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Introduction

Acetylene (C_2H_2) , which is a significant raw material used in chemical production, is of great importance in the petrochemical industry. In general, C_2H_2 is manufactured via the partial combustion of methane or cracking of hydrocarbons in which carbon dioxide (CO_2) will inevitably be present.^{1,2} On the one hand, C₂H₂ and CO₂ molecules have very similar molecular sizes with kinetic sizes of $3.32 \times 3.34 \times 5.7$ Å (C₂H₂) and $3.18 \times$ 3.33×5.36 Å (CO₂), which leads to significant difficulty in their separation.³ In addition, the similar physical properties of C₂H₂ and CO₂, with boiling points of 189.3 and 194.7 K, respectively, also hinder their separation.⁴ Consequently, there is a pressing need to develop efficient ways to purify C₂H₂ to better meet the demands for different domains. Currently, liquid absorption and cryogenic distillation processes are the two main techniques used to achieve the efficient purification of C₂H₂ from CO₂. However, these processes are highly energyintensive and often come with potential safety hazards.⁵ In

A Lewis basic site rich metal–organic framework featuring a hydrogen-bonded acetylene nano-trap for the efficient separation of C_2H_2/CO_2 ⁺

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The physical separation of C_2H_2 from CO_2 on metal–organic frameworks (MOFs) has received a substantial amount of research interest due to its advantages of simplicity, security, and energy efficiency. However, the exploitation of ideal MOF adsorbents for C_2H_2/CO_2 separation remains a challenging task due to their similar physical properties and molecular sizes. Herein, we report a unique C_2H_2 nano-trap constructed using accessible oxygen and nitrogen sites, which exhibits energetic favorability toward C_2H_2 molecules. This material exhibits a good acetylene capacity of 55.31 cm³ g⁻¹ and high C_2H_2/CO_2 selectivity of 7.0 under ambient conditions. We have combined *in situ* IR spectroscopy and in-depth theoretical calculations to unravel the synergistic interactions driven by the high density of accessible oxygen and nitrogen sites. Furthermore, dynamic breakthrough experiments confirmed the capability of TUTJ-201Ni for the separation of binary C_2H_2/CO_2 mixtures. This study on Ni-based MOFs will enrich Lewis basic site rich MOFs for gas adsorption and separation applications.

> this case, adsorption-based separation using porous solid adsorbents has attracted a great deal of research interest due to its lower cost and energy consumption.⁶ However, conventional adsorbents, such as activated carbon and zeolite, which were developed for the separation of C_2H_2 and CO_2 , exhibit relatively low separation selectivity and productivity.⁷

> Recently, metal-organic frameworks (MOFs), which are a new generation of high-capacity adsorbents, meet various separation needs and have exerted a huge amount of influence on gas separation and storage due to their high structural designability, tunable pore size, and adjustable internal surface properties.8-15 Many MOFs have been reported for the adsorption separation of C₂H₂/CO₂ in order to fulfill this important task. From previous studies, an effective strategy to improve the C₂H₂/CO₂ separation performance is the construction of strong C2H2 binding sites in the structure.16,17 Among them, C₂H₂ nano-traps with multiple adsorption sites can provide stronger binding interactions and high recognition capabilities.¹⁸⁻²⁴ Niu et al.²⁵ reported an ultra-strong acetylene nano-trap based on oppositely adjacent open metal sites in MOFs. Taking advantage of the designed C_2H_2 nano-trap, the anhydrous MOF²⁶ demonstrated the strongest C₂H₂ binding capability with the largest $Q_{\rm st}$ (79.1 kJ mol⁻¹) and highest uptake at ultra-low pressure (<0.001 bar), as well as benchmark C_2H_2/CO_2 selectivity at room temperature. Although the reported C₂H₂ nano-traps show a high separation performance, most of them tend to have high C₂H₂ binding energy,

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leading to a high desorption energy. Therefore, the construction of a new type of C_2H_2 nano-trap featuring both low heat of adsorption and high C_2H_2/CO_2 selectivity is urgently needed for large-scale applications.

