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Investigating CO\textsubscript{2} Sorption in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn) Through Computational Studies

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ABSTRACT: A combined Monte Carlo (MC) simulation and periodic density functional theory (DFT) study of CO\textsubscript{2} sorption was performed in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn), a family of hybrid ultramicroporous materials (HUMs) that consists of \textsuperscript{2+} ions coordinated to pyrazine ligands and are pillared with SiF\textsubscript{6}\textsuperscript{2−} (“SIFSIX”) anions. Grand canonical Monte Carlo (GCMC) simulations of CO\textsubscript{2} sorption in all five SIFSIX-3-M variants produced isotherms that are in good agreement with the corresponding experimental measurements. The theoretical isosteric heat of adsorption (Q\textsubscript{st}) for CO\textsubscript{2} as obtained through canonical Monte Carlo (CMC) simulations are also in close agreement with the experimental values. Consistent with experiment, the simulations generated the following trend in the CO\textsubscript{2} Q\textsubscript{st}: SIFSIX-3-Cu > SIFSIX-3-Ni > SIFSIX-3-Co > SIFSIX-Zn > SIFSIX-3-Fe. The magnitudes of the theoretical Q\textsubscript{st} and relative trend were further supported by periodic DFT calculations of the adsorption energy for CO\textsubscript{2} within the respective HUMs. We attribute the observed Q\textsubscript{st} trend in SIFSIX-3-M to their differences in pore size and lattice parameters. Specifically, the sorption energetics decrease with increasing pore size and a/b lattice constant. Simulations of CO\textsubscript{2} sorption in SIFSIX-3-Cu resulted in different profiles for the radial distribution function (g(r)) and dipole distribution than within the other analogues due to smaller pore size and much shorter a/b unit cell lengths of the crystal structure: this is a direct consequence of the Jahn-Teller effect. Although these HUMs are isostuctural, notable differences in the classical energy contributions for CO\textsubscript{2} sorption were observed from the GCMC simulations. Overall, this study demonstrates that the CO\textsubscript{2} Q\textsubscript{st} in SIFSIX-3-M can be controlled by the choice of the saturated metal, with values ranging from 42 to 54 kJ mol\textsuperscript{-1}.

I. INTRODUCTION

The concentration of CO\textsubscript{2} in the atmosphere is presently close to 410 ppm,\textsuperscript{1} which is about 45% greater than the CO\textsubscript{2} levels that are associated with pre-industrial times.\textsuperscript{2} The continued use of fossil fuels through industrial activity contributes to increasing CO\textsubscript{2} emissions. By 2050, the atmospheric CO\textsubscript{2} concentration is projected to be nearly double that of pre-industrial levels.\textsuperscript{3} The rapid buildup of CO\textsubscript{2} in the atmosphere causes the average temperature of the Earth to increase, an effect widely known as global warming. Thus, there is a pressing need to reduce CO\textsubscript{2} emissions in order to sustain life on Earth for future generations.

Methods to mitigate atmospheric CO\textsubscript{2} concentrations include separating CO\textsubscript{2} from post-combustion effluents or removing CO\textsubscript{2} directly from the atmosphere. A current technology for capturing CO\textsubscript{2} from flue gases or the air involves using aqueous alkaliamines, a process known as amine scrubbing.\textsuperscript{5} However, this method has been proven to be costly as there are extensive energy requirements for solvent regeneration since alkaliamines react chemically with CO\textsubscript{2}.\textsuperscript{6} Therefore, an efficient and inexpensive method for selectively removing CO\textsubscript{2} from anthropogenic sources is desired.

Metal–organic materials (MOMs) represent a class of crystalline solids that have been shown to be promising for applications in CO\textsubscript{2} capture and separation.\textsuperscript{7,8} Indeed, certain MOMs have the potential to separate CO\textsubscript{2} from flue gas and remove CO\textsubscript{2} directly from the air.\textsuperscript{9–12} These materials consist of metal ions that are coordinated to organic ligands (or “linkers”), with the resulting structure composed of a one-, two-, or three–dimensional framework that includes pores and channels.\textsuperscript{13} MOMs are capable of sorbing CO\textsubscript{2} molecules within their pores and channels and have the ability to release the sorbates freely through changes in thermodynamic conditions. Thus, unlike alkaliamines, MOMs rely on reversible physisorption to interact with the CO\textsubscript{2} molecules. In addition, most MOMs are fairly inexpensive to synthesize.

A number of different MOM structures can be synthesized by altering the metal ion and/or linker.\textsuperscript{14} A subclass of MOMs that combines short organic linkers (or interpenetration) to generate ultramicropores (< 0.7 nm) with inorganic anions (e.g., M\textsubscript{6}\textsuperscript{2−} (M = Si, Ti, Ge), M\textsubscript{2}\textsuperscript{2−} (M = Cr, Mo, W), Cr\textsubscript{2}O\textsubscript{5}\textsuperscript{2−}) that serve as “pillars” are hybrid ultramicroporous materials (HUMs).\textsuperscript{15–21} These materials are exceptional candidates for CO\textsubscript{2} capture and separation since they have been shown to display benchmark selectivity for
CO₂ over other gases, such as N₂, CH₄, and H₂O.\textsuperscript{22-25} The incorporation of strong electrostatics from the inorganic anions that line the pore walls allows HUMs to exhibit high affinity for CO₂.

