Exploiting thermodynamic-kinetic synergetic effect for C₃H₆/C₃H₈ separation in pillar-layer MOFs

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Abstract

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Abstract

Efficient adsorption separation of propylene (C₃H₆) and propane (C₃H₈) can largely lower the energy consumption compared to the current energy-intensive cryogenic distillation. Herein, we report an isoreticular family of pillar-layer metal-organic frameworks (MOFs), M(AIP)(BPY)_{0.5} (M = Co, Ni, and Zn), for efficient C₃H₆/C₃H₈ separation by exploiting thermodynamic and kinetic effects, circumventing disadvantages of each separation mechanism. The three MOFs feature an open metal site for each metal node and uniform but narrow one-dimensional (1D) channels, offering strong binding sites toward C₃H₆ via π -complexations while obstructing the diffusion of bulkier C₃H₈. The Ni-MOF shows the best separation performance based on the highest thermodynamic and kinetic C₃H₆/C₃H₈ selectivity, further verified by computational simulations. Ni(AIP)(BPY)_{0.5} has a moderate C₃H₆ uptake of 1.94 mmol/g but a remarkably high C₃H₆/C₃H₈ uptake ratio of 4.26 at 298 K and 1 bar. Efficient C₃H₆/C₃H₈ separation, good recyclability, moisture and water stability of Ni(AIP)(BPY)_{0.5} are confirmed.

KEYWORDS: pillar- layer MOFs, adsorption, separation, C₃H₆, C₃H₈

INTRODUCTION

Propylene (C_3H_6) is one of the most important building blocks in petrochemical industries that is widely used to produce polymers and high value-added organic chemicals.¹⁻³ In 2016, the worldwide production of C_3H_6 was up to 120 million tons,² and its global demand has been expected to increase faster than that of ethylene (C_2H_4) with an annual growth rate of 5%.⁴ C_3H_6 is typically produced by steam cracking of propane (C_3H_8) or naphtha that generally coexists with its saturated counterpart C_3H_8 .⁵ As a result, the separation of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ mixtures is an inevitable process to obtain polymer-grade ($> 99.5\%$) C_3H_6 . Due to their close similarity in physical properties including the small difference in boiling points (226 K for C_3H_6 and 231 K for C_3H_8), close molecular sizes ($6.5 \times 4.0 \times 3.8 \text{ \AA}^3$ of C_3H_6 and $6.8 \times 4.2 \times 3.8 \text{ \AA}^3$ of C_3H_8), and extremely close relative volatility (1.09-1.15),^{2, 6} $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation is listed as one of the seven chemical separations to change the world.⁷ To date, industrial separation of C_3H_6 and C_3H_8 is commonly achieved by the established energy-intensive cryogenic distillation method that requires to be performed under very harsh operation conditions, including more than 180 theoretical trays, reflux ratio as high as 12-20, ultra-low operation temperature of -30°C , and high operation pressure of 30 bar.^{2, 8, 9} It has been reported that the theoretical energy consumption during $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation process is estimated to be around 12.9 GJ per ton C_3H_6 , obviously higher than that of $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ separation which is theoretically calculated to be about 7.3 GJ per ton C_2H_4 ,^{10, 11} leading to huge energy consumption. Consequently, it is highly demanded to develop energy-efficient methods for the separation of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ mixtures, and $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation is viewed as one important industrial task to change the global energy footprint.¹²

Adsorption separation is an alternative technology to replace the traditional cryogenic distillation due to its energy-efficient feature and mild operation conditions.¹³ Moreover, adsorption separation has the potential capabilities of high separation selectivity, suitable for more difficult separation systems, such as ultra-low concentration removal and azeotropes separation that can overcome the thermodynamic limitations, attracting tremendous attention for gas separation and purification applications.¹⁴ However, the development of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation through adsorption method is stagnant due to the poor separation performance of traditional porous materials, which is the key factor for achieving highly efficient adsorption-based $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation.¹⁵

