary, we demonstrated the practical feasibility of incorporating polar and nonpolar sites synergistically into MOFs to promote the separation of CH₄ from natural gas. The obtained adsorbents exhibited significantly enhanced binding affinities for C₃H₈ and C₂H₆ compared to CH₄ by stepwise introducing methyl groups to enrich adsorption sites, as confirmed by comprehensive experimental and theoretical studies. Specifically, Zn-BPZ-MBDC and Zn-BPZ-DBDC demonstrated high adsorption capacities at low pressures, as well as improved IAST selectivity for C₃H₈/CH₄ and C₂H₆/CH₄. This overcomes the trade-off between adsorption capacity and selectivity. Theoretical calculations, including molecular simulations and DFT calculations, revealed that the synergy between polar and nonpolar sites facilitates multiple

strong interactions, enabling the efficient adsorption of C_3H_8 and C_2H_6 and the purification of CH_4 . Overall, this study provides insights into developing efficient adsorbents with high adsorption capacity and selectivity for natural gas separation.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (22208078) and the Fundamental Research Funds for the Central Universities (JZ2025HGTG0258). Partial support from the Robert A Welch Foundation (B-0027) (S.M.) and the Ongoing Research Funding Program (ORF2026-55), King Saud University, Riyadh, Saudi Arabia (A.M.A.) is also acknowledged. The analysis work of this article was partially carried out at the Instrumental Analysis Center, Hefei University of Technology.

Conflicts of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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