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Tuning gate-opening of a flexible metal-organic framework for ternary gas sieving separation

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Abstract: In comparison with the fast development of binary mixture separations, ternary mixture separations are significantly more difficult and have rarely been realized by a single material. Herein, a new strategy of tuning the gate-opening pressure of flexible MOFs is developed to tackle such a challenge. As demonstrated by a flexible framework NTU-65, the gate-opening pressure of ethylene (C₂H₄), acetylene (C₂H₂), and carbon dioxide (CO₂) can be regulated by temperatures. Therefore, efficient sieving separation of this ternary mixture was realized. Under optimized temperature, NTU-65 adsorbed a large amount of C₂H₂ and CO₂ through gate-opening and only negligible amount of C₂H₄. Breakthrough experiments demonstrated that this material can simultaneously capture C₂H₂ and CO₂, yielding polymer grade (>99.95 %) C₂H₄ from single breakthrough separation.

Introduction

In recent years, researchers have sought for energy-efficient separation technologies using advanced porous adsorbents. As a new type of crystalline material, metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), have demonstrated remarkable performance for gas separation thanks to the highly tunable pore size and surface functionality.^[11] Flexible MOFs are unique class of MOFs that undergo structural transformation with the variation of guest, pressure or temperature.^[2] Gate-opening adsorption of flexible MOF was first discovered in 2003, and the gate-opening pressure was found to be guest dependent.^[3] Strong gas-framework interaction usually leads to lower gate-opening pressure since the high adsorption enthalpy of such gas can overcome the energy requirement for

the phase transition even at low pressure.^[4] For smaller gas molecule, the gate-opening pressure is also lower as smaller degree of structural change is needed to accommodate smaller molecule in the pore.^[6] Selective gate-opening adsorption has realized several important binary gas separation^[6] with high sieving performance that is comparable to those of rigid sieving MOFs.

Ethylene (C₂H₄) is one of the most essential feedstocks and is widely used to produce polyethylene and other valued products in modern life.^[7] Generally, during C₂H₄ production such as oxidative coupling of methane process, acetylene (C_2H_2) and carbon dioxide (CO_2) coexist with C_2H_4 .^[8] These impurities must be removed to obtain high purity C2H4 for polyethylene production. Current purification technologies involve catalytic hydrogenation of C2H2 with precious metal catalyst at high temperature and basic solution for CO2 chemisorption, which require high capital and energy cost.^[9] For such ternary mixture, generally C2H2 is selectively adsorbed over $C_2H_4^{[8a, 10]}$, while CO_2/C_2H_4 separation is more challenging due to the smaller difference of their quadrupole moments (1.5 ×10⁻²⁶ esu cm² for C₂H₄, 4.3 ×10⁻²⁶ esu cm² for CO₂, and 7.2 ×10⁻²⁶ esu cm² for C_2H_2).^[11] Rigid MOFs with strong C_2H_4 binding sites also adsorb CO2 efficiently. For example, MOF-74 series and M₂(*m*-dobdc) series MOFs with open metal sites efficiently adsorbs both. CO_2 and C_2H_4 , which limited the separation performance.[12] Ideally, molecular sieving separation is favourable since the co-adsorption of C_2H_4 is precluded and most of the C_2H_4 in the mixture can be recovered. As most MOFs has certain degree of flexibility by linker rotation and distortion, it is quite challenging to design high sieving MOFs for hydrocarbon separation.^[10c, 13] Flexible MOFs with controllable

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gate-opening pressure offers new opportunity for such a challenging separation.

Scheme 1. Illustration of the temperature optimization for ternary mixture separation by flexible MOFs. At low temperature, all three gases can be adsorbed, which lead to co-adsorption of target gas and low productivity. At optimized temperature, two impurities are selectively adsorbed and pure target gas is obtained in high yield. At high temperature, only one type of impurity is adsorbed, therefore the product is not pure.