As an emerging class of porous crystalline materials, metal-organic frameworks (MOFs) assembled by inorganic metal nodes and organic linkers through coordination bonds have been widely studied in the field of gas separation and purification,¹⁶⁻²¹ including $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation,^{1, 22-24} due to their great structural diversity and easy tailorability. In terms of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation, the separation mechanisms in MOFs are classified into four categories: thermodynamic separation, kinetic separation, molecular sieve, and gate-opening separation.²⁵ With regard to kinetic separation, MOFs that separate $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ by utilizing the difference in C_3H_6 and C_3H_8 diffusion rates are still underexplored and have the common drawback of low uptakes due to their restricted and narrow channels, such as BTO (0.60 mmol/g),²⁶ DBTO (1.40 mmol/g),²⁶ and ELM-12 (1.47 mmol/g).²⁷ More importantly, most reports of kinetic $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation merely focus on the kinetic selectivity based on pure C_3H_6 and C_3H_8 sorption kinetics profiles, and breakthrough tests $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ mixtures were only performed on ELM-12²⁷ and Tb-ABTC²⁸ so far. For the gate-opening separation, separating $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ mixtures is realized by two flexible CPL-1⁹ and NJU-Bai8²⁹ through the differences in C_3H_6 and C_3H_8 gate-opening pressures. However, the dynamic $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation of CPL-1 was required to be conducted at 273 K rather than room temperature, and additional energy is consumed to cool down the operation temperature.⁹ For NJU-Bai8, since the relatively low gate-opening pressures of C_3H_6 and C_3H_8 were 4.5 and 24.4 kPa at 298 K, He as the balance gas was necessary to control each partial pressure of C_3H_6 and C_3H_8 to be 20 kPa that only C_3H_6 induced the gate-opening phenomenon during the breakthrough tests, making it impractical for industrial application.²⁹ Molecular sieving, as an ideal separation mechanism, is highly difficult to achieve by finely tune the MOF pore apertures that allow for the passing of smaller C_3H_6 molecules while excluding slightly bulkier C_3H_8 . Indeed, the construction of MOFs with such subtle pores remains a great intractable task to discriminate the small difference in molecular sizes. Until now, NbOFFIVE-1-Ni,²³ Y-abtc,²⁴ and Co-gallate MOF¹ have been exemplified in sieving separation of C_3H_6 and C_3H_8 . Compared to the above three mechanisms, thermodynamic separation of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ has

been the most widely explored as a feasible approach since the open metal sites (OMSs) within MOF frameworks can discriminately interact with C_3H_6 molecules via the formation of π -complexation interactions, such as MIL-100³⁰ and MOF-74 series.³¹ However, there usually exists the co-adsorption of the counterpart C_3H_8 and then hinders the high-purity C_3H_6 production, resulting in relatively moderate selectivity, such as the low C_3H_6 and C_3H_8 uptake ratio of MOF-74 series in the range of 1.12-1.31.² In addition, these MOFs generally have limited stability when exposed to water and moisture, because these OMSs are also strong binding sites toward water molecules and then induce the breakdown of weak coordination bonds.³²

Such disadvantageous effect on each separation mechanism may limit the utmost MOF separation performance of C_3H_6/C_3H_8 mixtures and means that there are still more efforts to further enhance the separation performance. On the other hand, the separation performance is simultaneously controlled by both thermodynamic and kinetic effects during a practical separation process.¹² Hence, developing MOF adsorbents that can simultaneously exploit thermodynamic and kinetic mechanisms is appealing for C_3H_6/C_3H_8 separation whereas intractable to design and construct. Only a few unique MOFs have been demonstrated as suitable materials for both thermodynamic and kinetic separation mechanisms.^{8, 33} Despite these efforts, it remains scarce investigation for high-efficiency C_3H_6/C_3H_8 separation on MOFs. Inspired by the unique type structure of pillar-layer MOFs with an OMS for each metal node and uniform but narrow one-dimensional (1D) channels, a series of pillar-layer MOFs, $M(AIP)(BPY)_{0.5}$ ($M = Co, Ni, \text{ and } Zn$; AIP, 5-aminoisophthalic acid; BPY, 4,4'-bipyridine) to study the effect of transition metal ions (Co^{2+} , Ni^{2+} , and Zn^{2+}) on C_3H_6/C_3H_8 separation by exploiting thermodynamic-kinetic synergetic effect. Herein, we demonstrate that $Ni(AIP)(BPY)_{0.5}$ has the best separation performance with the highest thermodynamic and kinetic selectivities of C_3H_6/C_3H_8 among the three MOFs.

