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Construction of a Ti-Based Bimetallic Metal–Organic Framework Using a One-Pot Method for Efficient C_2H_2/C_2H_4 and C_2H_2/CO_2 Separation

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ABSTRACT: Titanium (Ti)-based metal-organic frameworks (Ti-MOFs) have attracted intensive research attention due to their low toxicity and high abundance of titanium. However, limited by the high reactivity of titanium species in the reaction system, the construction of Ti-MOFs still faces great challenges. Herein, we successfully introduced Ti into MOF-74 using a one-pot method. Powder X-ray diffraction (PXRD) combined with X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma (ICP) spectroscopy confirmed that the Ti(IV) ions were uniformly inserted into the MOF-74 structure. Our scanning electron microscopy (SEM)/energy-dispersive spectrometry (EDS) analysis showed that the Ti content was up to 44% with good sample homogeneity. The adsorption selectivity of $Ti_{0.44}$ /Ni_{0.56}-MOF-74 at 1.0 bar and 298 K for C_2H_2/C_2H_4 and C_2H_2/CO_2 (50/50, v/v) mixtures was 4.9 and 6.8, respectively, which are higher than that of pristine Ni-MOF-74. The results of our breakthrough simulation experiments revealed that the adsorption and separation performances of Ti_{0.44}/Ni_{0.56}-MOF-74 were greatly



improved. This study provided insights for the construction of Ti-based bimetallic MOFs used for the separation of light hydrocarbons.

KEYWORDS: Ti-based bimetallic MOF, one-pot method, adsorption separation, C_2H_2/C_2H_4 , C_2H_2/CO_2

INTRODUCTION

Metal–organic frameworks (MOFs), which are constructed by connecting inorganic nodes and organic linkers,^{1,2} exhibit high porosity, large surface area, and highly ordered crystallinity, as well as structural and functional tailorability.³ These intrinsic features make MOFs an appealing class of materials for gas separation and storage,^{4–6} isotopologue separation,⁷ sensing, and heterogeneous catalysis.^{8–10} As one group of M(IV)-based metal–organic frameworks (M^{IV}-MOFs), Ti-MOFs have attracted considerable and sustained research attention due to the fascinating intrinsic characteristics of titanium, such as high abundance, low toxicity, and unique photo-oxidation properties.

Ti-MOFs have been widely studied by researchers in the field of low carbon hydrocarbon separation. Separation and purification of light hydrocarbons is a crucial process for the production of advanced energy and fine chemicals.¹¹ Ethylene (C_2H_4) and acetylene (C_2H_2) are the main raw material for the petrochemical industry.¹² The production process of C_2H_4 is often accompanied by a small amount of C_2H_2 impurities (<1%). In industry, the C_2H_2 content in polymer grade C_2H_4 should be less than 40 μ L/L; otherwise, it may cause catalyst

poisoning or even stop the polymerization reaction.¹³ In addition, CO₂ is produced together during the production of C_2H_2 through the thermal cracking process.¹⁴ Therefore, achieving efficient separation of C_2H_2/C_2H_4 and C_2H_2/CO_2 is very important.¹⁵ In 2020, Gao et al. studied the C_2H_2/CO_2 separation performance of NTU-9.¹⁶ Benefiting from the vast number of polar oxygen atoms on the surface of its one-dimensional (1-D) channel, this material has a high C_2H_2 adsorption capacity of 118 cm³·g⁻¹ and C_2H_2/CO_2 selectivity of 3.5 under ambient conditions. In our previous work, we synthesized a series of Ti-MOFs¹⁷ (MIL-125, NH₂-MIL-125, MUV-11, and ZSTU-2) and studied their $C_2H_2/C_2H_6/C_2H_4$ separation performance. The results showed that all MOFs exhibited high adsorption of C_2H_2 and C_2H_6 compared to

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 C_2H_4 , and low concentrations of C_2H_6 and C_2H_2 could be effectively separated from the $C_2H_2/C_2H_6/C_2H_4$ ternary mixtures. In 2022, Li et al. reported a titanium-based metal– organic framework, ZSTU-1, which could remove C_2H_6 from C_2H_6/C_2H_4 mixtures.¹⁸ As some of the terminal ligands, such as water and –OH groups, grafted on the Ti–O nanorods avoid the open metal sites (OMS), the π -complexation between the unsaturated olefin and the OMS can be suppressed, creating a suitable pore environment for C_2H_6 adsorption through multiple hydrogen bonds and C–H… π interactions.