HUMs belonging to the SIFSIX-3-M platform have been shown to display unprecedented selectivity and high isosteric heat of adsorption (Q_{st}) toward CO₂.\textsuperscript{22,24,26-28} These materials consist of M\textsuperscript{2+} ions that are coordinated to pyrazine (pyz) ligands to form a two-dimensional square grid; the M\textsuperscript{2+} ions are pillared in the third dimension with SiF\textsubscript{6}\textsuperscript{2-} ("SIFSIX") anions to create a three-dimensional pillared square grid that exhibits primitive cubic (pcu) topology and contains saturated metal centers (SMCs). The formula of these HUMs is therefore [M(pyz)\textsubscript{2}SiF\textsubscript{6}]. An illustration of the crystal structure of SIFSIX-3-M is shown in Figure 1.

The Zn analogue, SIFSIX-3-Zn, was the first member of the SIFSIX-3-M family to be synthesized.\textsuperscript{22,29} Although it was originally studied for its H₂ sorption properties,\textsuperscript{29} later experimental studies have shown that the HUM displayed remarkable CO₂/CH₄, CO₂/N₂, and CO₂/H₂ selectivity, even in the presence of moisture.\textsuperscript{22} The Q_{st} for CO₂ in SIFSIX-3-Zn was measured to be 45 kJ mol\textsuperscript{-1}, which was one of the highest for a material that does not possess open-metal sites or amine functional groups at the time. As revealed through computational studies, the high CO₂ Q_{st} for this material was attributed to the strong electrostatic interactions between the CO₂ molecules and the SIFSIX pillars in a confined space.\textsuperscript{22,30}

Later on, SIFSIX-3-Cu was synthesized and gas sorption measurements revealed that the HUM exhibited higher selectivity and Q_{st} for CO₂ than SIFSIX-3-Zn.\textsuperscript{24} Indeed, the CO₂ Q_{st} for the Cu variant was determined to be 54 kJ mol\textsuperscript{-1}. This enhancement in the Q_{st} could be attributed to the smaller pore size that SIFSIX-3-Cu displayed relative to SIFSIX-3-Zn. SIFSIX-3-Ni and SIFSIX-3-Co were synthesized shortly after,\textsuperscript{27} with the former being reported by two different groups.\textsuperscript{26,27} Although the CO₂ Q_{st} for SIFSIX-3-Ni and SIFSIX-3-Co are lower than that for SIFSIX-3-Cu, these variants displayed higher CO₂ uptake capacity for both pure component and 15:85 CO₂/N₂ mixtures under dry and wet conditions at 298 K/0.15 bar.\textsuperscript{27} More recently, SIFSIX-3-Fe was synthesized\textsuperscript{28} and we present experimental CO₂ sorption isotherms and Q_{st} values for this analogue herein.

Although members of the SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn) family are isostructural, they exhibit different CO₂ sorption properties that are dependent on the identity of the saturated metal. In addition, altering the M\textsuperscript{2+} ion causes differences in the bond lengths between various atoms within the crystal structure. As a result, these HUMs display distinct unit cell lattice parameters.\textsuperscript{24,27-29} The lattice parameters and unit cell volumes for all five HUMs based on previously reported single crystal X-ray data are displayed in Table 1. Differences in bond lengths and lattice constants lead to these HUMs exhibiting different pore sizes. For SIFSIX-3-M, pore size is defined as the diagonal F-F distance across the channel subtracted by the sum of the van der Waals radius of each F atom (2.94 Å). These values are summarized in Table 2 for the individual HUMs. A graphical representation of the pore size of these HUMs is shown in Figure 2. The pore size within the SIFSIX-3-M family ranges from 3.54 to 3.84 Å.

The experimentally measured Brunauer–Emmett–Teller (BET) surface areas\textsuperscript{31} for all five SIFSIX-3-M variants are displayed in Table 3. The trend in the BET surface areas within this series is not consistent with those observed for the a/b unit cell lengths and pore sizes of these materials (see Tables 1 and 2). This could be related to the difficulties of using the BET method to obtain accurate surface areas in materials with ultramicropores.\textsuperscript{32,33} Moreover, we calculated the accessible surface areas and theoretical pore volumes for these SIFSIX-3-M materials on the basis of their crystal structures and the results are also presented in Table 3. The former was calculated using a code developed by Dürer et al.,\textsuperscript{34} while the latter was calculated using the PLATON software.\textsuperscript{35} The trend for both of these quantities is the following: SIFSIX-3-Fe > SIFSIX-3-Zn > SIFSIX-3-Co > SIFSIX-3-Cu > SIFSIX-3-Ni. This is mostly consistent with the trends in the a/b lattice parameters and pore sizes for this family, although SIFSIX-3-Ni exhibits a smaller accessible surface area and theoretical pore volume than SIFSIX-3-Cu. This could presumably be due to the smaller unit cell volume for the Ni analogue (see Table 1). The accessible surface areas for these HUMs are much lower than the corresponding BET surface areas that were obtained through experiment. This could be attributed to regions in these materials that are inaccessible for the spherical probe molecule to "roll" over in the geometrical calculations.\textsuperscript{36}

In this work, we perform a combined Monte Carlo (MC) simulation and periodic density functional theory (DFT) study of CO₂ sorption in all five existing members of SIFSIX-3-M. Classical MC simulations are carried out within the grand canonical and canonical ensembles to generate theoretical CO₂ sorption isotherms and Q_{st} values, respectively. This was done in order to gain insights into the relative CO₂ sorption affinities for these HUMs. It will be shown that our simulated CO₂ sorption isotherms and Q_{st} values are in very good agreement with experiment for the individual HUMs. We also reproduce the relative trend that is observed for the experimental CO₂ Q_{st} within the SIFSIX-3-M platform. The magnitudes of the theoretical CO₂ Q_{st} values and relative trend will be further supported by periodic DFT calculations for a CO₂ molecule localized in the unit cell of the respective HUMs. It is expected that differences in the pore size and a/b unit cell lengths are mainly responsible for these HUMs displaying distinct Q_{st} for CO₂.

