Enhanced Gas Uptake in a Microporous Metal–Organic Framework via a Sorbate Induced-Fit Mechanism

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Supporting Information

ABSTRACT: Physical adsorption of gas molecules in microporous materials is an exothermic process, with desorption entropy driving a decrease in uptake with temperature. Enhanced gas sorption with increasing temperature is rare in porous materials and is indicative of sorbate initiated structural change. Here, sorption of C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{6}, and C\textsubscript{3}H\textsubscript{8} in a flexible microporous metal–organic framework (MOF) [Cu\textsubscript{12}(FPBDC)\textsubscript{12}(H\textsubscript{2}FPBDC = 5-(5-fluoropyridin-3-yl)-1,3-benzenedicarboxylic acid)] that increases with rising temperature over a practically useful temperature range is reported along with other small molecule and hydrocarbon sorption isotherms. Single X-ray diffraction studies, temperature-dependent gas sorption isotherms, in situ and variable temperature powder X-ray diffraction experiments, and electronic structure calculations were performed to characterize the conformation-dependent sorption behavior in NKU-FlexMOF-1. In total, the data supports that the atypical sorption behavior is a result of loading-dependent structural changes in the flexible framework of NKU-FlexMOF-1 induced by sorbate-specific guest–framework interactions. The sorbates cause subtle adaptations of the framework distinct to each sorbate providing an induced-fit separation mechanism to resolve chemically similar hydrocarbons through highly specific sorbate–sorbent interactions. The relevant intermolecular contacts are shown to be predominantly repulsion and dispersion interactions. NKU-FlexMOF-1 is also found to be stable in aqueous solutions including toleration of pH changes. These experiments demonstrate the potential of this flexible microporous MOF for cost and energy efficient industrial hydrocarbon separation and purification processes. The efficacy for the separation of C\textsubscript{2}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} mixtures is explicitly demonstrated using NKU-FlexMOF-1a (i.e., activated NKU-FlexMOF-1) for a particular useful temperature range.

INTRODUCTION

Among various porous materials, metal–organic frameworks (MOFs), also known as porous coordination polymers, are a promising class of crystalline materials with voids or internal surface areas that have become a focus in both chemistry and materials science.\textsuperscript{1–3} MOFs are inherently inorganic–organic hybrids with structural bond strengths that permit sorbate induced flexibility, distinguishing them from other porous solids.\textsuperscript{4–6} Considering extant MOFs, about 100 of some 20 000 reported MOFs exhibit breathing or flexibility, making them exciting candidates for storage, selectivity, separations, and sensing.\textsuperscript{7–9} The flexibility of MOFs can be attributed to many mechanisms, such as the rotation of the organic ligands, multiple accessible configurations of metal nodes and clusters, the sliding of interpenetrated subnetworks, and the inherent collective vibrational relaxation of a particular topology.\textsuperscript{10–12} Reversible motions result from external stimuli including changes in temperature or pressure, the presence or removal of guest molecules, photoactive moieties, or electrical and magnetic interactions that trigger structural flexibility.\textsuperscript{13–15} Understanding tailoring and exploitation of the dynamic phenomena occurring in flexible frameworks and their pores suggests tunable or desired properties that help realize the...
promote of smart materials. Therefore, focused efforts are underway to construct flexible MOFs and understand their structure–property relationships while tailoring them to specific aims. For example, NH$_2$-MIL-53(Al) is a flexible MOF that when mixed with PSF Udel P-3500 forms a nanocomposite membrane that produces increased CO$_2$/CH$_4$ selectivity up to 77 with increased pressure. The mixed matrix membrane’s (MMM) ability to achieve high selectivity was attributed to the dynamic behavior of NH$_2$-MIL-53(Al) particles. In addition, the MOF [Cu(aip)(H$_2$O)](solvent)$_n$ (aip = 5-azidoisophthalate) selectively sorbs CO with adaptable pores; unprecedented high selectivity was achieved by CO molecules coordinating with copper(II) ions, resulting in a global transformation of the framework. Flexible MOFs for light hydrocarbons applications, exhibiting selective sorption behavior, are desirable due to the importance of hydrocarbons as energy resources and commodity chemicals in the petrochemical industry.