Although Ti-MOFs have promising applications in the separation of low-carbon hydrocarbons, their synthesis still faces great challenges. Limited by the extreme reactivity of their titanium precursors, the synthesis of Ti-MOFs is relatively difficult when compared to other MOFs composed of di- and trivalence metal clusters. MOFs based on titaniumoxo clusters are rare and only provide a very small fraction (<0.1%) of those reported when compared to MOFs based other metal clusters.¹⁹ Over the past decades, researchers have exhausted many methodologies to overcome the challenges of synthesizing Ti-MOFs. Initially, in situ SBU (secondary building unit) construction methods link metal clusters as starting reagents with organic linkers, which can overcome the difficulty of the reversible bond association/dissociation process in Ti-MOF synthesis because of the strong Ti-O bond.²⁰⁻²² However, this method is extremely dependent on Ti-oxo clusters with moderate stability. Subsequently, researchers have creatively proposed the postsynthetic modification (PSEM),²³⁻²⁵ which has been used to synthesize a series of heterometallic Ti/M-MOFs.^{26,27} However, the PSEM strategy creates an MOF@TiO₂ composite rather than a mixed metal-organic framework.²⁸ Another synthesis strategy proposed by researchers is the one-pot Ti incorporation during the synthesis of MOFs. This method appears less controversial when compared with the two methods mentioned beforehand and does not question the actual Ti metathesis by PSEM, which presents unique advantages during the preparation of Ti-MOFs.²⁹⁻³¹

In this work, a new bimetal metal—organic framework (Ti/Ni-MOF-74) with a Ti/Ni ratio of 0.44/0.56 was synthesized using a one-pot method.³² Using a finely tuned organic solvent and ratio of the reacted solution mixture and, in particular, a slow heating rate, a series of Ti/Ni-MOF-74 were obtained with well-maintained crystallinity. In depth characterization demonstrated that Ti was inserted in the rodlike inorganic building unit and measured the ratio of Ti. In addition, single-component isotherm measurements and breakthrough simulation experiments revealed that separation performance of Ti/Ni-MOF-74 for C_2H_2/C_2H_4 and C_2H_2/CO_2 .

EXPERIMENTAL SECTION

Characterization. On a Bruker D8 ADVANCE X-ray diffractometer, powder X-ray diffraction (PXRD) patterns were obtained for Cu K α ($\lambda = 1.5418$ Å) radiation, operating at a voltage and current of 40 kV and 40 mA, respectively, and scanning over the 2θ range from 5 to 40° at a speed of 5° min⁻¹. Scanning electron microscopy (SEM) was performed on a ZEISS Gemini 300 instrument at an accelerating voltage of 3 kV. Energy-dispersive spectrometry (EDS) was carried out on a Smart EDX system with X-ray mapping at an accelerating voltage of 15 kV. Thermogravimetric (TGA) analysis of the samples was performed on a Netzsch STA449 F5 differential thermal analyzer with a temperature range of 300–1,073 K, a ramp rate of 10 K·min⁻¹, and an air purge of 100 mL·min⁻¹ maintained during the test. The N₂

adsorption–desorption isotherms at 77 K and the single-component gas adsorption isotherms for $C_2H_{2^{\prime}}$, $C_2H_{4^{\prime}}$ and CO_2 at 298 K were measured by an APSP 2460 and Intelligent Gravimetric Analyzer (IGA 001), respectively. Before the tests, the samples were degassed at 353 K and 1 × 10⁻⁵ mbar for 8 h. The X-ray photoelectron spectroscopy (XPS) spectra of Ni-MOF-74 and Ti/Ni-MOF-74 were obtained on a Thermo Scientific K-Alpha spectrometer using an excitation source composed of Al K α at 12 kV and 6 mA. The Ti and Ni contents were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) on an Agilent 5110 (OES) instrument.

Materials. The 2,5-dihydroxyterephthalic acid (H_4DOBDC , 99%) was obtained from Sinopharm Chemical Reagent Co., Ltd. Titanium-(IV) isopropoxide [Ti(OⁱPr)₄, 98%], nickel nitrate [Ni(NO₃)₂·6H₂O, AR, 98%], dimethylformamide (DMF, AR, >99.5%), and ethanol (EtOH, AR) were all used as received without further purification.

