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Mixed Metal-Organic Framework with Multiple Binding Sites for Efficient C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} Separation

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Abstract: The C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} separation is particularly challenging owing to their high similarity in physical properties and molecular sizes, but of industrial significance. Herein we report a mixed metal-organic framework (M-MOF) [Fe\textsubscript{2}(pyz)\textsubscript{4}Ni(CN)\textsubscript{4}]\textsubscript{4}\textsuperscript{-} (FeNi-M-MOF, pyz = pyrazine) with multiple functional sites and compact one-dimensional channels of ~4.0 Å for challenging C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} separation. This MOF shows not only a remarkable volumetric C\textsubscript{2}H\textsubscript{2} uptake of 133 cm\textsuperscript{3} g\textsuperscript{-1} but also an excellent C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} selectivity of 24 under ambient condition, resulting in the second highest C\textsubscript{2}H\textsubscript{2}-captured amount of 4.54 mol L\textsuperscript{-1} that outperforms most previous benchmark materials. The separation performance of this material has been validated by dynamic breakthrough and neutron diffraction experiments, which is driven by π-τ stacking and multiple intermolecular interactions between C\textsubscript{2}H\textsubscript{2} molecules and the binding sites of FeNi-M-MOF. Besides, this material can be facilely synthesized by mixing method at room temperature and is water stable, jointly highlighting FeNi-M-MOF as a promising material for C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{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 surface that can realize not only molecular sieving effect but also preferential gas binding.\textsuperscript{[1]} Plenty of MOFs have been explored for simplifying various gas separation and purification schemes, ranging from mature ones such as carbon dioxide capture (CO\textsubscript{2}) from methane and nitrogen to more challenging olefin/paraffin and alkyne/alkene separations.\textsuperscript{[2]} For C\textsubscript{2}H\textsubscript{2} and CO\textsubscript{2} gas molecules, their very high similarity in physical properties (differ in boiling point by ~3% and ~6 K), and identical molecular shapes/sizes (3.3 × 3.3 × 5.7 Å\textsuperscript{3} for C\textsubscript{2}H\textsubscript{2}, 3.2 × 3.3 × 5.4 Å\textsuperscript{3} for CO\textsubscript{2}) with both kinetic diameters of ~3.3 Å, make it very difficult and challenging to realize efficient porous materials for C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} separation under ambient conditions.\textsuperscript{[3]} A few ultramicroporous MOFs featuring bare oxygen or fluorine base sites have been developed to preferentially bind C\textsubscript{2}H\textsubscript{2} molecules through H-bonding interactions or bind CO\textsubscript{2} molecules through electrostatic interactions, showing high C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} selectivity but low C\textsubscript{2}H\textsubscript{2} uptake.\textsuperscript{[4]} Another approach is to incorporate strong adsorption binding sites mainly open metal sites into MOFs with large pore volumes to boost the uptake capacity of the preferred gas molecules.\textsuperscript{[5]} UTSA-74 represents a unique example with open metal centers of two accessible sites, which can bind two C\textsubscript{2}H\textsubscript{2} but only one CO\textsubscript{2} molecules, differing from its isomer MOF-74 which adsorbs similar amounts of C\textsubscript{2}H\textsubscript{2} and CO\textsubscript{2} under the same condition.\textsuperscript{[6]} Though progresses have been made over the past several years, the uptake capacity versus selectivity trade-off still poses a daunting challenge for addressing C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} separation.\textsuperscript{[6]}

The vast database of reported MOF structures enables comparative analyses to target potential candidates with dual functionalities, featuring moderate pore volumes and accessible functional sites, to realize both high gas uptake and separation selectivities. Among plentiful ligands, cyanide is a short and highly basic ligand that is feasible to construct robust MOFs with modest pore aperture size, such as Prussian blue and Hofmann-type compounds.\textsuperscript{[7]} For those MOFs with metaloligands, the open metal sites on ligands are accessible for gas molecules, whereas expected narrow pore structures originating from compact ligands enforce additional multiple intermolecular interactions to form, as demonstrated by a series of mixed metal-organic frameworks (M-MOFs).\textsuperscript{[8]} In this regard, a Hofmann-type MOF [Fe\textsubscript{2}(pyz)\textsubscript{4}Ni(CN)\textsubscript{4}]\textsuperscript{4}\textsuperscript{-} (FeNi-M-MOF, pyz = pyrazine) discovered in 2001, showing open nickel sites and polarized surfaces as well as compact pore channels of ~4.0 Å, is particularly interesting.\textsuperscript{[9]} The high density of functional sites and ultramicropore would collaboratively enforce gas separation with high gas uptake and separation selectivities. Herein we investigate the mixed iron/cyanid mixed metal MOF FeNi-M-MOF for potential C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} separation. In this MOF, C\textsubscript{2}H\textsubscript{2} molecules are found to preferentially bind onto the organic moieties and open Ni sites through π-τ stacking and multiple intermolecular interactions, respectively, whereas CO\textsubscript{2} molecules mainly distribute on the open Ni sites through relatively weak interactions. In this context, FeNi-M-MOF shows a very high C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} selectivity of 24 that is superior to the previous top-performing MOFs while retaining a remarkable C\textsubscript{2}H\textsubscript{2} uptake capacity of 133 cm\textsuperscript{3} g\textsuperscript{-1} and thus an excellent C\textsubscript{2}H\textsubscript{2}-captured capacity of 4.54 mol L\textsuperscript{-1} at 298 K and 1 bar for 50:50 C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} separation, which is close to that of the benchmark UTSA-74 and exceeds those of other out-performing MOFs.\textsuperscript{[8]}