Here, a flexible microporous MOF (Cu(FPBDC)]-DMF)$_n$ (NKU-FlexMOF-1) (H$_2$FPBDC = 5-(5-fluoropyridin-3-yl)-1,3-benzenedicarboxylic acid) was synthesized using [Cu$_2$(COO)$_4$N$_2$] paddle-wheel SBUs and FPBDC$^{2-}$ ligands. The MOF, [Cu(FPBDC)] (NKU-FlexMOF-1a), exhibits a guest-specific structural deformation of the flexible framework when activated. The material subtly adapts to each sorbent via an induced-fit mechanism where electronic repulsion and intermediate range dispersion interactions balance in a manner sufficiently distinct for each sorbate that the energetics allows for chemical resolution of similar species. To this point, as a result of the MOF’s framework responding to the presence of sorbates, NKU-FlexMOF-1a exhibits inversely temperature enhanced sorption behavior for C$_2$H$_6$, C$_3$H$_6$ and C$_3$H$_8$ over a measured temperature range. Distinct from conventional gas adsorption behaviors inherent in rigid porous materials, the maximum saturated uptake amounts gradually increase with temperature in a practically useful temperature and pressure range, as suggested in Scheme 1 and demonstrated in Figure 2.

**Scheme 1.** On the Basis of the Strongly Guest-Triggered Structure Deformation of the Flexible Framework, the Framework Exhibits Inversely Enhanced Adsorption Behaviors for C$_2$H$_6$, C$_3$H$_6$ and C$_3$H$_8$.

The unusual sorption behavior associated with the flexibility results from the framework adapting aptly with increased temperature to produce species-specific induced fits; NKU-FlexMOF-1a captures relatively large amounts of C$_3$H$_8$ at a higher temperature and can efficiently separate C$_2$H$_6$/C$_3$H$_6$ at the lower temperatures studied while maintaining a recognizably similar sorbate–sorbent structure and associated physical interactions. It was found that the repulsion and dispersion interactions are determined by small structural changes and the electrostatic environment remains very similar for the related chemical sorbates (e.g., C$_2$H$_6$/C$_3$H$_6$/C$_3$H$_8$).

### RESULTS AND DISCUSSION

**Synthesis, Crystal Structure, and Stability of NKU-FlexMOF-1.** The reaction of H$_2$FPBDC and CuCl$_2$·2H$_2$O under solvothermal conditions produced a porous framework NKU-FlexMOF-1. Single-crystal X-ray diffraction analysis of NKU-FlexMOF-1 (Table S1) showed that each Cu(II) ion is coordinated by four carboxylic oxygen atoms and one pyridine nitrogen atom from five FPBDC$^{2-}$ ligands and that the two adjacent Cu(II) ions constitute a [Cu$_2$(COO)$_4$N$_2$] paddle-wheel SBU (Figure 1a). Each FPBDC$^{2-}$ ligand coordinates to three paddle-wheel SBUs, giving a three-dimensional (3D) coordination framework with narrow open triangular 1D channels. The known flexibility of frameworks with rhombic channels led to investigating potential framework distortions in response to sorption.

![Figure 1. (a) Coordination environment of ligand FBDC$^{2-}$ and Cu(II). Key: Cu in turquoise, C in light gray, N in blue, O in red, and F in green. All H atoms were omitted for clarity. (b) 3D structure showing the narrow open triangular 1D channels. (c) Simplified 3D structure that suggests its continuous deformability via the “hinges.”](image)

The solvent and thermal stabilities of NKU-FlexMOF-1 were first demonstrated by PXRD and thermogravimetric (TG) analyses (Figures S1–S3). The TG curve and VT-PXRD patterns show that the thermal stability of NKU-FlexMOF-1 extends to about 340 °C. As shown in the PXRD pattern (Figure S3), NKU-FlexMOF-1 exhibits good stability to a wide pH range (3–11). After immersing in aqueous solutions with different pH values, the samples were analyzed by optical microscopy and scanning electron microscopy (SEM), demonstrating their crystalline state and stable morphology (Figures S4 and S5). The aqueous solutions were measured to assess the content of Cu$^{2+}$ by ICP, which results in Table S4 show that there are only small pH-independent concentrations.
of Cu$^{2+}$, confirming that NKU-FlexMOF-1 has good stability in pH range 3–11. These robust properties, especially water stability, which is uncommon and highly desired for MOFs, make NKU-FlexMOF-1 practically useful.

**Gas Adsorption Properties of NKU-FlexMOF-1a.** Prior to gas adsorption measurements, NKU-FlexMOF-1 was activated by heating the material to 140 °C under a dynamic vacuum to obtain the desolvated NKU-FlexMOF-1a. At 77 K, $N_2$ adsorption measurements were then used to assess the porosity and structural flexibility. The evacuated Brunauer–Emmett–Teller and Langmuir surface areas of NKU-FlexMOF-1a were calculated to be 952 and 993 m$^2$ g$^{-1}$, respectively (Figure S7). The $N_2$ adsorption isotherm exhibits a series of discrete steps apparent on a log plot at low pressure (Figure S6), indicating that NKU-FlexMOF-1a shrinks when solvent molecules are fully evacuated and responsively transforms to a series of expanded structures under increasing guest gas pressure, assuming a new conformation for each sorbed molecule. Thus, the transitions are gradual rather than an abrupt gated phenomena. At 1.0 bar, NKU-FlexMOF-1a reaches an expanded phase with a captured $N_2$ density of 270.9 cm$^3$ g$^{-1}$ (3.9 mol mol$^{-1}$).