Synthesis of Ni-MOF-74. H_4DOBDC (0.183 g, 1 mmol), Ni(NO₃)₂·6H₂O (0.291 g, 1 mmol), and DMF (6 mL) were added to a 25 mL glass bottle. After stirring at room temperature for 1 h, the solution was heated in a sealed glass vial for 24 h at 363 K, followed by being heated at 393 K for 55 h. After the reaction, the resulting precipitate was separated from the brownish-green suspension and thoroughly washed with fresh EtOH for 48 h (6 times). Subsequently, the sample was treated under a vacuum at 353 K for 8 h to obtain the final Ni-MOF-74.

Synthesis of Tix/Niy-MOF-74. H_4DOBDC (0.183 g, 1 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.262 g, 0.9 mmol), $Ti(OiPr)_4$ (0.03 mL, 0.1 mmol), and DMF (6 mL) were added to a 25 mL glass bottle. After stirring at room temperature for 1 h, the solution was heated in a sealed glass vial for 24 h at 363 K, followed by heating at 393 K for 55 h. After the reaction, the resulting precipitate was separated from the brown suspension and thoroughly washed with fresh EtOH for 48 h (six times). Subsequently, the sample was treated under vacuum at 353 for 8 h to obtain the final $Ti_{0.09}/Ni_{0.91}$ -MOF-74. Ti/Ni-MOF-74 with different Ti contents (the highest ratio of $Ti(OiPr)_4$ to $Ni(NO_3)_2 \cdot 6H_2O$ was 0.3) was also achieved by varying the Ti and Ni ratio used in the reaction solution. When the ratio of $Ti(OiPr)_4$ to $Ni(NO_3)_2 \cdot 6H_2O$ is 0.2, we get $Ti_{0.25}/Ni_{0.75}$ -MOF-74, and when the ratio is 0.3, we get $Ti_{0.44}/Ni_{0.56}$ -MOF-74. The resultant solids were activated via the same procedure as $Ti_{0.09}Ni_{0.91}$ -MOF-74.

Computational details and a theoretical model.

(1) Isosteric heats of adsorption (Q_{st}) : The Q_{st} of the samples was calculated from the adsorption isotherms of C_2H_2 , C_2H_4 , and CO_2 measured at 273 and 298 K, respectively. The isotherms were fitted to the virial equation shown in eq 1

$$\ln P = \ln q_{e} + \frac{1}{T} \sum_{i=1}^{m} a_{i} q_{e}^{i} + \sum_{i=0}^{m} b_{i} q_{e}^{i}$$
(1)

where *P* is the pressure of the gas phase, q_e is the total amount of gas adsorption equilibrium at pressure *P*, *a* and *b* are virial coefficients, and *m* and *n* are the numbers of coefficients required to describe the isotherm adequately. Using the fitting parameters obtained from eq 1, Q_{st} was calculated according to eq 2.

$$Q_{\rm st} = -R \sum_{i=1}^{m} a_i N^i \tag{2}$$

where R is the universal gas constant.

(2) Ideal adsorbed solution theory (IAST) gas selectivity: The IAST method was used to evaluate the competitive separation abilities of samples for different gases, as described by Myers and Prausnitz.³⁵ Initially, the dual-site Langmuir model, shown in eq 3, was used to fit the adsorption isotherms.

$$q_{\rm e} = \frac{q_{\rm l,m}p}{k_{\rm l}+p} + \frac{q_{\rm 2,m}p}{k_{\rm 2}+p}$$
(3)

where $q_{1,m}$ and $q_{2,m}$ are the saturation capacities of the adsorbate at sites 1 and 2, respectively, while k_1 and k_2 are the



Figure 1. One-step synthesis of Ti/Ni-MOF-74. Ti in yellow, Ni in green, Ti in orange, C in gray, and O in red. H atoms were omitted for clarity.



Figure 2. (a–d) Microphotograph and (e) PXRD patterns obtained for Ni-MOF-74, $Ti_{0.09}/Ni_{0.91}$ -MOF-74, $Ti_{0.25}/Ni_{0.75}$ -MOF-74, and $Ti_{0.44}/Ni_{0.56}$ -MOF-74.