2. RESULTS AND DISCUSSION

2.1. Structural analysis and characterization.

The solvothermal reaction of $M(CH_3COO)_2 \cdot 4H_2O$ ($M = Co$ and Ni), AIP, and BPY in a mixed solution of water and methanol at 80 °C for 3 days yielded crystals of $M(AIP)(BPY)_{0.5}$ ($M = Co$ and Ni). In contrast, $Zn(AIP)(BPY)_{0.5}$ crystals were synthesized via the solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$, AIP, and BPY in a mixed solution of water and *N,N*-dimethylformamide at 90 °C for 3 days. The three structures are isostructural and crystallized in the monoclinic space group of $P 2_1/c$.³⁴⁻³⁷ In the structure of $M(AIP)(BPY)_{0.5}$, each M in a distorted square pyramidal geometry is coordinated by three oxygen atoms from two AIP linkers (one monodentate mode and one bidentate mode from the carboxylate groups in two AIP linkers) and two nitrogen atoms (one in amino group in AIP and one from BPY), leaving an OMS for each metal node (Figure 1a). Structural analysis reveals that the coordination bonds between the metal node and AIP linker form a two-dimensional (2D) layer and then the adjacent layers are connected by BPY linker (Figure 1b), resulting in the three-dimensional (3D) network. In the pillar-layer framework, there exist 1D channels of dimension 8.8×8.1 , 8.8×7.9 , and $5.9 \times 8.1 \text{ \AA}^2$ for Co , Ni , and Zn -based frameworks along the y -axis, respectively.

Figure 1. Crystal structures of $M(AIP)(BPY)_{0.5}$ ($M = Co, Ni, \text{ and } Zn$): (a) the coordination mode of metal node, (b) the 3D structure of $M(AIP)(BPY)_{0.5}$ viewed along the y -axis. Color scheme: M ($Co, Ni, \text{ and } Zn$) (green), C (gray), N (blue), O (red). H atoms are omitted for clarity.

The bulk phase purities of the three $M(\text{AIP})(\text{BPY})_{0.5}$ materials were verified by powder X-ray diffraction (PXRD) patterns (Figure S1), matching well the simulated data with the experimental PXRD patterns. Generally, the permanent porosity of porous materials is evaluated by N_2 adsorption-desorption isotherms at 77 K. However, no uptake of N_2 at 77 K was observed for the three studied MOFs. Then CO_2 was selected as the probe gas molecule and the isotherms at 195 K were measured (Figure 2). For $\text{Co}(\text{AIP})(\text{BPY})_{0.5}$ and $\text{Ni}(\text{AIP})(\text{BPY})_{0.5}$, the type I isotherms of CO_2 sorption were observed, indicating the microporous frameworks. The saturated CO_2 uptakes reached 83 and 108 cm^3/g , respectively. However, the accessibility of CO_2 -induced gate-opening behavior at $P/P_0 = 0.506$ was observed for $\text{Zn}(\text{AIP})(\text{BPY})_{0.5}$ and the maximum CO_2 uptake reached 140 cm^3/g , in which the isotherm showed a type I characteristic with a steep uptake of CO_2 in a relatively low pressure region and then an abrupt increase in CO_2 uptake. It is probably due to the fact that the strength of Zn-N bond is weaker than that of Co-N and Ni-N, thereby resulting in more rotational flexibility of the pyridine ring in the BPY linker and then making it easier to trigger the structural transformation in $\text{Zn}(\text{AIP})(\text{BPY})_{0.5}$. The calculated Brunauer-Emmett-Teller (BET) areas were 260, 355, and 244 m^2/g for $\text{Co}(\text{AIP})(\text{BPY})_{0.5}$, $\text{Ni}(\text{AIP})(\text{BPY})_{0.5}$, and $\text{Zn}(\text{AIP})(\text{BPY})_{0.5}$, respectively. Besides, thermogravimetric analysis (TGA) confirmed that the three MOFs were stable below 350 $^\circ\text{C}$ under air (Figure S2). Scanning electron microscopy (SEM) images revealed that the crystal morphologies of the three MOFs were relatively long lamellate particles (Figure S3).