Next, single-component adsorption isotherms of guest-free NKU-FlexMOF-1a for $N_2$, CO$_2$, CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, and C$_4$H$_{10}$ were measured at 273 and 298 K and other temperatures for selected species. As shown in Figures S8–
S14, with the increase of sorbate size, correlating with stronger dispersion interactions, the adsorption isotherms become steeper for very low pressures. Consider the empirical kinetic diameters are 3.3 Å (CO₂), 3.758 Å (CH₄), 4.163 Å (C₂H₆), 4.443 Å (C₃H₆), 4.678 Å (C₄H₁₀), 4.3 – 5.118 Å (C₆H₁₄), and 4.687 Å (n-butane).⁴⁰ Note that the larger gas sorbates with electron rich double bonds have stronger host–guest interactions between these molecules and the NKU-FlexMOF-1a framework relative to those with single bonds; compared to molecules of similar size, the molecule with a double bond typically has a stronger binding with the framework via electrostatic and related interactions.

In addition, the isosteric heats of gas sorption (Qᵣ, Figure S26a), calculated via the common Clausius–Clapeyron approach using isotherm fits to a virial type equation, are consistent with this interpretation. The isosteric heats were also estimated using an integrated version of the Clausius–Clapeyron equation shown in Figure S26b,c.¹¹ The integrated form of the equation is equivalent to the differential form when employed over a small, effectively infinitesimal, temperature range. For the multitemperature measurements common in gas sorption, the integrated form has the advantage that multiple collinear points demonstrate that the inherent approximations are reasonable. This is especially important in the case of continuously flexible frameworks where a large change in structure or chemical environment makes Clausius–Clapeyron heats a reasonable estimate of the thermodynamics, but not a precise quantitative measure. The resulting temperature-dependent isosteric heats are reported and support the same conclusions. Note there is not a perfect way to extract sorption heats from isotherms in a continuously flexible material where Qᵣ will be everywhere loading and T dependent without performing calorimetry explicitly. This is also true for rigid frameworks if the sorption mechanism changes between isotherm temperatures. Nonetheless, the Clausius–Clapeyron Qᵣ values remain a valuable guide here. It is clear that specific sorbate–sorbent interactions are discernible from the neat isotherms, and this suggests their involvement in inducing sorbent conformational changes.

As shown in Figure S26a, the estimated initial Qᵣ⁰ values of NKU-FlexMOF-1a are 32.2 kJ mol⁻¹ for CO₂, 24.4 kJ mol⁻¹ for CH₄, 33.5 kJ mol⁻¹ for C₂H₆, 34.5 kJ mol⁻¹ for C₃H₆, 52.5 kJ mol⁻¹ for C₄H₁₀, and 61.6 kJ mol⁻¹ for C₆H₁₄, and 57.4 kJ mol⁻¹ for C₆H₁₄. While the adsorption isotherms of N₂, CO₂, CH₄, C₂H₆, C₃H₆, C₄H₁₀ and C₆H₁₄ are typical at 273 and 298 K, for C₆H₁₄ the behavior is anomalous. When the temperature is raised from 273 to 298 K, the overall C₆H₁₄ uptake increases as well; this phenomenon is rare in an exothermic physisorption system. Because entropic free energy contributions are favored at higher temperatures, sorption enthalpies must substantially increase with temperature. This too implies that collective structural changes take place in the porous material to account for the resulting stronger interactions.

Specifically, it is found that while the electrostatic environment remains remarkably similar for even different hydrocarbons (Table S8), the induced-fit nature of the compound provides repulsion and dispersion, aka van der Waals interactions, that lead to the observed distinct energetics. The structural changes are demonstrated to be small even in the fully loaded structures (Figure S45). However, the calculated energetics are still quite different, as shown in Table S7. The calculated energy differences are substantial and give rise to the observed separations and temperature enhanced sorption. The energetic differences necessarily arise largely from the repulsion and dispersion portions of the intermolecular potential energy. The repulsions are well thought of as exponentially distant dependent, and the dispersion attractions are a large inverse power of the distance. Thus, a subtle interplay between these functions gives rise to unique energetics for each sorbate and temperature. This situation is analogous to what is typically found in enzyme–substrate interactions with similar useful structure or function relationships.