Our classical potential energy function for the MC simulations consists of repulsion/dispersion, stationary electrostatic, and many-body polarization interactions. We examine the relative contribution of each energetic term toward CO₂ sorption in all five HUMs through grand canonical Monte Carlo (GCMC) simulations and show that there are various differences in the percent energy contributions between certain analogues. This study also presents an analysis of the radial distribution function (g(r)) of CO₂ molecules about the Si atom of the pillar and the distribution of induced dipoles on the sorbate molecules for each SIFSIX-3-M analogue. It will be revealed that one of the variants (SIFSIX-3-Cu) exhibit a notably different g(r) and dipole distribution than the other members.

### II. METHODS

A. Experimental Section

Experimental CO₂ sorption data for SIFSIX-3-Co, SIFSIX-3-Ni, SIFSIX-3-Cu, SIFSIX-3-Zn were re-
ported in previous work in references 27, 27, 24, and 22, respectively, and are shown here for comparison to simulations in this study. SIFSIX-3-Fe was prepared using the previously reported procedure by dissolving pyrazine (2 mmol, 0.16 g) with FeSiF₆·6H₂O (1 mmol, 0.31 g) in 20 mL of methanol and heating at 85 °C for 3 days. The as-synthesized samples of SIFSIX-3-Fe were exchanged with methanol for 3 days (2 times per day) prior to activation. The resulting solid was filtered and evacuated at 75 °C for 15 hours under dynamic pressure (< 5 μmHg). CO₂ sorption isotherms were collected for SIFSIX-3-Fe using an automatic gas sorption analyzer (Quantachrome Autosorb IQ, Quantachrome Instruments, Boynton Beach, FL, United States). The experimental CO₂ Qₘₚ for SIFSIX-3-Fe was obtained by directly applying the Clausius–Clapeyron equation to the experimental sorption isotherms at 278, 298, and 318 K (see Supporting Information for more details).

B. Theoretical Section

All MC simulations and periodic DFT calculations were performed in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn) using the crystal structure and associated lattice parameters shown in Table 1 for the respective analogues. We note that two different crystal structures have been published for SIFSIX-3-Ni.²⁶,²⁷ For this analogue, the results are presented for calculations within the crystal structure reported in reference 27. We also performed simulations within the other reported crystal structure for this variant, which exhibits different lattice parameters and pore size (see Supporting Information, Tables S9–S10). The results, however, are very similar to those obtained for simulations in the crystal structure reported by Elsaeid et al. (see Supporting Information, Figures S11–S13 and Table S11).

1. Grand Canonical Monte Carlo

GCMC simulations of CO₂ sorption were performed in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn) to generate theoretical sorption isotherms within the respective HUMs. This method keeps the chemical potential (µ), volume (V), and temperature (T) of a simulation box containing the HUM–CO₂ system constant while permitting other thermodynamic quantities, such as the number (N), to fluctuate.³⁸ The GCMC simulations were executed within the 3 × 3 × 3 system cell of the individual HUMs. All HUM atoms were constrained to be rigid for the simulations. CO₂ was modeled as a rigid five–site polarizable potential that was developed previously and has been shown to produce outstanding results within various HUMs.¹⁶–¹⁸,²²,²³,²⁷,³⁴,³⁰,³⁴,⁴¹ Notably, it was observed in certain cases that using a polarizable model resulted in CO₂ sorption isotherms and Qₘₚ values that were in better agreement with experiment compared to using nonpolarizable potentials.⁴²,⁴³ More details on the GCMC methods are provided in the Supporting Information.

The total potential energy (U) of the HUM–CO₂ system was calculated by summing the repulsions/dispersion, stationary electrostatic, and many-body polarization energies. These were calculated using the Leonard-Jones 12–6 potential, the Coulomb potential via Ewald summation, and a Thole-Applequist type polarization model.⁴⁶–⁴⁹ respectively. The inclusion of explicit polarization interactions in simulation was necessary to examine the distribution of induced dipoles on the CO₂ molecules in these HUMs. All HUM atoms were assigned Leonard-Jones ϵ and σ, point partial charges, and scalar point polarizabilities to model the corresponding interactions. Comprehensive details of obtaining these parameters are given in the Supporting Information. The GCMC simulations were executed with the Massively Parallel Monte Carlo (MPMC) code, an open-source code that is currently available for download on GitHub.⁵⁰

2. Canonical Monte Carlo

Canonical Monte Carlo (CMC) simulations of CO₂ sorption were performed in all five members of SIFSIX-3-M in order to evaluate the Qₘₚ for CO₂ in the individual HUMs. This method keeps N, V, and T of the HUM–CO₂ system constant while allowing other thermodynamic quantities to vary. Note, while GCMC methods can be used to calculate the Qₘₚ through fluctuations in N and U, the high affinity that these HUMs have toward CO₂ makes it difficult to obtain such Qₘₚ values at low loadings (< 2 mmol g⁻¹). Indeed, at 298 K/0.01 atm, the CO₂ uptakes for all five variants are already ≥ 2.00 mmol g⁻¹ according to the GCMC simulations. This demonstrates that all five SIFSIX-3-M materials exhibit exceptionally high CO₂ uptake at low pressures (< 0.10 atm). In order to better evaluate the Qₘₚ in these materials at lower loadings, it was necessary to perform CMC simulations with varying numbers of CO₂ molecules within the individual system cells.