Compared with the binary mixture, separation of ternary or quaternary mixture is more challenging and often requires multiple adsorbents.^[9, 14] Flexible MOFs through selective gateopening adsorption have great potential for this goal. For a certain gas, the gate-opening pressure is usually lower at low temperature, because adsorption is an exothermic process and lower temperature is thermodynamically favorable.^[15] Therefore, we can regulate the gate-opening pressure by temperature and realize the complete separation of multi-component mixture. For ternary mixture separation, as shown in Scheme 1, the desolvated flexible framework can adsorb three types of gases through phase transition to more opened structure at very low temperature. As the temperature increases, the gate-opening pressure increases. At certain temperature, the framework adsorbs two impurities of smaller size or with stronger gasframework interaction and produces desired gas in high purity. At higher temperature, only one impurity can induce the phase transition and be adsorbed, therefore the separation is incomplete. Herein, we demonstrate this strategy with a flexible framework NTU-65 for sieving separation of C2H4/C2H2/CO2 mixture. At optimized temperature (263 K), NTU-65 adsorbs large amount of C_2H_2 (86.3 cm³·g⁻¹), and CO_2 (79.5 cm³·g⁻¹) through gate-opening process, while only negligible amount of C₂H₄ (2.2 cm³·g⁻¹). As a result, this flexible MOF material captures C₂H₂ and CO₂ exclusively and produces polymer-grade

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 C_2H_4 (>99.95%) with very high recovered C_2H_4 percentage from $C_2H_4/C_2H_2/CO_2$ mixture in one-step.

Results and Discussion

The reaction of 1,4-di(1H-imidazol-1-yl)benzene (L1) in DMF and Cu(SiF₆)·6H₂O in H₂O at room temperature afforded the purple crystals of [Cu(L1)₂SiF₆)]·xSolvent (NTU-65).^[16] Single crystal X-ray measurements reveal that NTU-65 crystallizes in a monoclinic space group. The asymmetric unit of NTU-65 includes one Cu2+ cation, one SiF62- anion, and two L1 ligands (Figure S1). Each of the ligand and SiF62- ions coordinate to two Cu atoms, respectively (Figure 1a-b). In view of the metal centre, the Cu²⁺ cations are octahedrally coordinated by four imidazole N atoms at equatorial positions from four L1 and two F atoms in axial positions from two SiF62- ions (Figure 1c). Therefore, a three-dimensional (3D) framework with pcu topology was established (Figure S2). The ligands are further connected by multiple hydrogen bonds from all F atoms of the SiF₆²⁻ ion (Table S2). The NTU-65 framework has cross-linked 2D channels along the a-c plane (Figure S3), which are significantly different from the channels of typical SIFSIX materials (Figure S4) [6a, 17]. As a result, two types of channels that feature the rectangular and ultramicroporous window aperture of 2.6 \times 3.4 and 5.2 \times 6.3 ${\rm \AA^2}$ were observed (Figure 1d-g).

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The phase purity of the bulk crystals was identified by powder X-ray diffraction (PXRD) patterns and LeiBail fitting (Figures S5–S6). After exchanging the guest by dry methanol, the fully activated NTU-65 framework was obtained by degassing under high vacuum at 120 °C for 24 hours according to the thermogravimetric (TG) results. PXRD measurement revealed that NTU-65 underwent structural transformation after desolvation (Figure S5). The activated framework is thermally stable up to 300 °C according to the TG analysis (Figure S8).



Figure 1. Structure and channel of NTU-65. Coordination configuration of (a) L1, (b) SiF₆²⁻ ion, and (c) Cu centre. Brown red polyhedron represents octahedrally coordinated Cu atom. (d-e) Crystal structure view along a and c axis. (f-g) Channels along a axis and c axis with aperture size of 5.2×6.3 Å² and 2.6×3.4 Å² respectively. The colour codes: C, grey; N, blue; F, cyan; Si, yellow.

