Mixed Metal–Organic Framework with Multiple Binding Sites for Efficient C$_2$H$_2$/CO$_2$ Separation

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Abstract: The separation of C$_2$H$_4$/CO$_2$ is particularly challenging owing to their similarities in physical properties and molecular sizes. Reported here is a mixed metal–organic framework (M–MOF), [Fe(pyz)Ni(CN)$_4$] (FeNi-MOF, pyz = pyrazine), with multiple functional sites and compact one-dimensional channels of about 4.0 Å for C$_2$H$_2$/CO$_2$ separation. This MOF shows not only a remarkable volumetric C$_2$H$_2$ uptake of 133 cm$^3$ cm$^{-3}$, but also an excellent C$_2$H$_2$/CO$_2$ selectivity of 24 under ambient conditions, resulting in the second highest C$_2$H$_2$-capture amount of 4.54 mol L$^{-1}$, thus outperforming most previous benchmark materials. The separation performance of this material is driven by π–π stacking and multiple intermolecular interactions between C$_2$H$_2$ molecules and the binding sites of FeNi-MOF. This material can be facilely synthesized at room temperature and is water stable, highlighting FeNi-MOF as a promising material for C$_2$H$_2$/CO$_2$ separation.

Metal–organic frameworks (MOFs) have emerged as very promising porous materials for adsorptive gas separation because they integrate the merits of tunable pore sizes and functional pore surfaces that can realize not only a molecular sieving effect, but also preferential gas binding. Many MOFs have been explored for simplifying various gas separation and purification schemes ranging from mature ones, such as CO$_2$ separation. This MOF shows not only a remarkable volumetric C$_2$H$_2$ uptake of 133 cm$^3$ cm$^{-3}$, but also an excellent C$_2$H$_2$/CO$_2$ selectivity of 24 under ambient conditions, resulting in the second highest C$_2$H$_2$-capture amount of 4.54 mol L$^{-1}$, thus outperforming most previous benchmark materials. The separation performance of this material is driven by π–π stacking and multiple intermolecular interactions between C$_2$H$_2$ molecules and the binding sites of FeNi-MOF. This material can be facilely synthesized at room temperature and is water stable, highlighting FeNi-MOF as a promising material for C$_2$H$_2$/CO$_2$ separation.

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FeNi-M'MOF is a pillared-layer M'MOF, in which the Fe[Ni(CN)]₄ layer is connected by the pyz pillars. The Ni atoms show square-planar coordination geometry while Fe atoms are octahedrally coordinated. The Ni atoms are coordinated by carbon atoms of four different cyan groups, whereas the Fe atoms are fully coordinated by nitrogen atoms from four different cyan groups and two pyz linkers. Fe[Ni(CN)]₄ layers are then connected by pyz linkers into a three-dimensional network with one-dimensional channels of about 4.15 ± 0.08 or 3.94 ± 0.03 Å. The open metal site density of FeNi-M'MOF is about 9.2 mmol cm⁻³, which is higher than that of most MOFs, as shown in Table S2 (see the Supporting Information).

FeNi-M'MOF was synthesized at room temperature in water and methanol (Figure 1). By adding the solution of K₂[Ni(CN)]₄ into the mixed methanol and water solution of Fe²⁺ and pyz, the FeNi-M'MOF microcrystalline powders were obtained after stirring for 30 minutes. The powder X-ray diffraction (PXRD) of products indicated that those products have a good crystallinity and match well with the simulated XRD pattern, indicating the purity of FeNi-M'MOF. The resultant FeNi-M'MOF was further validated by elemental analysis (EA), thermogravimetry analysis (TGA), energy dispersive spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS) analysis (see the Supporting Information). This MOF also exhibits excellent water stability as shown in Figure S2. After soaking in water for 30 days, the crystallinity of FeNi-M'MOF is still retained. The TGA curve indicated that FeNi-M'MOF exhibits a considerable thermal stability up to 200°C (see Figure S4). The thermal stability of FeNi-M'MOF was also confirmed by variable-temperature PXRD (see Figure S5), indicating that FeNi-M'MOF can maintain its crystalline structure up to about 200°C. The fast and facile synthesis method, excellent water stability, and good thermal stability indicate FeNi-M'MOF is a promising separation material for scale-up synthesis.

The Brunauer-Emmett-Teller (BET) surface area of FeNi-M'MOF was measured to be 383 m² g⁻¹ by an N₂ sorption experiment at 77 K as shown in Figure 2a. The experimental total pore volume is about 0.25 cm³ g⁻¹, and slightly smaller than the theoretical one calculated from the crystal structure (0.30 cm³ g⁻¹), which can be attributed to the insufficient filling of N₂ molecules in the ultramicroporous pore channels.