Figure 3. Microphotograph of Ti/Ni-MOF-74 synthesized using (a) TiBALD and (b) Ti(OBu)₄. (c) PXRD of Ti/Ni-MOF-74 prepared from TiBALD and Ti(OBu)₄.

affinity parameters on sites 1 and 2, respectively, and P is the total pressure (bar).

According to the fitting parameters of $q_{1,m}$, $q_{2,m}$ and k_1 , k_2 , the two-component gas selectivity calculation formula was defined using eq 4.

,

$$S_{\rm ads} = \frac{q_1/q_2}{p_1/p_2} \tag{4}$$

where q_1 and q_2 are the equilibrium adsorption amounts of different gases at the corresponding partial pressures p_1 and p_2 in the gas-phase pressure, respectively.

(3) Breakthrough simulations were performed using a single tower direct breakthrough model for the feed gas and the adsorption bed parameters shown in Table S7. C₂H₂/C₂H₄ and C₂H₂/ $\rm CO_2$ mixtures with a volume ratio of 50/50 were evaluated, and the adsorption pressures (absolute pressures) set to 1.0 bar. In order to fully utilize the performance of the adsorption column, the feed gas flow rates in the simulation were set to 2 mL·min⁻¹. The modeling of the dynamic adsorption process in the adsorption bed and model simplification assumptions were adopted from our previous work.³⁴

RESULTS AND DISCUSSION

Ti-substituted Ni-MOF-74 (denoted as Ti_x/Ni_y -MOF-74, where *x* represents the ratio of Ti according to ICP-OES) was prepared by mixing a different ratio of the titanium precursor with Ni(NO₃)₂·6H₂O in the reaction solution (Figure 1). Titanium isopropoxide was used, and the ratio of Ti/Ni in the structure of MOF-74 reached 44% (detailed data in Table S1). As the ratio of Ti increased to 44%, the solid's color turned from yellowish-green to reddish-brown (Figure 2a-d).

The prepared Ni-MOF-74 samples have similar XRD spectra and comparable BET surface area (882.3 $m^2 \cdot g^{-1}$) compared to those previously reported,³⁵ which suggested that the prepared Ni-MOF-74 is of high quality. The as-synthesized series of Ti/ Ni-MOF-74 microcrystalline powders were characterized using PXRD. Figure 2e shows that the diffraction peaks of the modified material closely matched those of Ni-MOF-74, indicating that Ti/Ni-MOF-74 was successfully synthesized via the one-pot method. We performed the synthesis using various Ti/Ni ratios from 0 to 0.44, while further increasing the Ti content led to gelation of the sample and we were unable to synthesize the target materials.³⁶ To demonstrate the feasibility of the above idea, we used two other organic titanium precursors, TiBALD and Ti(OBu)₄, instead of $Ti(O^{1}Pr)_{4}$ in the synthesis, which could be successfully used (Figure 3, the specific synthesis process is described in the Supporting Information). We proposed a possible mechanism for the synthesis, in which, when titanium isopropyl alcohol was added into a DMF solution containing 2,5-dihydroxyterephthalic acid and nickel nitrate, the DOBDC replaced the methoxy group of $Ti(O'Pr)_4$ to form a complex. Ni ions in the solution then replaced the Ti ions in the complex and continued to grow, ultimately forming a bimetallic framework material (Figure 4).



Figure 4. Possible mechanism for the synthesis of Ti/Ni-MOF-74.

The collected SEM images were used to observe the crystal morphologies of Ni-MOF-74 and Ti/Ni-MOF-74. It is clear that the crystallite size and morphology of the mixed-metal samples are very similar up to a titanium content of 44%, but from this content onward, the particle size gradually decreases. The SEM images and diffraction peaks of Ti/Ni-MOF-74 showed that the crystallinity of the material decreased when the content of Ti increased (Figure S3). EDS was also performed to characterize the presence and dispersion of Ti ions in the Ti/Ni-MOF-74 sample. As expected, the Ti species in Ti/Ni-MOF-74 were uniformly spread over the whole crystalline particle (Figure Se,f).