Figure 2. CO_2 adsorption-desorption isotherms at 195 K of $M(\text{IPA})(\text{BPY})_{0.5}$ ($M = \text{Co}, \text{Ni}, \text{and Zn}$).

2.2. Thermodynamic adsorption of propylene and propane.

Due to the presence of OMS for each metal node in the pillar-layer structures, C_3H_6 can form strong π -complexation interactions with OMSs and thus the three MOFs have the feasibility of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation. Motivated by this point, single-component sorption isotherms of C_3H_6 and C_3H_8 at three temperatures (288, 298, and 308 K) were measured to test their $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation performances. As demonstrated in Figure 3a-3c, the C_3H_6 sorption isotherms of the three MOFs showed a type I feature that steep sorption curves were observed in the relatively low pressure region, meaning strong adsorption interactions between C_3H_6 and the three frameworks, due to the existence of π -complexation interactions toward C_3H_6 in these microporous materials. Particularly, no gate-opening behavior of C_3H_6 sorption was observed in $\text{Zn}(\text{AIP})(\text{BPY})_{0.5}$, excluding

the gate-opening separation mechanism. At 298 K and 1 bar, the saturated uptakes of C_3H_6 were 1.99, 1.94, and 1.87 mmol/g for $Co(AIP)(BPY)_{0.5}$, $Ni(AIP)(BPY)_{0.5}$, and $Zn(AIP)(BPY)_{0.5}$, respectively. As the temperature increased (308 K) or decreased (288 K), similar trends of the C_3H_6 sorption isotherms were retained. In contrast, the C_3H_8 sorption isotherms were nearly linear, in which the C_3H_8 uptakes monotonously increased with the increase of pressure under these measured conditions, due to the relatively weak MOF- C_3H_8 interactions. The C_3H_8 uptakes were remarkably lower than those of C_3H_6 for each MOF at the same measured temperature. Although the C_3H_6 uptakes of the three MOFs were closely similar, the differences in the C_3H_8 uptakes at the same temperature were more obvious. The Ni-based MOF had the smallest C_3H_6 uptakes among them. At 298 K and 1 bar, the C_3H_8 uptakes of $Co(AIP)(BPY)_{0.5}$, $Ni(AIP)(BPY)_{0.5}$, and $Zn(AIP)(BPY)_{0.5}$ were 0.49, 0.45, and 0.59 mmol/g, respectively. The obvious differences in C_3H_6 and C_3H_8 uptakes preliminarily verified the feasibility of the three MOFs for C_3H_6/C_3H_8 separation.

Figure 3. C_3H_6 and C_3H_8 sorption isotherms of (a) $Co(AIP)(BPY)_{0.5}$, (b) $Ni(AIP)(BPY)_{0.5}$, and (c) $Zn(AIP)(BPY)_{0.5}$. (d) Ratio of C_3H_6 and C_3H_8 uptakes at 298 K and 1 bar.