The C₂H₂ and CO₂ gas adsorption isotherms of FeNi-M'MOF were measured at both 273 and 298 K. As shown in Figure 2b, the volumetric C₂H₂ uptake capacity of FeNi-M'MOF is 133 cm³ cm⁻³ (4.29 mmol g⁻¹) at 1 bar and 298 K,
which is higher than those of many other MOFs, such as DICRO-4-Ni-i (52 cm$^3$ cm$^{-3}$),$^{[4]}$ ZJU-60a (96 cm$^3$ cm$^{-3}$),$^{[11]}$ Cu[Ni(pdt)$_2$] (108 cm$^3$ cm$^{-3}$),$^{[60]}$ SNNU-45 (113 cm$^3$ cm$^{-3}$),$^{[60]}$ TIFSIX-2-Cu-i (116 cm$^3$ cm$^{-3}$),$^{[4]}$ PCP-33 (128 cm$^3$ cm$^{-3}$),$^{[12]}$ and comparable to those of UTSA-74 (144 cm$^3$ cm$^{-3}$),$^{[5]}$ FJU-90a (146 cm$^3$ cm$^{-3}$),$^{[6]}$ and Zn-MOF-74 (150 cm$^3$ cm$^{-3}$).$^{[13]}$ The CO$_2$ uptake of FeNi-M/MOF is 84 cm$^3$ cm$^{-3}$ (2.72 mmol g$^{-1}$) at 1 bar and 298 K. At 1 bar and 273 K, C$_2$H$_2$ and CO$_2$ uptakes of FeNi-M/MOF are up to 145 and 102 cm$^3$ cm$^{-3}$, respectively, as shown in Figure S8. Interestingly, the Pt analogue [Fe(pyz)Pt(CN)$_4$] (FePt-M/MOF; see Figures S10–S12) shows much lower uptake capacities for C$_2$H$_2$ and CO$_2$ (100 and 105 cm$^3$ cm$^{-3}$), respectively, indicating the potential binding contribution of Ni sites in this type of MOF for C$_2$H$_2$ molecules. To evaluate the separation performance of this material, ideal adsorbed solution theory (IAST) was employed to calculate the adsorption selectivity. As shown in Figure 2c, at 100 kPa and 298 K, the C$_2$H$_2$/CO$_2$ (50:50) selectivity of FeNi-M/MOF is 24. The selectivity of FeNi-M/MOF is higher than those of most MOFs, such as Zn-MOF-74 (1.92),$^{[4]}$ FJU-90a (4.3),$^{[6]}$ UTSA-74a (8.2),$^{[4]}$ JCM-1 (13.4),$^{[6]}$ DICRO-4-Ni-i (13.9),$^{[4]}$ and benchmark HOF-3a (21).$^{[14]}$ It should be noted that both the uptake capacity and separation selectivity can significantly affect the practical performance of an adsorbent. HOF-3a has a high selectivity, but the low uptake of C$_2$H$_2$ reduced its separation performance. In contrast, FeNi-M/MOF can address such trade-offs between the adsorption capacity and selectivity as shown in Figure 2d. The high selectivity and high C$_2$H$_2$ adsorption capacity of FeNi-M/MOF jointly reveal its useful separation potential for C$_2$H$_2$/CO$_2$.

Transient breakthrough simulations were conducted to demonstrate the C$_2$H$_2$/CO$_2$ separation performance of FeNi-M/MOF. The simulations in Figure 3a demonstrate the FeNi-M/MOF is of potential use for this challenging separation of C$_2$H$_2$/CO$_2$ mixtures. The C$_2$H$_2$/CO$_2$ mixtures (50:50) were used as feeds to mimic the industrial process conditions. Pure CO$_2$ first eluted through the bed, where the CO$_2$ purity was 99.95%, followed by the breakthrough of C$_2$H$_2$ after a certain time, $t_{\text{break}}$, during which FeNi-M/MOF was saturated by C$_2$H$_2$. The C$_2$H$_2$ capture amount of FeNi-M/MOF is 4.54 mol L$^{-1}$ based on the simulated column breakthrough, which is close to that of the benchmark UTSA-74 (4.86 mol L$^{-1}$)$^{[5]}$ and higher than those of most out-performing MOFs, such as Zn-MOF-74 (4.06 mol L$^{-1}$),$^{[5]}$ FJU-90a (4.16 mol L$^{-1}$),$^{[6]}$ and PCP-33 (4.16 mol L$^{-1}$).$^{[12]}$ Accordingly, FeNi-M/MOF shows not only a high C$_2$H$_2$/CO$_2$ selectivity and high C$_2$H$_2$ uptake but also high C$_2$H$_2$-capture capability from gas mixtures, endowing this material with a useful C$_2$H$_2$/CO$_2$ separation potential. Based on experimental breakthrough studies, we further evaluated the performance of FeNi-M/MOF in near practical separation processes for a C$_2$H$_2$/CO$_2$ mixture (50:50 v/v) as shown in Figure 3b. Indeed, FeNi-M/MOF exhibits excellent C$_2$H$_2$/CO$_2$ mixture separation performance at 298 K. CO$_2$ was first eluted through the adsorption bed without any detectable C$_2$H$_2$, whereas the latter was retained in the MOF column for a remarkable period prior to saturate the MOF. The retention time of pure CO$_2$ and C$_2$H$_2$ for C$_2$H$_2$/CO$_2$ (50:50 v/v) mixture on FeNi-M/MOF are up to 24 and 40 min, respectively. Accordingly, the captured C$_2$H$_2$ was calculated to be 4.10 mol L$^{-1}$ with a separation factor of 1.7.