CMC simulations were carried within the 3 × 3 × 3 system cell of the respective HUMs with N = 1, 3, 6, 9, 12, 15, 18, 21, 24, and 27. These simulations utilized the same HUM force field and sorbate potential as described in section II.B.1. For all loadings considered, the simulations ran for a total of 1.0 × 10⁶ MC steps to ensure reasonable ensemble averages for U. The theoretical CO₂ Qₘₚ values were estimated by taking the ensemble averaged potential energy and dividing by N. Because there is only one type of CO₂ sorption site in these HUMs, this method to calculate the Qₘₚ appears to be appropriate for the system under the conditions considered.⁴⁰,⁵⁲ As with the GCMC simulations, all CMC simulations were performed using the MPMC code.⁵⁰

3. Periodic Density Functional Theory

Periodic DFT calculations were performed to evaluate the adsorption energy (ΔE) for CO₂ in SIFSIX-3-M. These calculations were implemented with the Vienna ab initio Simulation Package using the projector augmented wave (PAW) method, Perdew–Burke–Ernzerhof (PBE) functional, and DFT-D2 correction. Calculations within SIFSIX-3-Fe, SIFSIX-3-Co, SIFSIX-3-Ni, SIFSIX-3-Cu, and SIFSIX-3-Zn utilized multiplicity values of 5 (high-spin), 2 (low-spin), 3 (high-spin), 2, and 1, respectively, for the metal ions prior to relaxation. The optimizations were performed with the constraint that the total number of unpaired electrons in each crystal structure remained consistent with these spin states. The position of a single CO₂ molecule was initially optimized within the rigid unit cell of the respective HUMs. Next, another optimiza-
tion was performed in which the position of all atoms within the HUM–CO$_2$ system were allowed to vary, but under the constraint of the lattice parameters shown in Table 1. Afterwards, the $\Delta E$ for CO$_2$ in all five HUMs was calculated by the following:

$$\Delta E = E(\text{HUM + CO}_2) - E(\text{HUM}) - E(\text{CO}_2) \quad (1)$$

where $E(\text{HUM + CO}_2)$ is the energy of the unit cell of the HUM with the CO$_2$, $E(\text{HUM})$ is the energy of the empty unit cell, and $E(\text{CO}_2)$ is the energy of the CO$_2$. The calculated $\Delta E$ values for CO$_2$ in all five SIFSIX-3-M analogues are displayed in Table 5. In addition, the F(HUM)–C(CO$_2$) interaction distances based on the optimized CO$_2$ molecule positions within the respective HUMs are shown in Table 6.

### III. RESULTS AND DISCUSSION

#### A. Sorption Isotherms

The experimental and simulated CO$_2$ sorption isotherms for all five SIFSIX-3-M variants at 298 K and pressures up to 1 atm are displayed in Figure 3(a). The experimental isotherm shown for SIFSIX-3-Co, SIFSIX-3-Ni, and SIFSIX-3-Zn utilized the raw data taken from references 27, 27, and 22, respectively. The experimental data for SIFSIX-3-Cu were estimated from reference 24, while those for SIFSIX-3-Fe are newly reported in this work. We note that the experimental CO$_2$ sorption isotherm shown here for SIFSIX-3-Ni is similar to that reported in other CO$_2$ sorption studies on this variant.\textsuperscript{17,26} A plot of the CO$_2$ uptakes vs. the logarithm of the pressures is shown in Figure 3(b).

As seen in Figure 3(a), the experimental isotherms for all analogues show a significantly sharp increase in CO$_2$ uptake at very low loading (< 0.05 atm), indicating exceptionally strong interactions between the HUM and the sorbate molecules. CO$_2$ saturation was reached in these HUMs at ca. 0.20 atm. The simulated CO$_2$ sorption isotherms for the five variants show the same trend as experiment, with calculated uptakes that are in reasonable agreement with experiment for the pressure range considered. While the simulated uptakes for all SIFSIX-3-M variants are close to the corresponding experimental uptakes for pressures above 0.10 atm, such theoretical values overestimate experiment at lower pressures. This could be due to the fact that it may take some time for the CO$_2$ molecules to diffuse into the small channels of the materials in experiment at initial loading, resulting in measured low-pressure uptakes that are lower than those predicted through modeling. In this work, the simulated uptakes were produced by GCMC methods, which involve the random insertion, deletion, and movement of sorbate molecules in a simulation box containing the HUM. As a result, the effects of transport and associated kinetic phenomena are not an issue in GCMC simulations. A similar effect was observed for simulations of gas sorption in other porous materials with narrow pore sizes.\textsuperscript{62,63} Simulations of CO$_2$ sorption were also performed in SIFSIX-3-M at other temperatures and we observed decent agreement with the corresponding experimental data under these conditions as well (see Supporting Information, Figures S5–S9).

Although the experimental CO$_2$ sorption isotherms for all five SIFSIX-3-M analogues at 298 K display the same behavior, some differences in the uptakes can be observed at low and high pressures. These differences are also reflected in the simulated CO$_2$ sorption isotherms, especially at low pressures. A summary of the experimental and simulated CO$_2$ uptakes at 298 K and pressures of 0.10 and 1 atm for all five variants is presented in Table 4. At pressures approaching 0.10 atm, SIFSIX-3-Fe exhibits the lowest CO$_2$ uptake, followed by SIFSIX-3-Zn. The fact that these two SIFSIX-3-M analogues have the largest pore sizes within the series (see Table 2) could explain why these variants display lower CO$_2$ uptake than the other members under these conditions. Larger pore sizes lead to less optimal interactions between the framework and the sorbate molecules.