To evaluate the C_3H_6/C_3H_8 separation performance of the three MOFs, the C_3H_6/C_3H_8 uptake ratio at 298 K was calculated (Figure 3d), an important significant index for separation selectivity. The values of the record-high C_3H_6/C_3H_8 uptake ratios of $Co(AIP)(BPY)_{0.5}$, $Ni(AIP)(BPY)_{0.5}$, and $Zn(AIP)(BPY)_{0.5}$ were 4.07, 4.26 and 3.16, respectively. These values are highly higher than those of the MOFs based on the thermodynamic effect for C_3H_6/C_3H_8 separation, such as $Cu(0.6)@MIL-100(Fe)$ (1.34),³⁸ $Cu-BTC$ (1.12),³⁹ $Mn_2(m-dobdc)$ (1.25),²² $Mg-MOF-74$ (1.33),⁴⁰ $Mn_2(dobdc)$ (1.31),³¹ $MAF-23-O$ (1.17),⁸ $SIFSIX-2-Cu-I$ (1.59),² $ZnAtzPO_4$ (1.79),³³ but much lower than those of molecular sieving separation of C_3H_6/C_3H_8 including Co-gallate,¹ $NbOFFIVE-1-Ni$,²³ $Y-abtc$.²⁴ The results confirmed that the three MOFs would be new benchmark MOF adsorbents for C_3H_6/C_3H_8 separation via thermodynamic effect.

Then the adsorbed solution theory (IAST) was used to assess the separation selectivity of the C_3H_6/C_3H_8 (50:50, v/v) mixture.⁴¹ Although $Co(AIP)(BPY)_{0.5}$ and $Zn(AIP)(BPY)_{0.5}$ both had remarkably high C_3H_6/C_3H_8 selectivities of 21 and 20 at 1 bar, $Ni(AIP)(BPY)_{0.5}$ showed the highest IAST-predicted selectivity of C_3H_6/C_3H_8 at 298 K among the three MOFs in Figure 4a. It means that the Ni mode in the pillar-layer structure has the best separation performance among a series of transition metals (Co, Ni,

and Zn). The selectivity was calculated to be 31 at 1 bar, which is remarkably higher than most reported MOFs under similar conditions, such as $\text{Fe}_2(\text{dobdc})$ (15), $^{42}\text{Cr}_3(\text{btc})_2$ (3), $^{42}\text{Cu}_3(\text{btc})_2$ (6), $^{42}\text{MAF-23}$ (3),⁸ and MAF-23-O (9),⁸ meaning the potential for efficient $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation.

Moving forward, the isosteric heat of adsorption (Q_{st}), a key thermodynamic parameter, was calculated to evaluate the interactions between C_3H_6 molecules and the three MOF frameworks by using the Virial equation and the isotherms at the three temperatures (Figures 3a-3c, S4-S6, and Table S1). The Q_{st} values of $\text{Ni}(\text{AIP})(\text{BPY})_{0.5}$ (48.70-49.75 kJ/mol) and $\text{Co}(\text{AIP})(\text{BPY})_{0.5}$ (41.79-40.22 kJ/mol) slightly decreases as the adsorbed uptake increased while the Q_{st} values of $\text{Zn}(\text{AIP})(\text{BPY})_{0.5}$ remained almost constant (40.67-40.64 kJ/mol), indicating that the pore surfaces of $\text{Zn}(\text{AIP})(\text{BPY})_{0.5}$ are more homogeneous than those of $\text{Ni}(\text{AIP})(\text{BPY})_{0.5}$ and $\text{Co}(\text{AIP})(\text{BPY})_{0.5}$.⁴³ It is observed that the Q_{st} values of $\text{Ni}(\text{AIP})(\text{BPY})_{0.5}$ are much higher than those of Co-MOF and Zn-MOF, meaning that the interactions of C_3H_6 toward the Ni-based framework are much stronger than those of Co- and Zn-based frameworks. Furthermore, the interactions between C_3H_6 and the Co-MOF or Zn-MOF are closely similar due to the close Q_{st} values under each C_3H_6 loading. Compared to the Zn-MOF, the Co-MOF had higher Q_{st} values at the initial C_3H_6 loading due to the larger steric hindrance in the narrow channels within the pillar-layer framework. The related reasons will be further discussed in the following section. From the perspective of thermodynamic effect, it further confirms that the Ni-MOF shows the best $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation performance among the three MOFs.