To further explore this unusual behavior, the adsorption isotherms for C₄H₁₀ at different temperatures (258, 268, 273, 278, 288, 298, 308, 318, 328, 338, and 348 K) were measured. As shown in Figure 2a, in the range 258 – 318 K, the maximum saturated uptake amounts at 113 kPa gradually increase with increasing temperature. The sorbed amount reaches a maximum at about 318 K. At temperatures above 318 K, NKU-FlexMOF-1a exhibits typical adsorption behavior, where the sorption decreases as the temperatures increase (Figure 2b). From 258 to 318 K, the C₄H₁₀ uptake capacity in NKU-FlexMOF-1a increases considerably from 52.2 cm³ g⁻¹ (258 K) to 66.8 cm³ g⁻¹ (318 K), a change of 14.6 cm³ g⁻¹.

Considering the typical sorption behavior of NKU-FlexMOF-1a for C₄H₁₀, the adsorption isotherms for C₂H₆, C₃H₆ and C₃H₈ at different temperatures were also measured (Figure 2c–f). Interestingly, the sorption behaviors of C₂H₆ and C₃H₆ are similar to that of C₄H₁₀. Maximum saturated uptake amounts appear at 273 K for C₂H₆ and at 268 K for C₃H₆ subsequently, the uptake amounts gradually decrease with increasing temperature (Figure 2c–e). The magnitude of increasing sorption with temperature is different for C₂H₆, C₃H₆ and C₄H₁₀. For C₂H₆ when the temperature is increased from 248 to 273 K, the maximum saturated uptake increased by 6.8 cm³ g⁻¹, from 65.6 cm³ g⁻¹ (248 K) to 72.4 cm³ g⁻¹ (273 K). Considering C₃H₆, the maximum saturated uptake amount increased by 2.0 cm³ g⁻¹, from 71.7 to 73.7 cm³ g⁻¹ over a temperature range of 258 – 268 K. The resulting rates of change are 0.27, 0.20, 0.24 cm³ g⁻¹·K⁻¹ for C₂H₆, C₃H₆ and C₄H₁₀ respectively.

Conversely, the adsorption isotherms for C₆H₁₄ are typical with respect to uptake with temperature, but with an inflection clearly visible in the lower temperature isotherms (Figure 2f), reflecting the flexibility of the framework. The more typical uptake pattern indicates the sorbate–sorbent interactions are not strongly increasing with temperature; the larger size sorbate likely inhibits the ability to interact as effectively with the framework. Interestingly, the estimated isosteric heat still increases with loading on the basis of the differential, virial form analysis of the isotherms. Figure 2g shows the variation of saturated uptakes for C₂H₆, C₃H₆, C₄H₁₀, and C₆H₁₄ at different temperatures highlighting the temperature enhanced sorption for C₂H₆, C₃H₆, and C₆H₁₄ within a particular temperature and pressure range.

Analysis of Framework Flexibility. The adsorption isotherms of NKU-FlexMOF-1a for N₂ and CO₂ at 77 and 195 K, respectively (Figures S6 and S16), exhibit a series of distinct steps at very low pressures from the framework flexibility. The structural changes resulting from guest loading conditions are challenging to characterize but can lead to an understanding of host–guest interactions and the corresponding framework flexibility.⁵² Although some techniques, such as IR/Raman spectroscopy, NMR, and powder X-ray diffraction, have been used to probe the nature of sorbates in MOF
structures, the use of in situ single-crystal X-ray diffraction (SCXRD) is useful because it provides unequivocal structural information relating to different sorbent conformational states. Thus, single-crystal X-ray diffraction and in situ powder X-ray diffraction experiments were performed to characterize the flexibility of the framework NKU-FlexMOF-1a in the presence of sorbates.

Analyzing crystal data parameters (Table 1), the b-axis and c-axis of NKU-FlexMOF-1a change by $-0.464 \text{ Å}$ and $+0.215 \text{ Å}$, respectively, compared with solvated NKU-FlexMOF-1, which demonstrates that the framework has shrunk after removing guest solvent DMF molecules. In addition, the crystal structures containing N$_2$ molecules at low or high pressures were obtained, respectively (the pressure of NKU-FlexMOF-1a-N$_2$-a < the pressure of NKU-FlexMOF-1a-N$_2$-b). With increasing N$_2$ pressure, the number of N$_2$ molecules in the channels increases and induces a swelling of the framework. This is evidenced by distinct changes of the framework flexibility. However, as shown in Figure S43, at 273 K the F-group on the ligand adds lability to the torsion, resulting in the stepwise N$_2$ adsorption behavior at 77 K. Thus, the functional group on the organic linker plays a significant role for the flexibility of the final MOF framework.