We next evaluated the permanent porosity of NTU-65 by N₂ adsorption at 77 K. A sudden increase of adsorption at pressure of P/P₀ =0.12 was observed indicating a gate-opening process (Figure S11). In the desorption process, the isotherm showed a certain hysteresis, which is typical for flexible frameworks^[1c, 18]. Based on N₂ adsorption isotherm, NTU-65 has a BET (Langmuir) surface area of 680 (1002) m²·g⁻¹ and a pore volume of 0.372 cm³·g⁻¹ (Figures S12-S13), which is almost same as the calculated values (0.379 cm³·g⁻¹) from single crystal data. In addition, the cavity size distribution (5-6 Å) is also close to the determined values from the crystal structure (Figure S14). The softness of the framework and the microporous environment prompted us to evaluate the potential of NTU-65 for gas separation. We first measured the C₂H₂ adsorption under the temperature range of 195 to 333 K. As shown in Figure S15, the gate-opening pressure increases from 1.2 kPa (263 K) to around 20 kPa (313 K) and 42 kPa (333 K) indicating that the gate-opening pressure is temperature dependent. Such temperature dependent gate-opening has also been observed for CO₂ and C₂H₄ which possess higher gate-opening pressure (Figure S16-17). At 298 K, the C₂H₂ adsorption capacity of NTU-65 (3.36 mmol·g⁻¹, 75.4 cm³·g⁻¹) is comparable to that of UTSA-300^[6a] (3.41 mmol·g⁻¹, 76.4 cm³·g⁻¹) and SIFSIX-3-Zn^[10a] (3.86 mmol·g⁻¹, 86.5 cm³·g⁻¹). Interestingly, only negligible amount of CO₂ (2.3 cm³·g⁻¹) and C₂H₄ (1.2 cm³·g⁻¹) can be adsorbed at 298 K showing a guest dependent gate-opening phenomenon (Figure 2c). The selective gate-opening by C₂H₂ is likely due to strong binding affinity to the framework, as suggested by density functional theory (DFT) calculations. According to the structural model (Figure S19-22), we found hydrogen bonds between terminal H_{C2H2} atoms and the F atoms from SiF₆²⁻ anions (*d*_{H...F}: 1.88 Å and 1.99 Å), and multiple C-H•••C van der Waals (vdW) interactions between the **C**_{C2H2} atoms and adjacent H_L (*d*_{H...C}: 2.49 to 2.93 Å).

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Figure 2. Temperature dependent adsorption of NTU-65. $C_2H_2,\ C_2H_4$ and CO_2 adsorption (solid symbol) and desorption (hollow symbol) isotherms at 195 K (a), 263 K (b) and 298 K (c).

To simultaneously encapsulate the two impurities $(C_2H_2$ and $CO_2)$ from a ternary mixture, significant CO_2 adsorption is required. Adsorption measurement at 195 K showed uptake of all three gases (Figure 2a), which is not promising for efficient separation of ternary mixture because the high C_2H_4 uptake would result in significant amount of co-adsorption of C_2H_4 and

low percentage of recycled C₂H₄. Since C₂H₄ showed highest gate-opening pressure, it is likely that at some temperature between 195 and 298 K, only C₂H₂ and CO₂ can open the pore and be captured. At 263 K, NTU-65 showed remarkable adsorption of C₂H₂ (86.3 cm³·g⁻¹) and CO₂ (79.5 cm³·g⁻¹), and only negligible amount of C₂H₄ (2.2 cm³·g⁻¹) as shown in Figure 2b. Therefore, it is promising to simultaneously capture C₂H₂ and CO₂ from the ternary mixture of C₂H₄/C₂H₂/CO₂ by NTU-65 at 263 K. Adsorption isobar results (Figure S 18) indicated simultaneously high C₂H₂/C₂H₄ and CO₂/C₂H₄ uptake ratios between 250 to 270 K, which further supported our temperature choice.