Figure 4. (a) IAST-predicted selectivities of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ (50:50, v/v) at 298 K for $\text{M}(\text{IPA})(\text{BPY})_{0.5}$ ($\text{M} = \text{Co}, \text{Ni}, \text{and Zn}$). (b) Isosteric heats of isotherms of C_3H_6 on $\text{M}(\text{IPA})(\text{BPY})_{0.5}$ ($\text{M} = \text{Co}, \text{Ni}, \text{and Zn}$).

2.3. Kinetic adsorption of propylene and propane.

For the industrial applications, kinetic adsorption tests were also performed by measuring the time-dependent adsorbed amount profiles of C_3H_6 and C_3H_8 at 303 K and 0.5 bar to provide more insights into the sorption behaviors of the three MOFs (Figure S7-S9). As shown in Figure S7, the C_3H_6 and C_3H_8 uptakes of $\text{Co}(\text{AIP})(\text{BPY})_{0.5}$ reached equilibrium within about 36 and 81 min at 303 K, respectively. For the kinetic sorption of $\text{Ni}(\text{AIP})(\text{BPY})_{0.5}$ in Figure S8, the kinetic uptake of C_3H_6 was highly faster than that of C_3H_8 . The initial C_3H_6 uptake increased steeply within 1 min and reached 1.21 mmol/g at 1 min. Then continuous increase in C_3H_6 uptake was observed until 100 min. In contrast, it was observed a nearly linear increase in the uptake of C_3H_8 as the function of time, indicating its slow diffusion. However, the respective equilibrium times of C_3H_6 and C_3H_8 for $\text{Zn}(\text{AIP})(\text{BPY})_{0.5}$ were about merely 1 and 4 min, demonstrating the corresponding fastest diffusion rates of C_3H_6 and C_3H_8 in the three pillar-layer structures. Then the micropore diffusion model was selected to fit the dynamic adsorption profiles (Figure 5). The diffusion time constants (D') of C_3H_6 were calculated to be 0.0036, 0.1012, and 0.4934 at 303 K for $\text{Co}(\text{AIP})(\text{BPY})_{0.5}$, $\text{Ni}(\text{AIP})(\text{BPY})_{0.5}$, and $\text{Zn}(\text{AIP})(\text{BPY})_{0.5}$, respectively, following the order of $\text{Co-MOF} < \text{Ni-MOF} < \text{Zn-MOF}$ toward C_3H_6 diffusion in the pillar-layer frameworks. Meantime, the corresponding values of C_3H_8 were 0.0005, 0.0011, and 0.0348 for the three MOF frameworks, obviously lower than that of respective C_3H_6 , due to the bulkier C_3H_8 molecule resulting in larger steric hindrance and consequently leading to lower diffusion rate within the micropores. As a result, the kinetic selectivities of $\text{Co}(\text{AIP})(\text{BPY})_{0.5}$, $\text{Ni}(\text{AIP})(\text{BPY})_{0.5}$, and $\text{Zn}(\text{AIP})(\text{BPY})_{0.5}$ were determined to be 7.2, 92.0, and 14.2, respectively. From the perspective of kinetic effect, it also verifies

that the Ni-MOF has the best C_3H_6/C_3H_8 separation performance among the three MOFs, which Ni-MOF can shorten the industrial operating time and enhance the whole productivity of C_3H_6/C_3H_8 separation.

Figure 5. Linear fittings of C_3H_6 (solid) and C_3H_8 (open) on $M(AIP)(BPY)_{0.5}$ ($M = Co, Ni, \text{ and } Zn$) for the calculation of diffusional time constant at 303 K.