The N₂ adsorption–desorption isotherms of pristine Ni-MOF-74 and Ti/Ni-MOF-74 were measured at 77 K to investigate the effect of introducing metal atoms on the BET surface area and pore size distribution of the framework (Figure 6b, Figure S1b, and Figure S2). The obtained isotherms exhibit a typical type I profile, indicating that the structures of both materials have a microporous structure. The experimentally measured BET surface area obtained for Ti_{0.44}/Ni_{0.56}-MOF-74 was 402.4 m²·g⁻¹ (Langmuir Surface Area 519.8 m²·g⁻¹), which was lower that of Ni-MOF-74 (BET Surface Area 882.3 m²·g⁻¹) or Langmuir Surface Area 1097.1 m²·g⁻¹). Under the reaction conditions (using DMF/water as solvent), the high reactivity and easy hydrolysis of titanium isopropoxide were expected to be accountable for the poor crystallinity.³⁶

The thermal stabilities of Ni-MOF-74 and Ti/Ni-MOF-74 were examined using TGA. Figure 6a and Figure S1a show Ti/ Ni-MOF-74 was less stable than Ni-MOF-74. The chemical state of Ti in the framework was probed by XPS (Figure 6c,d and Figure S1c,d). Compared with Ni-MOF-74, Ti/Ni-MOF-74 showed two distinct peaks at 457.88 and 464.78 eV, representing the binding energies of Ti 2p1/2 and 2p3/2, respectively.³⁷ This result suggested that the charge state of Ti in the framework was +4.

Encouraged by the pore environment changed with Ti(IV) sites, the adsorption behaviors of Ti/Ni-MOF-74 and Ni-MOF-74 were investigated using pure-component CO_2 , C_2H_4 , and C_2H_2 at 298 and 273 K up to 1.0 bar. The C_2H_2 , C_2H_4 , and CO_2 isotherms are depicted in Figure 7 and Figures S8 and S9, respectively, and a summary of the gas adsorption data is given in Table 1. By analyzing the data, we found that Ti_{0.44}/Ni_{0.56}-MOF-74 adsorbed more C_2H_2 than C_2H_4 under the same conditions. At 298 K and 1.0 bar, the C_2H_2 uptake of Ti_{0.44}/Ni_{0.56}-MOF-74 was 127.5 cm³·g⁻¹, while the C_2H_4 and CO_2 uptake was almost one-third of C_2H_2 (45.3 and 46.6 cm³·g⁻¹, respectively). The reason is that the crystallinity of Ti/Ni-MOF-74 decreases and the BET area decreases after Ti is introduced. Although the adsorption capacity of Ti_{0.44}/Ni_{0.56}-MOF-74, was lower than the benchmark material, Ni-MOF-74,



Figure 5. SEM/EDX mapping of Ni-MOF-74 (a-c) and Ti_{0.44}/Ni_{0.56}-MOF-74 (d-f).



Figure 6. (a) TGA curves, (b) N_2 adsorption isotherms obtained at 77 K, (c) XPS spectra, and (d) local XPS spectra (Ti 2p spectra) obtained for Ni-MOF-74 and Ti_{0.44}/Ni_{0.56}-MOF-74.



Figure 7. Dual-site Langmuir (DSL) fit of C_2H_2 , C_2H_4 , and CO_2 adsorption isotherms in Ni-MOF-74 (a) and $Ti_{0.44}/Ni_{0.56}$ -MOF-74 (b).

Table 1. Gas Adsorption and Selectivity Results (298 K)

	adsorption uptake $(cm^3 \cdot g^{-1})$			selectivity	
	C_2H_2	C_2H_4	CO ₂	$\begin{array}{c} C_2H_2/\\ C_2H_4 \end{array}$	$\begin{array}{c} C_2H_2/\\CO_2 \end{array}$
Ni-MOF-74	182.2	100.5	95.9	3.3	6.1
Ti _{0.09} /Ni _{0.91} -MOF-74	151.6	76.4	74.5	3.5	5.9
Ti _{0.25} /Ni _{0.75} -MOF-74	138.1	61.4	57.8	4.2	8.2
${\rm Ti}_{0.44}/{\rm Ni}_{0.56}$ -MOF-74	127.5	45.3	46.5	4.9	6.8

this value is still high and comparable to many adsorbents, such as UTSA-74a (107.4 cm³·g⁻¹),³⁸ UTSA-300a (69.0 cm³·g⁻¹),³⁹ and Cu@FAU (79.5 cm³·g⁻¹)⁴⁰ under the same

conditions. An adsorption relationship for CO₂, C₂H₄, and C₂H₂ was observed for these materials experimentally with the capacity order C₂H₂ > C₂H₄, C₂H₂ > CO₂ at both temperatures, showing that C₂H₂ could be selectively adsorbed over C₂H₄ and CO₂ on these MOFs and the excellent potential of the Ti/Ni-MOF-74 series to separate C₂H₂/C₂H₄ and C₂H₂/CO₂ mixtures.