FeNi-M-MOF is a pillared-layer M-MOF, in which the Fe[Ni(CN)\textsubscript{4}]\textsubscript{2} 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 moieties, whereas the Fe atoms are fully coordinated by nitrogen atoms from four different cyan moieties and two pyz linkers. Fe[Ni(CN)\textsubscript{4}]\textsubscript{2} layers are then connected by pyz linkers into a three-dimensional network with one-dimensional channels of about 4.15 × 4.27 or 3.94 × 4.58 Å\textsuperscript{2}.\textsuperscript{[8]}

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The open metal sites 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.

**Figure 1.** The crystal structure of FeNi-M'MOF viewed along the a/b axis. Fe, Ni, C, N, H in FeNi-M'MOF are represented by orange, green, gray, blue and white, respectively.

FeNi-M'MOF was synthesized at room temperature in water and methanol.\(^{[10]}\) By adding the solution of K\(_2\)[Ni(CN)\(_4\)] into the mixed methanol and water solution of Fe\(^{2+}\) 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 supporting information). This MOF also exhibits an 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 (Figure S4). The thermal stability of FeNi-M'MOF was also confirmed by variable temperature PXRD (Figure S5), indicating that FeNi-M'MOF can maintain its crystalline structure until ~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 m\(^2\) g\(^{-1}\) by N\(_2\) sorption experiment at 77 K as shown in Figure 2a. The experimental total pore volume is ~0.25 cm\(^3\) g\(^{-1}\), and slightly smaller than the theoretical one calculated from the crystal structure (0.30 cm\(^3\) g\(^{-1}\)), which can be attributed to the insufficient filling of N\(_2\) molecules in the ultramicroporous pore channels.
The C₂H₂ and CO₂ gas adsorption isotherms of FeNi-M’MOF were measured at 273 K and 298 K. As shown in Figure 2b, the volumetric C₂H₂ uptake capacity of FeNi-M’MOF is 133 cm³ g⁻¹ at 1 bar and 298 K, which is higher than those of many other MOFs, such as DICY-4-Ni-I (52 cm³ g⁻¹),[9a] ZJU-60a (96 cm³ g⁻¹)[11] Cu[Ni(pdt)]₂ (108 cm³ g⁻¹),[6d] SNNU-45 (113 cm³ g⁻¹),[6b] TIFSIX-2-Cu-I (116 cm³ g⁻¹),[6g] PCP-33 (128 cm³ g⁻¹),[12b] and comparable to those of UTSA-74 (144 cm³ g⁻¹).[8c] FJU-90a (146 cm³ g⁻¹),[6d] and Zn-MOF-74 (150 cm³ g⁻¹).[13] The CO₂ uptake of FeNi-M’MOF is 84 cm³ g⁻¹ (2.72 mmol g⁻¹) at 1 bar and 298 K. At 1 bar and 273 K, C₂H₂ and CO₂ uptakes of FeNi-M’MOF are up to 145 and 102 cm³ g⁻¹ respectively, as shown in Figure S8. Interestingly, the Pt analogue [Fe(pz)₂Pt(CN)₄] (FePt-M’MOF Figure S10-12) shows much lower uptake capacities for C₂H₂ and CO₂ (100 and 105 cm³ g⁻¹ respectively), indicating the potential binding contribution of Ni sites in this type of MOF for C₂H₂ 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 C₂H₂/CO₂ (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),[6c] FJU-90a (4.3),[6d] UTSA-74a (8.2),[6b] JCM-1 (13.4),[4c] DICRO-4-Ni-I (13.9),[4a] 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 C₂H₂ reduced its separation performance. In contrast, FeNi-M’MOF can address such trade-off between the adsorption capacity and selectivity as shown in Figure 2d. The high selectivity and high C₂H₂ adsorption capacity of FeNi-M’MOF jointly reveal its bright separation potential for C₂H₂/CO₂.