2.4. Molecular simulations of gas adsorption mechanism.

To reveal the adsorption mechanism in the three pillar-layer structures, molecular simulations were performed to investigate the preferential binding sites of C_3H_6 in the frameworks. The calculated results in Figure 6 demonstrated that C_3H_6 molecules were mainly concentrated in the center of the 1D channels in Co- and Zn-based pillar-layer frameworks, whereas Ni-based counterpart exhibited a more dense and bulky binding space for C_3H_6 molecules in the channels. In addition, the interaction energy distributions of a single C_3H_6 molecule in the three MOFs were calculated in Figure S10, in which the interaction energy distributions were located in the ranges of -16.55 -9.15, -16.55 -9.45, and -15.75 -8.55 kcal/mol for $Co(AIP)(BPY)_{0.5}$, $Ni(AIP)(BPY)_{0.5}$, and $Zn(AIP)(BPY)_{0.5}$, respectively. Although the interaction energy distributions in the Co-MOF are close to those in Ni-MOF, the peak width of C_3H_6 could be another way to reveal the interaction affinity between C_3H_6 and the framework. The peak width follows the order: $Ni(AIP)(BPY)_{0.5}$ (2.04 kcal/mol) > $Zn(AIP)(BPY)_{0.5}$ (1.90 kcal/mol) > $Co(AIP)(BPY)_{0.5}$ (1.45 kcal/mol), well consistent with the results of C_3H_6 adsorption density distributions in Figure 6, further verifying that the Ni nodes are more preferential for adsorbing C_3H_6 compared to the corresponding Co and Zn nodes in the targeted structures. Moreover, the adsorption configuration of C_3H_6 also demonstrated a relatively closer interaction distance from the wall of pores in $Ni(AIP)(BPY)_{0.5}$ and $Zn(AIP)(BPY)_{0.5}$ compared to that of $Co(AIP)(BPY)_{0.5}$. These observations explained why the C_3H_6 uptake and C_3H_6/C_3H_8 selectivity of the Co-MOF in the low pressure region are relatively lower than those of the corresponding Ni- and Zn-MOFs in Figure 3a and 4a under the same conditions.

Figure 6. Adsorption density distribution at 298 K and 1 bar, and the adsorption configuration of C_3H_6 in $M(AIP)(BPY)_{0.5}$ ($M = Co, Ni, \text{ and } Zn$).

Apart from the thermodynamic differences in the three MOFs, the diffusion behaviors of C_3H_6 in the pores were also examined by using molecular dynamic simulations to investigate the kinetic characteristics. As shown in Figure 7, we simulated a 20 ns diffusion process of C_3H_6 passing through the 1D channels in the three MOFs. In the case of $Zn(AIP)(BPY)_{0.5}$, the C_3H_6 molecule migrated forward about 6.73 Å in the first 10 ns and 7.95 Å in the second 10 ns, which is faster than that in the case of $Ni(AIP)(BPY)_{0.5}$. It is interesting that in the case of $Co(AIP)(BPY)_{0.5}$, the C_3H_6 molecule migrated backward in the second 10 ns, indicating that the diffusion of C_3H_6 has been hindered in the 1D narrow channels of $Co(AIP)(BPY)_{0.5}$. These calculated results are consistent with our experiments in Figure 5.

Figure 7. Molecular dynamic (MD) simulation of C_3H_6 passing through the 1D channels of $M(AIP)(BPY)_{0.5}$ ($M = Co, Ni, \text{ and } Zn$). The metal atoms color code: Zn (green), Ni (cyan), Co (pink). The C_3H_6 molecule colored by brown, red and salmon indicated a snapshot of MD simulation in 0, 10, and 20 ns, respectively.