These single gas adsorption isotherms prompted us to analyze the separation performance of $Ti_{0.44}/Ni_{0.56}$ -MOF-74 for binary gas mixtures composed of C_2H_2/C_2H_4 (50/50, v/v) and C_2H_2/CO_2 (50/50, v/v) (Figure 8 and Figure S15). For this purpose, the adsorption selectivity of $Ti_{0.44}/Ni_{0.56}$ -MOF-74 was calculated using ideal adsorbed solution theory (IAST),⁴¹



Figure 8. (a) IAST calculations for the C_2H_2/CO_2 (50/50, v/v) adsorption selectivity of Ni-MOF-74 and $Ti_{0.44}/Ni_{0.56}$ -MOF-74 at 298 K. (b) IAST calculations for the C_2H_2/C_2H_4 (50/50, v/v) adsorption selectivity of Ni-MOF-74 and $Ti_{0.44}/Ni_{0.56}$ -MOF-74 at 298 K.



Figure 9. Isosteric heat of adsorption (Q_{st}) obtained for C_2H_2 , C_2H_4 , and CO_2 on Ni-MOF-74 (a) and $Ti_{0.44}$ /Ni_{0.56}-MOF-74 (b).



Figure 10. Simulated breakthrough curves obtained for (a) $50/50 C_2H_2/C_2H_4$ and (b) $50/50 C_2H_2/CO_2$ over Ni-MOF-74 and Ti_{0.44}/Ni_{0.56}-MOF-74 at 298 K and 1.0 bar.

and then the single component isotherms were fitted using the dual-site Langmuir equation (Figures S4–S7). The IAST selectivity of the C_2H_2/CO_2 (50/50, v/v) mixtures was calculated. At 298 K, the C_2H_2/CO_2 (50/50, v/v) separation selectivity of Ti_{0.44}/Ni_{0.56}-MOF-74 was 6.8 (1.0 bar). As shown in Figure 8a, the separation selectivity of Ti_{0.44}/Ni_{0.56}-MOF-74 was comparable to that of the previous benchmark substance, Ni-MOF-74 (6.1, at 298 K and 1.0 bar), and is higher than that of other promising MOFs, such as UTSA-68a (3.5–5.0)⁴² and ZJU-199 (4.0–5.8).⁴³ Figure 8b shows the selectivity for

 C_2H_2/C_2H_4 (50/50, v/v) as a function of the total gas pressure at different temperatures. For 50/50 v/v C_2H_2/C_2H_4 mixtures, the selectivity of $Ti_{0.44}/Ni_{0.56}$ -MOF-74 at 298 K and 1.0 bar was 4.9. In addition, the separation selectivity of $Ti_{0.44}/Ni_{0.56}$ -MOF-74 was higher than the benchmark material Ni-MOF-74 (3.3) and was higher than some adsorbents such as NOTT-300 (2.2)⁴⁴ and Fe-MOF-74 (2.1)⁴⁵ under the same conditions. These excellent results implied that $Ti_{0.44}/Ni_{0.56}$ -MOF-74 was a promising material for the removal of C_2H_2 from excess C_2H_4 under ambient conditions and to separate C_2H_2/CO_2 mixtures to acquire high grade C_2H_2 .