The structural change during adsorption process was studied by *in-situ* coincident PXRD/sorption measurements during the C₂H₂ adsorption at 189 K and 333 K. ^[19] As shown in Figure S23, we observed two phases transitions at 189 K and one phase transition at 333 K. The phase transition pressure is much higher at 333 K (Figure S24). These results showed that the phase transition and gate-opening pressure are temperature dependent. Further, the varied cell parameters that determined from synchrotron-based PXRD measurements validate again the phase transitions ^[20] (Figures S25-286, Table S3).



Figure 3. CO_2/C_2H_4 separation performance. Amount and percentage of C_2H_4 recovered from CO_2/C_2H_4 (75/25, v/v) by NTU-65 in comparison with benchmark materials.

Next, we calculated the amount and percentage of recovered C₂H₄ from binary mixtures of C₂H₂/C₂H₄ and CO_2/C_2H_4 for NTU-65. The percentage of recovered C_2H_4 is defined as amount of recovered pure C₂H₄ divided by the total amount of C₂H₄ in the feed gas mixture. High percentage of recovered C₂H₄ means that most of the valuable C₂H₄ molecules can be recovered from the mixture in a single breakthrough cycle. As shown in Figure 3, the amount of C₂H₄ recycled by NTU-65 from the CO_2/C_2H_4 (75:25, V/V) mixture is quite high compared with some representative zeolite materials in a recent study ^[22]. At the same time, 99.87 % of the C_2H_4 in the mixture can be recycled thanks to the low C₂H₄ adsorption. Likewise, large amount (3.7 mmol/g) and high percentage (97.7 %) of C_2H_4 can be recovered from the C_2H_2/C_2H_4 (50:50, $V\!/V)$ mixture by NTU-65, which is higher or comparable to the current benchmark materials^{[21] [10a, 10b]}, as shown in Figure S29.

Gas separation under dynamic process is important for application. Transient breakthrough practical simulation indicates that NTU-65 would be efficient adsorbent for C_2H_2/C_2H_4 and CO_2/C_2H_4 separations (Figure S30-S32). Experimental breakthrough was carried out with handmade equipment ^[21a, 23]. The initial activated sample bed was swept by He flow at 100 °C for 8 hours to remove impurities from the system. We first carried out breakthrough experiments with the feed gas of C_2H_2/C_2H_4 , where the gas ratio is 1/99 (v/v) at 263 K. (Figure 4a). As expected, C_2H_4 with high purity >99.95% was the first effluent, while C₂H₂ was selectively absorbed by the sample bed with long retained time of ~100 min. After the breakthrough experiment, the sample was regenerated under He flow for 20 min at 358 K which is lower temperature than that of a flexible MOF with open metal site (393 K) [24]. Furthermore, same breakthrough curves were observed during the cycling breakthrough experiments (Figure S33), indicating the excellent stability and reversible pore opening/closing of NTU-65. The C_2H_2/C_2H_4 separation can also be realized at higher temperature of 298 K and 333 K (Figure S34-37). Next, the binary gas separation of CO_2/C_2H_4 (1/9, v/v) was also investigated at 263 K. Likewise, NTU-65 selectively captured CO2 molecules, and yielded purity C_2H_4 (>99.95%) in the outlet of column (Figure 4b). The CO₂/C₂H₄ separation performance was retained during another ten cycling breakthrough experiments (Figure S38). In light of the excellent separation performance for the binary mixture at 263 K, we then conducted ternary separation of $C_2H_4/C_2H_2/CO_2$ (Figure 4c). After introducing the $C_2H_4/C_2H_2/CO_2$ mixture (90/1/9, v/v/v) inside the system, the effluent of polymergrade C₂H₄ (>99.95%) was detected at 11.2 min, while the outflow of CO₂ and C₂H₂ from the sample bed was around 23.0 min and 174.4 min. The industrial mixtures generally contain 1 % of C_2H_2 and up to ~30 % of CO_2 . ^{[10] [25]} We therefore altered the mixture ratios by tuning CO₂ percentage and kept C₂H₂/C₂H₄ ratio of 1/99. As shown in Figure S39 and S40, C₂H₄/C₂H₂/CO₂ mixtures with volume ratio of 95.7/0.967/3.33 (V/V/V) and 66.00/0.67/33.33 (V/V/V) can be separated by NTU-65 yielding pure C₂H₄. Low percentage of CO₂ can be efficiently captured. when the CO₂ percentage increased to 33.33 %, the separation performance decreased slightly. These breakthrough experiments demonstrated that NTU-65 maintained the selective adsorption under dynamic process and high purity C₂H₄ can be separated from the ternary mixture in one step.