As a result, shown in Figure S34, the dihedral angle between pyridyl and phenyl rings was enlarged by 3.489°, changed from 45.094 to 48.583°, when the number of N$_2$ molecules in the asymmetric unit increased. Further, the twist of the FBDC$^-$ ligand results in the angle between paddle-wheel SBUs and phenyl rings changing by $-5.207$ from $46.929$ to $41.722$°, and $-0.996$ from $21.482$ to $20.486$°.

![Figure 3](image)

Figure 3. (a) With increasing N$_2$ pressure, the sizes and angles of triangular channels for NKU-FlexMOF-1a-N$_2$-a and NKU-FlexMOF-1a-N$_2$-b are shown from SCXRD. (b) In situ powder X-ray diffraction patterns are shown for NKUFlexMOF-1a at 83 K and variable N$_2$ pressures (as indicated) and are consistent with the structures seen in SCXRD.

Next, in order to understand the structural transformation in depth, in situ powder X-ray diffraction experiments were performed under various pressures of N$_2$ at 83 K. As shown in Figure 3b, from 0 to 5 kPa, there are substantial changes of the positions of the diffraction peaks, but between 5 and 101 kPa, there are only very small changes in position and minor changes to the intensities of some diffraction peaks. In the vacuum state, the PXRD pattern is the same as that of the sample at 0 kPa, which indicates that the expanded phase is reversibly converted back to the collapsed phase.

Further, the refinement of the in situ PXRD patterns of NKU-FlexMOF-1a at different N$_2$ pressures was performed. The results, as shown in Table S5, revealed that unit cell volume increases slowly followed by the increase of pressure, which shows the framework has the property of guest-induced flexibility. However, as shown in Figure S35, at 273 K the PXRD pattern does not exhibit obvious changes with an increase in N$_2$ pressure. Thus, the guest N$_2$ gas molecules at...
low temperatures are sorbed with stronger framework interactions that trigger the ligand torsion leading to the structural changes reflected in the isotherms and a PXRD consistent with the low thermal barrier noted above with an energy corresponding to a temperature of about 200 K, as shown in Figure S43.

**Guest-Induced Flexibility.** In order to further explore the effect of CO$_2$ and hydrocarbon guest molecules on the flexible behavior of framework, the *in situ* powder X-ray diffraction patterns were measured at 298 K under different gas atmospheres ($P = 100$ kPa) corresponding to the asymptotic region of the gas isotherms where structural changes are complete for the sorbates considered. As shown in Figure 4.

**Figure 4.** *In situ* powder X-ray diffraction patterns for NKU-FlexMOF-1a at room temperature and variable gas atmosphere (as indicated).

cmpared with NKU-FlexMOF-1a under a vacuum condition, the structural transformations induced by the guest molecules are evident. The changes are characteristic of the sorbate as reflected in the changes to the positions of the diffraction peaks in Figure 4 and correspond to distinct fits to each sorbate adapting to their mutual steric and attractive interactions. The diffraction peaks moving toward low angles indicate pore size increase, and the degrees of movement increase with the size of the guest molecules. Furthermore, considering a sample loaded with propane, the positions of the diffraction peaks exhibit mild shifts with varied temperature (Figure S40). This reflects that the framework loaded with propane changing with temperature.

In addition to *in situ* powder X-ray diffraction measurements, the crystal structures containing C$_2$H$_6$, C$_3$H$_8$, or CO$_2$ molecules were measured. When the crystal data of NKU-FlexMOF-1a-C$_2$H$_6$, NKU-FlexMOF-1a-C$_3$H$_8$, and NKU-FlexMOF-1a-CO$_2$ are compared with the crystal data of NKU-FlexMOF-1a (Table 1), the unit parameters of NKU-FlexMOF-1a-C$_2$H$_6$ are similar to the parameters of NKU-FlexMOF-1a, which coincides with *in situ* PXRD result that exhibits relatively small changes compared with those of other gas molecules. For NKU-FlexMOF-1a-C$_2$H$_6$ and NKU-FlexMOF-1a-CO$_2$, their unit cell parameters show obvious changes. In the NKU-FlexMOF-1a-C$_2$H$_6$, all axes increase mildly and the $\beta$ angle increases by 1.65°. When CO$_2$ molecules are entered into the channel of NKU-FlexMOF-1a, the unit cell parameter of the $b$-axis increases 0.9 Å and the $c$-axis decreases 0.7 Å. On the basis of above results, it can be confirmed that the different guest molecules lead to distinct conformational accommodations. At the room temperature, the sample was kept in equilibrium for long times in a C$_3$H$_8$ atmosphere, and the phase was assessed by using *in situ* powder X-ray diffraction; the sample was activated under a dynamic vacuum and the recovered phase was characterized. The experiments were recorded over four cycles, which exhibited good reversibility (Figure S41). Furthermore, the morphologies of NKU-FlexMOF-1, NKU-FlexMOF-1a, and the crystals after multiple cycles were compared by optical microscopy and scanning electron microscopy (SEM). As shown in Figure S42, the morphologies of the crystals after multiple cycles are retained.