Overall, there is a small, but noticeable difference in the experimental CO$_2$ uptakes at 298 K and 0.10 atm as a result of metal substitution in the SIFSIX-3-M series, with uptakes ranging from 2.43 to 2.68 mmol g$^{-1}$ at this state point (see Table 4). The simulations revealed a smaller range in the CO$_2$ uptakes within the SIFSIX-3-M family under the same condition (2.65 to 2.75 mmol g$^{-1}$). This could be attributed to the fact that each material already contains close to 1 CO$_2$ molecule per unit cell at 298 K/0.10 atm, arising from the absence of dynamic accessibility issues in GCMC simulations as explained above.

In general, experiment and simulation suggest the following trend in the CO$_2$ uptake at 298 K and 0.10 atm: SIFSIX-3-Ni > SIFSIX-3-Co > SIFSIX-3-Cu > SIFSIX-3-Zn > SIFSIX-3-Fe. Although SIFSIX-3-Co and SIFSIX-3-Ni exhibit higher CO$_2$ uptake than SIFSIX-3-Cu at 298 K/0.10 atm, the Cu variant shows greater uptake at ca. 0.001 atm than the other two analogues according to a close-up view of the experimental and simulated isotherms from 0–0.10 atm (see Supporting Information, Figure S4(a)). This is because SIFSIX-3-Cu has the smallest pore size within the series, which allows for this HUM to interact more strongly with the CO$_2$ molecules at very low loading. This also explains why SIFSIX-3-Cu displays higher $Q_{st}$ for CO$_2$ than SIFSIX-3-Co and SIFSIX-3-Ni as shown and discussed in section III.B.

At 298 K/1 atm, the trend in the experimental CO$_2$ uptake is SIFSIX-3-Ni > SIFSIX-3-Fe > SIFSIX-3-Co > SIFSIX-3-Zn > SIFSIX-3-Cu. Any difference in the experimental uptakes between the SIFSIX-3-M variants under this condition could be a consequence of sample preparation and the type of gas adsorption equipment utilized. On the other hand, the simulations revealed that all five SIFSIX-3-M materials display nearly the same CO$_2$ uptake at 298 K and 1.0 atm. This is because the materials already reached CO$_2$ saturation (1 molecule per unit cell) under this condition. Therefore, the simulated uptake values shown in Table 4 at 298 K/1.0 atm correspond to the CO$_2$ uptake at 1 molecule per unit cell loading for the individual HUMs. Since the molar mass of the system cell is used to calculate the GCMC-calculated average particle number to a gravimetric uptake quantity (i.e., mmol g$^{-1}$), the slight difference in the simulated CO$_2$ uptakes within the SIFSIX-3-M series at this state point can be attributed to differences in the molar mass of the metal.

#### B. Isosteric Heats of Adsorption and Adsorption Energies

A comparison of the experimental CO$_2$ $Q_{st}$ values with those determined from CMC simulations for all five
SIFSIX-3-M analogues is shown in Figure 4. The experimental \( Q_{st} \) plot shown for SIFSIX-3-Co, SIFSIX-3-Ni, and SIFSIX-3-Zn were taken from references 27, 27, and 22, respectively, while the plot for SIFSIX-3-Cu was estimated from reference 24. The experimental \( Q_{st} \) values for CO\(_2\) in SIFSIX-3-Fe were determined through applying the Clausius–Clapeyron equation\(^{37} \) to the experimental sorption isotherms collected in this work. More details of this process are provided in the Supporting Information. We obtained an initial \( Q_{st} \) value of 42 kJ mol\(^{-1} \), which is consistent with what was reported recently for this analogue.\(^{64} \) Note, the experimental CO\(_2\) \( Q_{st} \) shown here for SIFSIX-3-Ni is similar to those reported in other CO\(_2\) sorption studies on the HUM.\(^{17,26} \)

As shown in Figure 4, the simulated CO\(_2\) \( Q_{st} \) for all five HUMs are in excellent agreement with experiment in both magnitude and general shape. Notably, the theoretical \( Q_{st} \) values for the SIFSIX-3-M variants are essentially constant for all uptakes considered, indicating that there is only one type of CO\(_2\) sorption site in these HUMs. The experimental and simulated CO\(_2\) \( Q_{st} \) values for SIFSIX-3-M are summarized in Table 5. Experimental measurements show the following trend in the \( Q_{st} \) for CO\(_2\) within the SIFSIX-3-M family: SIFSIX-3-Cu > SIFSIX-3-Ni > SIFSIX-3-Co > SIFSIX-3-Zn > SIFSIX-3-Fe. This trend in the CO\(_2\) \( Q_{st} \) has been reproduced by our simulations.

Note, previous theoretical studies of CO\(_2\) sorption in SIFSIX-3-Cu, SIFSIX-3-Ni, and SIFSIX-3-Zn produced \( Q_{st} \) values of 51, 47, and 43 kJ mol\(^{-1} \) for the respective analogues.\(^{65} \) Our calculated CO\(_2\) \( Q_{st} \) values are 55.4, 51.9, and 45.2 kJ mol\(^{-1} \) for the Cu, Ni, and Zn variants, respectively, which are closer to the corresponding experimental values (see Table 5). The variation in the calculated \( Q_{st} \) for the individual HUMs in this work and the study presented in reference 65 can be attributed to differences in the force field that was utilized for the HUM and sorbate. Specifically, our simulations account for explicit many-body polarization interactions, which the earlier study omits. It is expected that the inclusion of this energetic term allows for more realistic modeling of the HUM–CO\(_2\) interaction in SIFSIX-3-M, resulting in \( Q_{st} \) values that are in line with experiment.