Accessible oxygen and nitrogen sites on the surface of MOFs have demonstrated the preferential binding of C_2H_2 .^{27,28} However, previously reported C2H2 sorbents based on isolated oxygen or nitrogen binding sites are limited by their weak C-H…O and C-H…N interactions and often show low separation performance.²⁹⁻³⁴ Presumably, a C₂H₂ nano-trap based on accessible oxygen and nitrogen sites would improve the C₂H₂ adsorption capacity. More importantly, this new type of C₂H₂ nano-trap will exhibit excellent C2H2/CO2 separation performance under low C₂H₂ binding energy due to the weak recognition of CO₂ by the oxygen and nitrogen sites. Upon consideration of these factors, we have prepared an ultra-microporous MOF (TUTJ-201Ni) taking advantage of C-H···O and C-H…N hydrogen bonding as nano-traps for C2H2 molecules, which features multiple accessible oxygen and nitrogen sites to increase the energetic favorability toward C2H2 molecules. The C₂H₂ and CO₂ adsorption properties of TUTJ-201Ni have been characterized using isotherms, the heat of adsorption $(Q_{\rm st})$, and ideal adsorbed solution theory (IAST) selectivity. Breakthrough experiments were performed to evaluate its C₂H₂/CO₂ separation performance under dynamic conditions. Moreover, theoretical calculations combined with in situ infrared (IR) spectroscopy were performed to further decipher the separation mechanism. Upon combining our experimental and computational results, TUTJ-201Ni can efficiently realize the separation of C_2H_2 and CO_2 , thus achieving the goal of enriching the C₂H₂ stream target.

Experimental section

Analysis of the gas adsorption and separation properties

 C_2H_2 and CO_2 single-component gas adsorption and desorption isotherms of the samples were measured at 273 and 298 K using a BSD-660 M analyzer (Beishide Instrument Technology

(Beijing) Co., Ltd) applying the volumetric technique to precisely measure the amount of gas adsorbed.

In situ IR spectroscopic analysis

The *in situ* IR spectra of adsorbed C_2H_2 and CO_2 were obtained using a Bruker V70 instrument equipped with an MCT detector, a stainless steel high-temperature *in situ* IR cell, and a KBr window. The resolution of the IR spectrometer was set at 4 cm⁻¹. For analysis, a specified amount of the adsorbent powder was placed in the sample cup of the high-temperature reaction cell and the powder scraped flat. The TUTJ-201Ni samples were activated at 423 K and 1 × 10⁻¹ mbar for 6 h. During the activation process, the heating and cooling rates of the adsorbent were both 5 K min⁻¹. After the adsorbent was cooled to the test temperature, the IR spectrum of the activated sample was recorded as the background spectrum. The tested gas was passed into the test system and the IR data were collected until the adsorbent was saturated.

Breakthrough experiments

The breakthrough curves of TUTJ-201Ni were obtained at a mixed gas flow rate of 5–15 mL min⁻¹. The prepared TUTJ-201Ni (1.2 g) particles were activated at 443 K and 1×10^{-1} mbar for 6 h and then placed in the adsorption column (Ø 4.0 mm × 100 mm) under anhydrous conditions. Before starting the test, the adsorption column was flushed with He gas at a flow rate of 15 mL min⁻¹ and a temperature of 298 K, and the inlet gas was then switched to the test mixture at a total gas flow rate of 5–15 mL min⁻¹. The spectra of the gas at the outlet of the adsorption column were recorded using an online mass spectrometer (HPR-20 EGA, Hiden, with a detection limit of 0.01%) to obtain the final breakthrough curves.

Results and discussion

TUTJ-201Ni was synthesized based on our previously reported work. The framework is formed from the hydroxide groups bridging the regular octahedra of nickel atoms and organic linkers (Fig. 1). Each nickel metal center exhibits an octahedral



Fig. 1 (a) 3D structures showing uniform one-dimensional channels. (b) Selective capture of the target molecule by the hydrogen-bonding nanotrap *via* host-guest multiple hydrogen-bonding interactions.

coordination environment *via* its connection with four oxygen atoms and two nitrogen atoms, where three oxygen atoms and two nitrogen atoms are from five different organic linkers, whereas the remaining oxygen atoms originate from the bridging hydroxide group. TUTJ-201Ni exhibits rhombic-shaped one-dimensional channels ~6.2 Å along the crystallographic *b*-axis and the pore walls are decorated by multiple oxygen and nitrogen sites.