2.5. Breakthrough Experiments and Cycling Tests.

Motivated by the corresponding highest thermodynamic and kinetic selectivities of C_3H_6/C_3H_8 mixture among the three MOFs, breakthrough experiments of the pillar-layer Ni-based MOF with uniform but narrow pore structure were performed to assess the actual separation performance of C_3H_6/C_3H_8 under ambient conditions. From the breakthrough curves illustrated in Figure 8a, the results indicated that $Ni(AIP)(BPY)_{0.5}$ could be a highly promising adsorbent for efficient C_3H_6/C_3H_8 separation. Obviously, C_3H_8 component was quickly eluted through the packed column after 3.4 min whereas C_3H_6 was trapped in the adsorption bed until nearly 8.5 min. The retention time of C_3H_6 is 2.5 times more than that of C_3H_8 . The obvious breakthrough time interval between C_3H_6 and C_3H_8 means that $Ni(AIP)(BPY)_{0.5}$ is highly effective for C_3H_6/C_3H_8 separation. The high practical C_3H_6/C_3H_8 selectivity of $Ni(AIP)(BPY)_{0.5}$ should be contributed by the thermodynamic-kinetic synergetic effect. Furthermore, the elution of C_3H_6 was accompanied by an obvious roll-up phenomenon of C_3H_8 with a C/C_0 value up to 1.4, suggesting that the already adsorbed C_3H_8 molecules were largely displaced by C_3H_6 , indicative of the stronger competition adsorption of C_3H_6 over C_3H_8 on the OMSs of $Ni(AIP)(BPY)_{0.5}$. In addition, cycling breakthrough experiments were performed to check the recycle ability. During 5 consecutive cycles, there were no obvious

differences in the breakthrough time and time interval for C_3H_6/C_3H_8 mixtures, confirming good recycle ability of $Ni(AIP)(BPY)_{0.5}$ and favorable feature for industrial applications.

Figure 8. (a) Breakthrough curves of C_3H_6/C_3H_8 (50/50, v/v) mixture on $Ni(AIP)(BPY)_{0.5}$ at 298 K and 1 bar for five cycles. (b) C_3H_6 sorption isotherms at 298 K of $Ni(AIP)(BPY)_{0.5}$ after moisture and water tests.

2.6. Moisture and Water Stability Tests.

Since material stability is another important factor to be considered in practical applications, moisture and water tests were carried out after being exposed to humid conditions (RH 80%) and soaked in water for 3 days, respectively. The PXRD patterns in Figure S11 showed no obvious difference in the crystallinity of the robust $Ni(AIP)(BPY)_{0.5}$ framework, confirming that the structure remained intact and no phase transition occurred. Moreover, the C_3H_6 sorption isotherms revealed that the C_3H_6 uptakes of the moisture-exposed and water-soaked $Ni(AIP)(BPY)_{0.5}$ remained almost no decreased (Figure 8b). These results allow for $Ni(AIP)(BPY)_{0.5}$ as a promising adsorbent for industrial separation of C_3H_6/C_3H_8 separation.

3. CONCLUSIONS

In summary, we have reported a series of pillar-layer MOFs constructed by different transition metals (Co, Ni, and Zn) for C_3H_6/C_3H_8 separation. For the three MOFs, thermodynamic and kinetic results confirm that $Ni(AIP)(BPY)_{0.5}$ has the best of C_3H_6/C_3H_8 separation performance. The origin of the thermodynamic-kinetic synergetic effect on C_3H_6/C_3H_8 separation simultaneously comes from the OMSs on the metal node and optimal pore structure, enabling strong adsorption interactions toward C_3H_6 molecules while impeding the diffusion of bulkier C_3H_8 molecules. In this context, $Ni(AIP)(BPY)_{0.5}$ ranks as a new benchmark for efficient purification of C_3H_6 with a remarkably high C_3H_6 and C_3H_8 uptake ratio of 4.26 at 298 K and 1 bar. Computational results reveal the most uniform binding sites of C_3H_6 within these 1D narrow channels and also verify the obvious difference in diffusion rates of C_3H_6 among the three MOFs. The outstanding C_3H_6/C_3H_8 separation performance on $Ni(AIP)(BPY)_{0.5}$ is confirmed by breakthrough experiments. In addition, $Ni(AIP)(BPY)_{0.5}$ has good recycling capability, excellent water and moisture stabilities, which are favorable features for practical applications. This work provides an example that capitalizing on both thermodynamic and kinetic separation mechanisms is an effective strategy to achieve efficient C_3H_6/C_3H_8 separation.

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