Comparing the CO\(_2\) \( Q_{st} \) for the SIFSIX-3-M variants with the \( a/b \) lattice constants and pore sizes (shown in Tables 1 and 2, respectively) for the individual HUMs reveals a strong correlation between such quantities. SIFSIX-3-Cu exhibits the shortest \( a/b \) unit cell lengths, which results in the HUM having the smallest pore size of the series. This allows for stronger interactions between the HUM and the CO\(_2\) molecule, thus explaining why this analogue displays the highest CO\(_2\) \( Q_{st} \) within the family. It has been well-documented in the MOM literature that smaller pore sizes lead to greater concurrent interactions between the sorbate molecules and the framework.\(^{52,66–68} \)

In accord with trends in the pore size, SIFSIX-3-Ni has the next highest CO\(_2\) \( Q_{st} \) followed by SIFSIX-3-Co. SIFSIX-3-Fe and SIFSIX-3-Zn have essentially the same value for the pore size, but the former displays a lower CO\(_2\) \( Q_{st} \) due to having the longer \( a/b \) unit cell lengths. We have therefore attributed the trend in the CO\(_2\) \( Q_{st} \) within SIFSIX-3-M to differences in the pore sizes and lattice parameters for these HUMs. In general, the smaller the pore size and \( a/b \) lattice constants, the greater the \( Q_{st} \) for CO\(_2\).

The magnitudes of the theoretical \( Q_{st} \) values in SIFSIX-3-M are close to the calculated \( \Delta E \) values for CO\(_2\) within the individual HUMs as determined through periodic DFT calculations that were implemented with VASP (see section II.B.3). The calculated \( \Delta E \) values for CO\(_2\) localized within the unit cell of the respective SIFSIX-3-M analogues are also shown in Table 5. It can be observed that the trend in the \( \Delta E \) is consistent with the \( Q_{st} \) values determined from experiment and CMC simulations.

It has been well-established through theoretical studies\(^{17,22,30,65} \) and in situ powder X-ray diffraction\(^{27} \) in SIFSIX-3-M that the CO\(_2\) molecules reside in the center of the channel with the C atom of the sorbate participating in favorable electrostatic interactions with the equatorial F atoms of four different SIFSIX pillars. An illustration of the optimized position of a CO\(_2\) molecule within SIFSIX-3-Ni as determined through periodic DFT calculations using VASP is shown in Figure 5. A graphically similar picture can be observed for CO\(_2\) localized within the other four variants.

The interaction distances between the C atom of the DFT-optimized CO\(_2\) molecule and the surrounding equatorial F atoms of the SIFSIX pillars for all five SIFSIX-3-M analogues are presented in Table 6. It can be deduced that shorter F(HUM)···(CO\(_2\)) distances lead to greater calculated \( \Delta E \) values. Note, the F(HUM)···(CO\(_2\)) distance obtained in this work for SIFSIX-3-Ni (3.23 Å) is very close to the corresponding distance that was observed for the HUM through powder X-ray diffraction (3.24 Å).\(^{57} \) In addition, the F(HUM)···(CO\(_2\)) distances shown in Table 6 for SIFSIX-3-Cu, SIFSIX-3-Ni, and SIFSIX-3-Zn are comparable to those obtained in reference 65 for the respective variants using similar periodic DFT methods.

### C. Radial Distribution Functions

As shown through periodic DFT calculations, the most optimal position of a CO\(_2\) molecule in SIFSIX-3-M is within the center of the pore. However, our GCIMC simulations show that the CO\(_2\) molecules can adopt a number of distinct positions within the channel, with varying distances from the pillars. For instance, it is possible for a CO\(_2\) molecule to sorb closer to one of the pillars within the square grid than the others. The modeled system cell for SIFSIX-3-Ni displaying the sites of CO\(_2\) occupancy in the material from GCMC simulations at 298 K and 1 atm is shown in Figure 6. A very similar distribution of sites was observed in the system cell for the other variants at this state point.

In order to examine the different distances that were obtained between the CO\(_2\) molecules and the pillars from the GCMC simulations, we plot the normalized CO\(_2\) population as a function of the Si(HUM)···(CO\(_2\)) distance in an equilibrated HUM–CO\(_2\) system for all five variants. Thus, Figure 7 shows the g(\( r \)) of CO\(_2\) carbon atoms about the Si atom of the SIFSIX pillars in the five SIFSIX-3-M analogues at 298 K and 1 atm. While CO\(_2\) sorbs directly between the equatorial F atoms of the SIFSIX groups in these materials, the g(\( r \)) was taken about the Si atom to provide clearer distinctions of the nearest-neighbor peaks in the resulting distribution. Since these F atoms extend from the Si atom toward the center of the channel, the F(HUM)···(CO\(_2\)) distance can be determined by subtracting the equatorial Si···F distance from the nearest-neighbor distances reported. Note, the g(\( r \)) plots shown herein are normalized to a total magnitude of 1 over a distance of 8.0 Å. Further, the g(\( r \)) at other...
state points are very similar to that shown in Figure 7 for the individual analogues.