Fig. 2a shows the adsorption behavior of TUTJ-201Ni for C_2H_2 and CO_2 measured using the single-component gas adsorption isotherms obtained at 273 and 298 K, respectively. The C_2H_2 uptake capacity of TUTJ-201Ni was apparently higher than that of CO_2 . TUTJ-201Ni rapidly takes up C_2H_2 , reaching a value of 36.1 cm³ g⁻¹ at 298 K under 0.1 bar, but has a much lower CO_2 uptake capacity of 14.2 cm³ g⁻¹. As the pressure increased and reached 1.0 bar, the uptake of C_2H_2 reached as high as 55.3 cm³ g⁻¹. In contrast, the CO_2 uptake value was

only 40.1 cm³ g⁻¹. A comparison of the C_2H_2 and CO_2 adsorption isotherms obtained for TUTJ-201Ni indicated the strong affinity for C₂H₂ over CO₂. The C₂H₂ sorption amount observed at 298 K and 1.0 bar for TUTJ-201Ni was comparable to the values for some previously reported MOFs, including Cu@FAU $(33.8 \text{ cm}^3 \text{ g}^{-1})$,³⁵ FJU-36 (52.2 cm³ g⁻¹),³⁶ ZNU-11 (45.5 cm³ g⁻¹),³⁷ NKMOF-1-Ni (61.0 cm³ g⁻¹),³⁸ Cu(bpy)NP (50.7 cm³ g⁻¹),³⁸ Cu(bpy)NP g^{-1}),³⁹ and NbU-7 (47.3 cm³ g⁻¹)⁴⁰ (Table S3[†]). The C₂H₂/CO₂ uptake ratio reached up to 1.37 at 298 K and 1.0 bar, which is higher than the values previously reported for TIFSIX-2-Cu-I (1.05),⁴¹ MUF-17 (1.2),⁴² and Cu-AD-GA (1.28).⁴³ In addition, successive adsorption/desorption cycles were measured at 298 K and a testing pressure of up to 1.0 bar without a regeneration process. TUTI-201Ni exhibits excellent adsorption recyclability for C_2H_2 and CO_2 , as demonstrated by our cyclic C_2H_2 and CO₂ adsorption measurements (Fig. 2b). To probe the porous nature of TUTJ-201Ni, we produced nitrogen adsorp-



Fig. 2 (a) C_2H_2 and CO_2 adsorption isotherms obtained for TUTJ-201Ni at 273 and 298 K. (b) The recycling performance of TUTJ-201Ni obtained at 298 K and a testing pressure up to 1.0 bar without the regeneration process. (c) IAST selectivity of C_2H_2/CO_2 . (d) Q_{st} curves calculated for C_2H_2 and CO_2 sorption. (e) A comparison of the Q_{st} value at zero coverage and IAST selectivity at 1 bar with other porous materials.

tion and desorption isotherms of the samples at 77 K (Fig. S6†). The resulting N_2 adsorption isotherms exhibit a typical type-I behavior, validating its inherent micro-porous structures.

To determine the separation performance of TUTJ-201Ni, the C_2H_2/CO_2 selectivity was calculated using ideal adsorbed solution theory (IAST). Fig. 2c shows that the selectivity increases as the pressure decreases. At 298 K and 1.0 bar, the calculated C_2H_2/CO_2 selectivity for the corresponding binary equimolar mixture is up to 7.0. This value is higher than those of most of the previously reported materials, including FJU-83 (4.8),⁴⁴ CoV-bdc-ppy (2.7),⁴⁵ Cu-AD-GA (2.6),⁴³ and CAU-23 (3.8).⁴⁶