These transformations reflect different intermolecular interactions between the guest molecules and the framework; a structure that responds distinctly, i.e., adapts subtly but meaningfully, to an array of chemically related species is a promising candidate for applications where physical sorbate–sorbent interactions seek to resolve similar molecules. This makes NKU-FlexMOF-1 a desirable platform for hydrocarbon capture and separation, as the flexible framework response to sorption acts to distinguish between the chemical entities by more extensive interactions, e.g., through shape, charge, dispersion, or polarization, that are not possible in rigid sorbate–sorbent systems. In rigid platforms, only a small subset of physical and chemical interactions are sampled, as the sorbate is in contact with the sorbent for a restricted set of orientations and distances that cannot be mutually optimized, interacting with a rigid substrate. This limits the potential chemical resolution achievable through the rigid interactions, while a flexible material can capture the differences in structures through enhanced sampling of the interactions via the adaptable solid state structure as seen in NKU-FlexMOF-1a.

**First-Principles Calculations on Framework Flexibility.** In order to further explore the flexible nature of NKU-FlexMOF-1a, we compare the SCXRD structure of the as-synthesized NKU-FlexMOF-1 with that of the activated sample NKU-FlexMOF-1a. Upon desolvation, the lattice unit cell shrinks slightly, mainly within the $b$–$c$ plane. The overall unit cell volume decrease is quite small (only $\sim$2.4%); however, the decrease in PLATON pore volume resulting from the structural change is significant at $\sim$17% (0.291 vs 0.242 cc g$^{-1}$). This demonstrates how small structural accommodations can meaningfully adapt to sorbates.

To elucidate the mechanism of the structural flexibility, a detailed computational first-principles investigation was performed on the basis of dispersion-corrected density functional theory (DFT-D). The as-synthesized structure NKU-FlexMOF-1, using the coordinates with the solvent removed *in silico*, and the activated structure NKU-FlexMOF-1a were first fully geometry optimized. Then nudged elastic band calculations were performed to find a minimum energy path for the structural change between the two phases. An animation consisting of snapshots of the transformation clearly shows how the pore shrinks smoothly and continuously along the structural change coordinate (see Animation of transformations Supporting Information).

In the NKU-FlexMOF-1 structure, the [Cu$_2$(COO)$_2$N$_2$] paddle-wheel, the linker phenyl ring, and the linker pyridine ring are relatively rigid, while the joints connecting these three types of rigid units are flexible, particularly in terms of the relative orientation of the linked units. These flexible
coordination bonds are largely responsible for the flexibility of the NKU-FlexMOF-1a framework.

Our lattice dynamics calculation on the activated structure NKU-FlexMOF-1a further shows that there are several low energy “soft” phonons, i.e., collective structural relaxation coordinates, resulting from these flexible coordination bonds (see Figure S44). Shown as an example in Supporting Information as Animation of transformations-2 is a phonon with ~4 meV energy (32 cm$^{-1}$), involving the rotation of the pyridyl rings. Upon guest inclusion, internal structural distortion takes place, mediated by the low frequency collective coordinates and may further couple with lattice distortions. Subtle conformational changes then mutually “optimize” the structure to interact effectively with different sorbates.