Essentially two broad peaks can be observed in the g(r) for all five SIFSIX-3-M members. These peaks correspond to the sorption of CO₂ between four independent SIFSIX groups within the channel of the material. The estimated locations of these peaks for all analogues are summarized in Table 7. It can be observed that the closest nearest-neighbor interaction distance with the highest occupancy for four of the five variants is 4.6 Å. The g(r) for SIFSIX-3-Fe, SIFSIX-3-Co, and SIFSIX-3-Zn are very similar to each other, with essentially the same locations for the nearest-neighbor peaks. SIFSIX-3-Ni displays greater occupancy for both of these interaction distances, presumably because this variant has smaller pore sizes than the other three aforementioned members. Smaller pore sizes would allow for stronger interactions between the CO₂ molecules and the pillars at such short distances. Otherwise, the location of the nearest-neighbor peaks in the g(r) for SIFSIX-3-Ni are similar to that for the Fe, Co, and Zn analogues.

SIFSIX-3-Cu exhibits a notably different g(r) than the other analogues, with the closest Si(HUM)···C(CO₂) interaction distance observed at 4.4 Å for this variant. Further, while the distance corresponding to the next closest nearest-neighbor interaction for SIFSIX-3-Fe, SIFSIX-3-Co, and SIFSIX-3-Zn is at ca. 5.6 Å, this distance is shortened to 5.4 Å for SIFSIX-3-Cu. Compared to what was observed for some of the other variants, the g(r) for SIFSIX-3-Cu shows a clear bimodal distribution. These results indicate that the CO₂ molecules are not only closer to the SIFSIX pillars in this analogue, but are also less frequently situated at the center of the channel according to our GCMC simulations. We also performed control simulations of CO₂ sorption for SIFSIX-3-Zn in which the parameters for this analogue were utilized in the crystal structure of SIFSIX-3-Cu (see Supporting Information). The resulting g(r) plot for this control case is very similar to what was obtained for simulations in SIFSIX-3-Cu using its normal force field (see Figure S15), which indicates that the Cu variant exhibits a unique crystal structure for CO₂ sorption compared to that for the other members.

The fact that SIFSIX-3-Cu displays a shorter nearest-neighbor interaction distance relative to the other analogues can be attributed to the Jahn–Teller effect participation of the octahedral Cu²⁺ ions in this HUM. Such an effect causes contraction in bond lengths along the a/b axes and elongation in the c direction. This explains why SIFSIX-3-Cu has the shortest a/b and longest c lattice constants compared to the other analogues (see Table 1). The relatively small a/b unit cell length results in SIFSIX-3-Cu having the smallest pore size within the series (see Table 2). This leads to shorter average distances between the CO₂ molecules and the SIFSIX pillars in this variant. The g(r) for SIFSIX-3-Ni also shows somewhat of a bimodal distribution, at least more noticeable than that for SIFSIX-3-Fe, SIFSIX-3-Co, and SIFSIX-3-Zn. This could be related to the fact that the Ni variant exhibits smaller pore sizes and a/b lattice constants than the other three members.

Note, the distance between the Si and equatorial F atoms in the crystal structure of SIFSIX-3-Fe, SIFSIX-3-Co, SIFSIX-3-Ni, SIFSIX-3-Cu, and SIFSIX-3-Zn was measured to be 1.68732, 1.66539, 1.69288, 1.65062, and 1.65721 Å, respectively. Subtracting these distances from the closest Si(HUM)···C(CO₂) interaction distances observed in the g(r) plot for the individual analogues results in F(HUM)···C(CO₂) distances that are notably shorter than those obtained through periodic DFT calculations (see Table 6). This is because classical GCMC simulations are able to capture CO₂ molecule positions that are very close to one of the pillars through trial insertion (see Figure 6), while DFT determines a single optimal position of the sorbate molecule based on quantum mechanics.

D. Dipole Distributions

In vacuum, the net dipole moment of a single CO₂ molecule averages 0 D. However, as the CO₂ molecules are sorbed within the pores of SIFSIX-3-M, the electrostatic field provided by the environment of the HUMs induces a dipole moment on the sorbates molecules. This phenomenon is captured in our GCMC simulations that include explicit many-body polarization interactions. A plot of the normalized distribution of induced dipoles on the CO₂ molecules in all five SIFSIX-3-M analogues at 298 K and 1 atm are shown in Figure 8. Specifically, the normalized CO₂ population is plotted as a function of the induced dipole magnitudes on the sorbate molecules in all five HUMs at the considered state point.

It can be seen that all five SIFSIX-3-M variants exhibit essentially a single peak within their dipole distribution. As shown in previous experimental and theoretical studies on these materials, only one unique CO₂ sorption site is observed in SIFSIX-3-M. Particularly, the CO₂ molecule is sorbed between the equatorial F atoms of four different SIFSIX pillars as displayed in Figure 5. This sorption site is responsible for the unimodal dipole distribution that was observed for all analogues. Note, because there is only one type of CO₂ sorption in these HUMs, the dipole distribution at other state points are very similar to that shown in Figure 8 for all variants.