The Q_{st} values of C₂H₂ and CO₂ were further calculated using the dual-site Langmuir-Freundlich model in order to evaluate the interactions formed between the adsorbents and gases (Fig. 2d). The Q_{st} values of C_2H_2 were in the range of 28.86-34.66 kJ mol⁻¹, which is notably higher than those of CO_2 (27.46–29.84 kJ mol⁻¹). The near zero coverage Q_{st} values of C₂H₂ and CO₂ are 34.66 and 29.84 kJ mol⁻¹, respectively, which are in accordance with the above-mentioned gas adsorption results. The higher Qst observed for C2H2 over CO2 indicates the strong affinity of TUTJ-201Ni toward C2H2. The Qst value of C₂H₂ near zero coverage was lower than those of the previously reported top materials SIFSIX-DPA-Cu-I (46.53),47 ATC-Cu (79.1),²⁵ UTSA-300a (57.6),⁴⁸ and JXNU-18 (37.4)⁴⁹ (Fig. 2e). From an industrial application perspective, the moderate adsorption enthalpy implies the potential to achieve regeneration under mild conditions, showing its promising potential for energy-friendly C₂H₂ purification from mixtures.

In order to better understand the ultra-high C_2H_2 storage density and separation performance of TUTJ-201Ni, Grand Canonical Monte Carlo (GCMC) simulations were performed to investigate the different binding sites of C₂H₂ and CO₂. Fig. 3a and b show that the C_2H_2 and CO_2 gas molecules both appear around the center of the rhombic pore, indicating that the pore centers were the most energetically favorable binding sites for both adsorbates. The density of C2H2 adsorbed in TUTJ-201Ni is obviously higher than that of CO₂ and is in full agreement with their adsorption capacities. Subsequently, DFT calculations were carried out to directly visualize the locations of C₂H₂ and CO₂ within TUTJ-201Ni. Simulations show that multiple binding sites existed. Fig. 3c and d show that the C_2H_2 molecule was preferentially adsorbed at the center of the MOF pore, where it formed three cooperative C-H...O interaction and one C-H...N hydrogen-bonding interaction with the nearby uncoordinated oxygen and nitrogen atoms with interaction distances ranging from 2.53 to 4.08 Å. The uncoordinated accessible oxygen and nitrogen sites can form preferential C₂H₂ binding interactions with the acidic H atoms via H-bonding and such interactions usually have moderate sorption heats according to the literature.⁵⁰ Simulations show that multiple binding sites existed. In this case, plenty of carboxylate oxygen atoms were exposed on the pore walls. In contrast to C₂H₂, each CO₂ molecule could only form four weak C-O…H interactions with distances of 3.31-4.45 Å. Such oxygen atoms can form hydrogen bonds with the acidic H atoms of C₂H₂ molecules but are unfavorable for adsorbing CO₂ molecules with two electronegative O atoms due to the electrostatic repulsion interaction. Such subtle differences between C₂H₂ and CO₂ can be maximized by the MOF bearing the Lewis base sites, thus enabling C₂H₂-selective C₂H₂/CO₂ separation. The binding energies for the framework-C₂H₂ and framework-CO₂ were calculated to be 34.66 and 29.84 kJ mol⁻¹, which confirmed a stronger interaction formed between the framework and C2H2 molecules, and this order was consistent with our



Fig. 3 (a) and (b) Density distributions of C_2H_2 and CO_2 within TUTJ-201Ni at 298 K; the red dashed circles indicate the favorable adsorption sites. (c) and (d) The DFT-optimized adsorption configurations of C_2H_2 and CO_2 in TUTJ-201Ni.

experimental data. *In situ* IR spectroscopy was carried out to probe further the interactions of C₂H₂ within TUTJ-201Ni. Fig. 4 shows the change in the stretching bands upon C₂H₂ loading. The adsorption bands at 3237 cm⁻¹ that were assigned to $\nu (\equiv C-H)$ gradually increased with dosing C₂H₂, indicating the interaction of C₂H₂ molecules with the framework *via* C-H···O and C-H···N. This weak interaction leads to changes in the intensity of the C-H peak in the *in situ* IR spectra. Similarly, $\nu (C=O) = 2333$ cm⁻¹ proves the presence of

 C_2H_2 and CO_2 adsorbed in the MOF. Upon adsorption of C_2H_2 on TUTJ-201Ni, the intensity of the stretching band was significantly increased. This may be attributed to the high gas adsorption capacity of this material.