**Breakthrough Experiments for Binary C$_3$H$_6$/C$_3$H$_8$ Mixtures.** Remarkably, due to the unique adsorption behaviors for C$_3$H$_6$ and C$_3$H$_8$, as shown in Figure S23, at a lower temperature range (258–273 K), the uptake amount of C$_3$H$_6$ is distinctly larger than that of C$_3$H$_8$, indicative of the C$_3$H$_6$/C$_3$H$_8$ selectivity in this range. This is confirmed via a breakthrough experiment for a C$_3$H$_6$/C$_3$H$_8$ (50/50, v/v) mixture on NKU-FlexMOF-1a material at 273 and 298 K (Figure S46), to check its actual separation ability for the gas mixture. As shown in Figure S5b,c C$_3$H$_6$ first broke through the adsorption bed and yielded a high purity gas (>99.99%), whereas after a certain time C$_3$H$_8$ slowly eluted. The long breakthrough time interval between C$_3$H$_6$ and C$_3$H$_8$ suggests that NKU-FlexMOF-1a material is effective for practical C$_3$H$_6$/C$_3$H$_8$ separation as was suggested by the thermodynamic and structural results above. According to the breakthrough experiment, as shown in Table S6 and Figure S23, the calculated adsorption capacity of C$_3$H$_6$ is 1.96 mmol g$^{-1}$ and the selectivity is 2.31 at 1 bar at 298 K, and the adsorption capacity and selectivity are 2.13 mmol g$^{-1}$ and 2.66 at 1 bar at 273 K, respectively. The calculated adsorption capacity of C$_3$H$_8$ at 298 K is higher than that at 273 K, which is in line with the adsorption results. In addition, after the breakthrough experiment, the purity of desorbed propylene is 85.2%, as shown in Figure S24, which was consistent with the calculated selectivity. Afterward, cycling breakthrough experiments on NKU-FlexMOF-1a material were carried out under the same conditions. The breakthrough time intervals for C$_3$H$_6$/C$_3$H$_8$ mixtures in five cycles (Figure S5d) are close (~24 min), showing that this material has a good regenerability. Note the difference of adsorption capacity is the largest at 258 K, but our current laboratory setup is unable to perform the analogous colder experiments. Then we carried out breakthrough simulations for a C$_3$H$_6$/C$_3$H$_8$ (50/50, v/v) mixture, in a fixed bed to demonstrate the feasibility of separation of propylene and propane in a pressure swing adsorption operation at 258 K (Figure S25). The simulations also demonstrate the NKU-FlexMOF-1a is of potential use for this challenging separation of C$_3$H$_6$/C$_3$H$_8$ mixtures.

**Analysis of Gas Adsorption and Separation Behavior.** Flexible MOFs have transformable frameworks that are able to reversibly respond to external stimuli such as temperature, pressure, light, electric/magnetic fields, or the presence of particular species. Understanding how these materials change when perturbed will have applications in the development of smart materials and superior separations. Ideally, identification of extant and design of aspirational materials with adaptive properties is possible given a detailed understanding of relevant intermolecular interactions.

Here, a flexible microporous MOF showing inversely enhanced adsorption behavior for C$_2$H$_6$, C$_3$H$_6$, and C$_3$H$_8$ in a defined temperature and pressure range is presented. The increase in sorption with temperature is attributed to the dynamic behavior of NKU-FlexMOF-1a where guest molecules subtly interacting with an adaptive framework lead to an induced-fit specific to each sorbate. Notably, the material geometry and chemical environment is little changed between sorbates and the energetic differences are attributable to the
detailed changes in the van der Waals, aka repulsion and dispersion, interactions similar to enzyme–substrate interaction mechanisms. Further, to confirm that equilibrium phenomena is not the determining factor, the C\textsubscript{3}H\textsubscript{6} isotherm at 258 and 298 K was obtained with long equilibration intervals between two points (at least 124 min). As shown in Figure S15, the adsorption amount at 298 K is consistently larger than that at 258 K, which is consistent with the trend reported in the pristine measurement. These results indicate that the inversely increased gas uptake at higher temperature should be due to the structure change of the NKU-FlexMOF-1a at different temperatures instead of the different diffusion resistances.

To understand why it is requisite that the framework is adaptive in response to sorbate contact, examine the thermodynamics of sorption. Because the magnitude of thermodynamic sorption at constant pressure (P) and temperature (T) is governed by the Gibbs free energy $G = H - TS$, an increase in temperature will necessarily lead to decreased sorption if the material can be considered a rigid framework. Consider the entropy of the sorbate is decreased with substantial interaction with a rigid or flexible framework as the conformational space it can explore is restricted; for example, the rotations are hindered, and the relatively large translational entropy contribution is greatly diminished. Thus, the entropy change upon “binding” is negative. Because the intermolecular interactions are temperature independent (i.e., the potential energy function is not T dependent), the only way for the free energy to decrease is for the enthalpy to sharply decrease with increasing temperature.

Given the enthalpy, $H = E + PV$, there is no significant differential contribution from the PV term upon contact, and thus the interaction energy must substantially decrease as T increases. This can only happen as a result of the material changing its conformation to produce more stable interactions with sorbates, implying closer contacts with more favorable molecular interactions than were present in the lower T structure. To this point, consider that a single structure will have larger amplitude thermal motions with increasing temperature that would tend to decrease the sorbate–sorbent system enthalpy, and only a mutually beneficial structural change can explain the observed increase in sorption that is referred to herein as an induced-fit mechanism. This is what is observed in the case of NKU-FlexMOF-1a, a flexible MOF that has adaptive conformational transformations in response to contact with the different sorbate molecules tested. Many of them show atypical increases in sorption with temperature, all of which have isotherms characteristic of material structural changes in response to sorption and similar structures for comparable loadings.