To better understand the strength of the interaction between the gas molecules and $Ti_{0.44}/Ni_{0.56}$ -MOF-74, the isosteric heat of adsorption (Q_{st}) values of C_2H_2 , C_2H_4 , and CO_2 were calculated based on the adsorption data collected at 273 and 298 K, using the virial equation (Figure 9, Figures S10–S14, and Tables S2–S6). From the curves obtained for Q_{st} at all gas loadings, the Q_{st} values of C_2H_2 , C_2H_4 , and CO_2 at zero loading were 54.3, 11.1, and 30.0 kJ·mol⁻¹, respectively. Interestingly, the Q_{st} value of C₂H₂ decreased with an increase in the uptake for $Ti_{0.44}/Ni_{0.56}$ -MOF-74, and the Q_{st} of CO_2 increased slightly, while the Q_{st} of C₂H₄ increased slightly with an increase in the loading. The reason for the upward trend in the Q_{st} curve may be due to the interaction between adsorbed gas molecules. Furthermore, compared to C₂H₄ and CO₂, the higher Q_{st} of C_2H_2 further confirmed the favorable interactions of $Ti_{0.44}/Ni_{0.56}$ -MOF-74. Interestingly, the Q_{st} of C_2H_2 for Ni-MOF-74 decreased with an increase in uptake and the Q_{st} of CO_2 decreased slightly with an increase in uptake, while the Q_{st} of C₂H₄ increased slightly and then decreased with increasing loading. The adsorption gap of C_2H_2/C_2H_4 and C_2H_2/CO_2 of $Ti_{0.44}/Ni_{0.56}$ -MOF-74 was greater than that of Ni-MOF-74, and Ti/Ni-MOF-74 exhibits greater adsorption differences for different molecules, which is why the former can better obtain pure C_2H_2 (Table S6).

This excellent adsorption performance and selection encouraged us to further explore the actual adsorption separation performance of Ti/Ni-MOF-74. The breakthrough curves obtained for Ni-MOF-74 and Ti/Ni-MOF-74 for C_2H_2/C_2H_4 and C_2H_2/CO_2 at 298 K were obtained by using breakthrough simulation experiments. Figure 10 and Figure S7, corresponding to the previous results, show that C_2H_4 and CO_2 first passed through the adsorption bed to yield high purity gases, and then C_2H_2 broke through the bed after reaching a dynamic adsorption equilibrium. For C_2H_2/C_2H_4 , the enhanced selectivity of $Ti_{0.44}/Ni_{0.56}$ -MOF-74 compared to Ni-MOF-74 led to a further reduction in the co-adsorption time during the adsorption separation process from 1445 to 831 s and a significant reduction in the ratio of the coadsorption time to the separation time from 16.4 to 2.5, which led to higher yields with $Ti_{0.44}/Ni_{0.56}$ -MOF-74 in the prospective application of pressure swing adsorption for C_2H_2/C_2H_4 . Similarly, the ratio of co-adsorption time to separation time is reduced from 9.0 to 1.5 in the C_2H_2/CO_2 separation, where more CO_2 is expelled at the separation time to obtain a higher concentration of C_2H_2 gas. As shown in Figure S17, the separation effect of Ti_{0.44}/Ni_{0.56}-MOF-74 was well verified by actual breakthrough experiments. These results implied that regulation over the pore environment and chemistry by altering the metal node may have implications for the separation of C_2H_2 from C_2H_4 or CO_2 .

CONCLUSIONS

We synthesized a new bimetallic metal—organic framework, Ti/Ni-MOF-74, using a one-pot method. According to PXRD, the diffraction peaks of the bimetallic-MOF closely matched those of pristine Ni-MOF-74. The particle size slightly decreased with the increase of the Ti content due to the high reactivity of titanium. The ratio of Ti/Ni in the MOF-74 structure reached 44% and SEM-EDS mapping showed that titanium was uniformly distributed inside the particles rather than at the edges of the particles, suggesting that the coordination of the linker in the MOF structure is the same as in the case of Ni. Upon ultra-fine tuning of the coordination metal, $Ti_{0.44}/Ni_{0.56}$ -MOF-74 achieved a high C_2H_2 capture ability and storage density (127.5 cm³·g⁻¹ at 298 K and 1.0 bar) and realized the effective separation of C_2H_2/C_2H_4 (S = 4.9) and C_2H_2/CO_2 (S = 6.8) mixtures under ambient conditions. In addition, the actual separation performance was tested using breakthrough simulation experiments and showed that Ti/Ni-MOF-74 was more suitable for the separation of light hydrocarbons. Therefore, we have successfully synthesized a new material with C_2H_2/C_2H_4 and C_2H_2/CO_2 separation potentials, which demonstrated that bimetallic strategies had great potential in developing MOFs with specific functions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/cbe.3c00037.

Full experimental details; ICP data; TGA curves; adsorption-desorption isotherms; XPS spectra; pore size distribution; SEM images; DSLF and DSL fits; fitting isotherms and parameters; isosteric heat of adsorption; IAST calculations; physical properties of adsorption; simulated breakthrough curves (PDF)

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Notes

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