Dynamic breakthrough experiments for an equimolar C_2H_2/CO_2 mixture were carried out under different conditions in order to verify the adsorptive separation performance of binary mixtures under continuous flow conditions. Fig. 5a shows the dynamic breakthrough experiments carried out for an equi-



Fig. 4 In situ IR spectra obtained for C₂H₂ (a) and CO₂ (b) adsorbed on TUTJ-201Ni with different gas dosing durations at 298 K.



Fig. 5 (a) Experimental breakthrough cycles obtained for C_2H_2/CO_2 (50/50) separation on TUTJ-201Ni at 298 K and 1.0 bar. (b) Breakthrough curves obtained for TUTJ-201Ni with C_2H_2/CO_2 (50/50) mixtures at 298 K and flow rates of 5, 10, and 15 mL min⁻¹. (c) Experimental breakthrough curves obtained for TUTJ-201Ni during the separation of C_2H_2/CO_2 (50/50) at 1.0 bar and different temperatures. (d) Experimental breakthrough curves obtained for 50/50, 75/25, and 90/10 mixtures at 298 K and 1.0 bar.

molar C_2H_2/CO_2 mixture at a total flow rate of 5 mL min⁻¹ under ambient conditions. CO₂ first penetrated the adsorption bed and C₂H₂ was detected after a long period of time. The difference between the breakthrough times of the two gases reached 25.0 min, which offers a large operating window for C_2H_2 release during the pressure-swing adsorption process. Furthermore, five continuous cycling breakthrough experiments were performed on TUTJ-201Ni. No appreciable change in the retention time was observed, proving its good recyclability for C₂H₂/CO₂ separation. After each cycle, the TUTJ-201Ni in the column can be readily regenerated within 30 min upon purging with He. To further achieve the target of practical applications, we also investigated the C₂H₂/CO₂ separation performance at different gas flow rates of 10.0 and 15.0 mL min⁻¹ (Fig. 5b). Although the breakthrough time decreased when the flow rate increased, the separation performance remained almost unchanged. Fig. 5c shows the breakthrough curves obtained under different temperatures and the results indicate that TUTJ-201Ni exhibited an excellent separation performance. In addition, the separation capacity of this material for high concentrations of C_2H_2 was also tested (Fig. 5d). When the C₂H₂/CO₂ ratio was adjusted to 75/25 and 90/10, TUTJ-201Ni still exhibited a good separation effect. All of the breakthrough curves under various separation scenarios demonstrated that TUTJ-201Ni can effectively separate C2H2 and CO_2 .

Considering that the C_2H_2 raw stream is produced from the combustion of natural gas or cracking of hydrocarbons, the C_2H_2/CO_2 separation process will be performed under harsh conditions in industrial applications. This requires adsorbent candidates with extremely high and long-term pH stability. Thus, we investigated the chemical stability of TUTJ-201Ni after treatment under different conditions. Fig. S3 and S4† show that TUTJ-201Ni exhibits no loss of crystallinity and no phase change after exposure to air for 1 week and different pH aqueous solutions using PXRD, indicating its good chemical stability.

Conclusions

In summary, we reported an oxygen and nitrogen based C_2H_2 nano-trap for the separation of C_2H_2 and CO_2 . The high C_2H_2 uptake capacity, remarkable C_2H_2/CO_2 IAST selectivity, prominent experimental breakthrough performance, and theoretical calculation indicate that this C_2H_2 nano-trap is an ideal acetylene trapper for practical applications. Our work enriches the study of Lewis basic site rich MOFs with hydrogen-bonded acetylene nano-traps and provides an efficient functional porous adsorbent to address challenging gas separation applications.

Author contributions

MYL: investigation, visualization, and writing original draft; ZWZ and YHT: investigation and visualization; YTW: visualization, validation and review; FFZ: in charge of conceptualization, data analysis, writing – review and editing. JPL and JFY: supervised and administered the project.

Data availability

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

Conflicts of interest

The authors declare no competing financial interest.

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