The nature of the conformational changes observed is guest specific and related to the detailed sorbate–sorbent interactions in the adaptive micro pores of NKU-FlexMOF-1a. The maximum saturated uptake amounts of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} and C\textsubscript{3}H\textsubscript{8} gradually increase, which is an atypical behavior compared with conventional physical adsorption. CO\textsubscript{2}, N\textsubscript{2}, and C\textsubscript{3}H\textsubscript{10} also induce structural changes but show typical diminished sorption as temperature is increased. Understanding the detailed nature of the different behaviors requires further investigation and careful molecular modeling. Nonetheless, the distinct temperature dependence of the sorbent enthalpies and the material stability make NKU-FlexMOF-1a an exciting candidate for hydrocarbon and potentially other small molecule separations via the induced-fit mechanism.

Further, on the basis of the observed adsorption behavior at the different temperatures considered, there is a useful difference in adsorption capacity between C\textsubscript{3}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} that can be employed for selective separation of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8}. Along this line, the breakthrough experiment and simulation both demonstrate NKU-FlexMOF-1a is of potential use for this challenging separation of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} mixtures.

To better understand the separation mechanism, the saturated crystal structures, reported here, of C\textsubscript{3}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} were taken and optimized using dispersion-corrected periodic DFT calculations in the program CP2K.\textsuperscript{45} C\textsubscript{3}H\textsubscript{6} calculations serve as a point of calibration and reference in interpreting the results. Next, the C\textsubscript{3}H\textsubscript{8} molecules were mutated to C\textsubscript{3}H\textsubscript{6} in silico and optimizations were performed with a resulting 0.204 Å RMSD between the resulting framework coordinates. The resulting structures are shown superimposed (Figure S45) and have analogous structures that imply separation mechanisms that are similarly mediated by different detailed energetics via van der Waals repulsions and attractions, consistent with the induced-fit mechanism.

The nature of the sorption is similar; the separation chemistry and surface areas will be comparable for the separations considered. This was further confirmed by examining derived partial charges for saturated structures that demonstrate the commensurate chemistry evidenced by the highly similar electrostatic environment (Table S8). The energy per sorbate was also calculated in the loaded, effectively zero temperature configuration, and calculations consistently show the sorption energy averaged over fully loaded configurations with $E(C_3H_6) \approx E(C_3H_8) \approx E(C_3H_8)$; values are presented in Table S7. While the double bonded C\textsubscript{3}H\textsubscript{6} will clearly have enhanced electrostatic interactions, the conformational adaptation leads to enough increase in van der Waals energies that both propane and propene are substantially higher in binding energy than ethane that are similarly bound.

\section{CONCLUSION}

In summary, we report a flexible microporous MOF (NKU-FlexMOF-1), which exhibits sorbate induced-fit dynamic behavior. On the basis of the behavior, sorption of C\textsubscript{3}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8} and C\textsubscript{3}H\textsubscript{8} in NKU-FlexMOF-1a increases with rising temperature over a practically useful temperature and pressure range. Then the difference in adsorption capacity between C\textsubscript{3}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} can induce the selective separation of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8}. Therefore, this work provides not only a new flexible MOF with distinct and useful adsorption behaviors for C\textsubscript{3}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8} and C\textsubscript{3}H\textsubscript{8} but also a design strategy of seeking and constructing flexible, induced-fit MOFs with flexible ligand motions; the material responds distinctly to sorbates of interest for gas capture and separation, exploiting the extreme sensitivity of repulsion and dispersion interactions to small changes in distance. Materials with adaptive structural characteristics and tunable host–guest interactions as a function of both sorbate and temperature have a much wider range of utility than rigid materials. The induced-fit mechanism revealed in this study provides new directions for the design of flexible MOFs for the development of adsorption-based separation and capture technologies.
Materials and measurements, details of syntheses, gas sorption data, calculations on framework flexibility, and gas adsorption tables of crystal data and structure refinement parameters, Cu$^{+}$ in aqueous solutions, unit cell parameters, PXRD patterns, binding energies, and average partial charges, figures of TG curves, VT-PXRD patterns, images of crystals, adsorption isotherms, adsorption points, calculated selectivity, components of desorbed mixtures, breakthrough simulations, isosteric heats, details of virial equations, structure analysis, X-ray diffraction patterns, torsional landscape, DFT-D calculated phonon density of states, and schematic diagram of device of breakthrough experiments (PDF)

Animation of transformations-1 (GIF)

Animation of transformations-2 (GIF)

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