Figure 4. Breakthrough curves of NTU-65 at 263 K. (a) Binary mixture separation of C_2H_2/C_2H_4 , (b) Binary mixture separation of CO_2/C_2H_4 . (c) Ternary separation of $C_2H_4/C_2H_2/C_2H_4/C_2H_2/C_2H_4/C_2H_2/C_2H_4$. (c) Ternary separation of $C_2H_4/C_2H_2/C_2H_4/C_2H_2/C_2H_4/$

In comparison with NTU-65, we also measured high surface area activated carbon (S_{BET}~1100 m²/g) with no phase transition and a gate-opening MOF ZIF-7 [26] (Figure S7) with two porous phases. The activated carbon material exhibits typical adsorption isotherms of rigid porous materials. The C2H4 and C₂H₂ adsorption are very close and higher than CO₂ adsorption at corresponding temperatures (263 K to 318 K, Figure S41). The corresponding column breakthrough experiments (Figure S43) showed that C_2H_4 and C_2H_2 are preferably captured and simultaneously broke through, which could not produce pure C₂H₄ like NTU-65. The adsorption isotherms of ZIF-7 showed gate-opening effect for all three gases and C₂H₄ exhibits slightly lower gate-opening pressure than C2H2 and CO2 at different temperatures (263 K to 318 K, Figure S42). Breakthrough experiments (Figure S44) showed that C₂H₄ and C₂H₂ eluted out simultaneously at very early stage yielding incomplete separation. The results of activated carbon and ZIF-7 together indicated that a material with temperature-regulated phase transition from less porous phase to open phase might be essential for such separation strategy.

Moreover, NTU-65 also possesses remarkable water/chemical stability. From PXRD analysis, NTU-65 showed the same diffraction and cell parameters after a long-term treatment where the crystals were soaked in water for two months at 298 K (Figure S45). In addition, the crystallinity of NTU-65 retained after immersing the crystal in water of pH 2 \sim 12 at 298 K (24 h) and pH 2 \sim 7 at 373 K (24 h) as shown in Figure S46. More importantly, the N₂ adsorption isotherm showed that acid-treated NTU-65 features an almost identical pore opening feature and total pore volume as those with the fresh sample (Figure S47).

Conclusion

Guest dependent gate-opening phenomenon of flexible porous MOFs is promising for selective gas adsorption and separation. In this work, we demonstrated that the separation performance can be optimized through tuning gate-opening pressure by temperature and realized the ternary mixture separation with a

flexible framework NTU-65. Under optimized temperature, NTU-65 adsorbed large amount of C_2H_2 and CO_2 through gateopening and only negligible amount of C_2H_4 . Such selective adsorption enabled one-step separation of C_2H_4 from a ternary mixture of $C_2H_4/C_2H_2/CO_2$ and high purity C_2H_4 can be obtained through single breakthrough cycle. The ultralow C_2H_4 uptake also prevented its co-adsorption therefore yielded high percentage of recovered C_2H_4 . Such gate-opening pressure optimization strategy would be broadly useful for separations by flexible MOFs. It is foreseeable that more multi-component separations will be realized by flexible MOFs in the near future.

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One-step sieving separation of ternary gas mixture ($C_2H_2/CO_2/C_2H_4$) has been realized by a flexible MOF NTU-65. Such successful separation relies on tuning the gate-opening pressure of this flexible framework to optimize the separation performance. Under an optimized temperature, NTU-65 adsorbed large amount of C_2H_2 and CO_2 while negligible amount of C_2H_4 , readily producing high purity of C_2H_4 through a separation column.

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