Transient breakthrough simulations were conducted to demonstrate the C₂H₂/CO₂ 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 C₂H₂/CO₂ mixtures. The C₂H₂/CO₂ mixtures (50/50) were used as feeds to mimic the industrial process conditions. Pure CO₂ first eluted through the bed, where the CO₂ purity is 99.95%, and followed by the breakthrough of C₂H₂ after a certain time break that FeNi-M’MOF has been saturated by C₂H₂. The C₂H₂-captured 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)[8c] and higher than those of most out-performing MOFs, such as Zn-MOF-74 (4.06 mol L⁻¹),[6d] FJU-90a (4.16 mol L⁻¹),[6d] PCP-33 (4.16 mol L⁻¹).[12b] Accordingly, FeNi-M’MOF shows not only a high C₂H₂/CO₂ selectivity and high C₂H₂ uptake but also high C₂H₂-captured capability from gas mixture, enabling this material a huge C₂H₂/CO₂ separation potential. Based on experimental breakthrough studies, we further evaluated the performance of FeNi-M’MOF in near practical separation processes for C₂H₂/CO₂ mixture (50/50 v/v) as shown in Figure 3b. Indeed, FeNi-M’MOF exhibits excellent C₂H₂/CO₂ mixtures separation performance at 298 K. CO₂ was first eluted through the adsorption bed without any detectable C₂H₂, whereas the latter was retained in the MOF column for a remarkable period prior to saturate the MOF. The retained time of pure CO₂ and C₂H₂ for C₂H₂/CO₂ (50/50 v/v) mixture on FeNi-M’MOF are up to 24 and 40 min respectively. Accordingly, the captured-C₂H₂ was calculated to be 4.10 mol L⁻¹ with a separation factor of 1.7.

The isosteric heat of adsorption (Qₑ) has been used to evaluate the strength of interaction between the adsorbent and the adsorbate, which is calculated (Figure S13) from the adsorption isotherms at 273 and 298 K. The Qₑ values are 27.32±8.0 and 24.5 kJ mol⁻¹ of FeNi-M’MOF for C₂H₂ and CO₂, respectively. The Qₑ value of C₂H₂ in FeNi-M’MOF is lower than those of other MOFs such as HKUST-1 (39 kJ mol⁻¹),[15a] FeMOF-74 (47.5 kJ mol⁻¹),[15b] and SIFSIX-2-Cu-I (41.9 kJ mol⁻¹,[15c] and is comparable to that of UTSA-74 (31 kJ mol⁻¹).[9c] These data indicate FeNi-M’MOF has a lower regeneration energy for C₂H₂ production, which would be beneficial for practical application.

To understand the separation performance of FeNi-M’MOF, the adsorption modes of C₂H₂ in FeNi-M’MOF were established by DFT-D calculations (Figure S14). The modeling structures indicated that there are two binding sites for C₂H₂ in FeNi-M’MOF. Site I located in the middle of two adjacent pyz rings, where C₂H₂ was adsorbed through the π-π interactions between C₂H₂ and pyz rings (Figure S14a). The C₂H₂ 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 C₂H₂ molecule was adsorbed through the interactions between C₂H₂ and Ni open metal sites and was perpendicular to c axis. The C₂H₂ static binding energy in this site is 29.9 kJ mol⁻¹, which is smaller than that of site I (Figure S14b).

Further visualization of these host-guest interactions was carried out through high-resolution neutron powder diffraction experiments. The crystal structure under low C₂D₂ loading was measured first (Figure 4a). As expected, C₂D₂ molecules preferentially distribute on site I. C₂D₂ molecules were identified between the two pyz rings through π-π stacking (3.552 Å). The C₂D₂ molecules show a tilting angle of 27.4° from the [001] direction (crystallographic c axis) (Figure S15a). In addition, multiple intermolecular interactions were also observed between C₂D₂ and FeNi-M’MOF (D···π*: 2.977 Å, O···N*: 3.080 Å, Figure 4c and Figure S15b). In contrast, the preferential CO₂ binding site is located at the open Ni site (Figure 4b). The electronegative O⁻ atoms of CO₂ interact with the positive open metal site Ni⁵⁺. However, the distance across the channel is insufficient for favorable Ni⁵⁺·O⁻↔C=O⁻·Ni⁵⁺ interactions to form in the structure. Thus, CO₂ molecules were adsorbed near the center of the channel and parallel to the channel. O⁰ atom of

![Figure 3](image-url)
Figure 4. Neutron diffraction crystal structure of FeNi-M'MOF (a) and FeNi-M'MOF-2 CO₂ (b), viewed from a/b axis. Adsorption binding sites of C₂D₂ (c) and CO₂ (d) for FeNi-M'MOF. Fe, Ni, C, N, O, H in FeNi-M'MOF and CO₂ are represented by orange, green, grey, blue, red, white, respectively. C and D in C₂D₂ are represented by orange and white, respectively. The labelled distance is measured in Å.

In summary, the highly selective C₂H₂/CO₂ separation has been successfully realized by a mixed iron/nickel MOF FeNi-M'MOF from metalloidigan approach. The structural features of cyanocarikolate and optimal pore channels in this MOF allow C₂H₂ molecules to interact on multiple binding sites, with both very high C₂H₂ uptake and C₂H₂/CO₂ selectivity in volumetric ratio. The so-called dual functionality in this material enable this MOFs to serve as one of the best materials for C₂H₂/CO₂ separation in terms of C₂H₂-captured capability. 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.

Keywords: metal-organic frameworks • gas separation • acetylene • Hofmann • open metal sites

FeNi-M’MOF with a microporous one-dimensional channel decorated with multiple binding sites shows a high CH₂ uptake (133 cm³ cm⁻³) and high CH₂/CO₂ selectivity (24).