The isosteric heat of adsorption ($Q_{st}$) has been used to evaluate the strength of interaction between the adsorbent and the adsorbate, which is calculated (see Figure S13) from the adsorption isotherms at 273 and 298 K. The $Q_{st}$ values are 27–32.8 and about 24.5 kJ mol$^{-1}$ of FeNi-M/MOF for C$_2$H$_2$ and CO$_2$, respectively. The $Q_{st}$ value of C$_2$H$_2$ in FeNi-M/MOF is lower than those of other MOFs such as HKUST-1 (39 kJ mol$^{-1}$)$^{[15]}$ and FeNi-MOF-74 (47.5 kJ mol$^{-1}$)$^{[16]}$ and SIFSIX-2-Cu-i (41.9 kJ mol$^{-1}$)$^{[16]}$ and is comparable to that of UTSA-74 (31 kJ mol$^{-1}$).$^{[5]}$ These data indicate FeNi-M/MOF has a lower regeneration energy for C$_2$H$_2$ production, which would be beneficial for practical applications.

To understand the separation performance of FeNi-M/MOF, the adsorption modes of C$_2$H$_2$ in FeNi-M/MOF were established by DFT-D calculations (see Figure S14). The modeling structures indicated that there are two binding sites for C$_2$H$_2$ in FeNi-M/MOF: Site I, located in the middle of two adjacent pyz rings, where C$_2$H$_2$ was adsorbed through the π–π interactions between C$_2$H$_2$ and the pyz rings (see Figure S14a). The C$_2$H$_2$ static binding energy in site I is up to 41.4 kJ mol$^{-1}$. Site II, located in the middle of two adjacent Ni open metal sites, where C$_2$H$_2$ a molecule is adsorbed through the interactions between C$_2$H$_2$ and Ni open metal sites and is perpendicular to c axis. The C$_2$H$_2$ static binding energy in this site is 29.9 kJ mol$^{-1}$, which is smaller than that of site I (see Figure S14b).

Further visualization of these host–guest interactions was carried out through high-resolution neutron powder diffraction experiments. The crystal structure under low C$_2$H$_2$ loading was measured first (Figure 4a). As expected, C$_2$H$_2$ molecules preferentially distribute on site I. C$_2$H$_2$ molecules were identified between the two pyz rings through π–π stacking (3.552 Å). The C$_2$H$_2$ molecules show a tilting angle of 27.4° from the [001] direction (crystallographic c axis; see Figure S15a). In addition, multiple intermolecular interactions were also observed between C$_2$D$_2$ and FeNi-M/MOF (D···N$^\text{v}$: 2.977 Å, C$^6$···N$^\text{v}$: 3.808 Å, Figure 4c; see Figure S15b). In contrast, the preferential CO$_2$ binding site is located at the open Ni site (Figure 4b). The electronegative O$^\text{v}$ atoms of CO$_2$ interact with the positive open-metal site Ni$^6$. However, the distance across the channel is insufficient.
sites, with both very high C$_2$H$_2$ uptake and C$_2$H$_2$/CO$_2$ selectivity. The so-called dual functionality has been successfully realized by a mixed iron/nickel MOF FeNi-MOF using a metalloligand approach. The structural features of the cyanonickelate and optimal pore channels in this MOF allow C$_2$H$_2$ molecules to interact at multiple binding sites, with both very high C$_2$H$_2$ uptake and C$_2$H$_2$/CO$_2$ selectivity in volumetric ratio. This work also illustrates an outstanding example to further reveal the huge separation potential of MOF adsorbents, especially for challenging gas separation and purification. The active ongoing research affords tremendous opportunities for energy-efficient separation.

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**Conflict of interest**

The authors declare no conflict of interest.

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