While the dipole distribution for SIFSIX-3-Fe, SIFSIX-3-Co, SIFSIX-3-Ni, and SIFSIX-3-Zn are similar to each other, the distribution for SIFSIX-3-Cu is notably different from the other variants. Indeed, for the Fe, Co, Ni, and Zn analogues, a single peak can be observed from 0 to 0.4 D, with the apex at ca. 0.12 D. These four SIFSIX-3-M analogues also display similar intensities for this peak as well. On the other hand, a broader distribution of induced dipoles was observed for SIFSIX-3-Cu, with the peak spanning from 0 to 0.65 D and the summit shifting to about 0.16 D. The former indicates that there are more CO₂ molecules with higher induced dipoles in SIFSIX-3-Cu relative to the other four analogues. As a result, the population of CO₂ molecules having lower induced dipoles in SIFSIX-3-Cu is reduced, thus explaining why the height at the summit in the dipole distribution for this variant is roughly two-thirds that as the other members.

A possible explanation for why SIFSIX-3-Cu has a different dipole distribution than the other variants could be due to this member exhibiting the smallest pore size and shortest a/b unit cell length within the series. SIFSIX-3-Cu displays relatively short a/b lattice constants due to the Jahn–Teller effect exhibited by the octahedral Cu²⁺ ions. This effect is also responsible for elongation of the axial Si···F and Cu···F bonds, which explains why the crystal structure for SIFSIX-3-Cu has a notably longer c unit cell length compared to the other analogues (see Table 1). The contracted
pore size of SIFSIX-3-Cu results in shorter average distances between the CO₂ carbon atom and the equatorial fluorine atoms at the sorption site. This greater general proximity between such atoms allows for higher induced dipole magnitudes on the sorbate molecules due to librational effects. This results in both higher dipole magnitudes and an increase in occupancy of CO₂ molecules with these dipoles in SIFSIX-3-Cu. Note, simulations of CO₂ sorption in the crystal structure for SIFSIX-3-Cu with the force field that was developed for SIFSIX-3-Zn produced a similar dipole distribution (see Supporting Information, Figure S16).

E. Energy Contributions

As stated in section II.B.1, the total potential energy for GCMC simulations within the HUM-CO₂ system consists of repulsion/dispersion, stationary electrostatic, and many-body polarization interactions. A decomposition of the total energy for simulations of CO₂ sorption within SIFSIX-3-M was carried out to examine the contributions of each energy component toward CO₂ sorption in the respective variants at certain state points. Figure 9 shows the averaged percent contributions of the energy components in all five HUMs at 298 K and pressures up to 1 atm. The relative percentage of each energetic term for simulations at 298 K and 0.10 atm are listed in Table 8 for the five SIFSIX-3-M analogues.

It can be observed that repulsion/dispersion interactions are the main contributor to the total energy for every member of the SIFSIX-3-M family except SIFSIX-3-Cu at all state points considered. The narrow pore size displayed by these SIFSIX-3-M materials allows for favorable repulsion/dispersion interactions between the HUM and the sorbate molecules. In addition, as the CO₂ molecules are sorbed within the confined pores of the material, they can also interact with the electronegative F atoms of four different SIFSIX pillars. The combination of the small pore size and proximity of the SIFSIX pillars provides for significant contributions from electrostatic interactions for CO₂ sorption in these HUMs.

The significantly small pore size and a/b lattice constants exhibited by SIFSIX-3-Cu causes the four neighboring SIFSIX pillars within a square grid to become closer to one another relative to what was observed in the other SIFSIX-3-M analogues. As such, these SIFSIX pillars can interact more synergistically with the CO₂ molecule in the Cu variant, resulting in shorter F(HUM)···C(CO₂) interaction distances. Because the negatively charged equatorial F atoms of the pillars are closer to the sorbate molecule in SIFSIX-3-Cu, this causes electrostatic interactions to enhance substantially in this variant. This could explain why electrostatic interactions contribute mostly to the total energy for CO₂ sorption in SIFSIX-3-Cu for all pressures considered.

As shown in Figure 9 and presented in Table 8, polarization interactions contribute minimally to CO₂ sorption within SIFSIX-3-M, with percentages of no greater than 7% for four of the five members. SIFSIX-3-Cu displays the highest percentage from polarization effects within the platform by having essentially 10% attributed to this energetic term for all pressures considered. This could be related to the reason for the notably high electrostatic contribution in this variant as described in the preceding paragraph. Although the contribution from classical polarization is small within SIFSIX-3-M, we expect that the inclusion of this energetic term allows for the generation of theoretical CO₂ Qₐ values that are better representative of experiment for the respective HUMs. Indeed, previous theoretical studies on these materials have shown that simulations of CO₂ sorption in which only repulsion/dispersion and stationary electrostatic interactions were considered resulted in simulated CO₂ Qₐ values that mildly underestimated experiment for certain SIFSIX-3-M analogues.⁶⁵

Interestingly, SIFSIX-3-Co and SIFSIX-3-Ni have a very similar breakdown of the energetic terms toward CO₂ sorption even though they exhibit notably different pore sizes (see Table 2). This could be attributed to differences in their charge environment, especially on the equatorial F atoms (see Supporting Information, Table S6). Although SIFSIX-3-Ni has the smaller pore size, perhaps the higher partial negative charge on the equatorial F atoms in SIFSIX-3-Co causes electrostatic interactions to increase, thus providing a percent contribution that is comparable to that for SIFSIX-3-Ni.

Even though SIFSIX-3-Zn displays higher CO₂ Qₐ than SIFSIX-3-Fe (see Figure 4 and Table 5), the contributions from electrostatic interactions is greater in the Fe variant. This could be due to SIFSIX-3-Fe having the higher partial negative charge on the equatorial F atoms than SIFSIX-3-Zn according to our electronic structure calculations (see Supporting Information, Table S6). When comparing these two variants that exhibit the same pore size, the greater partial negative charge on the equatorial F atoms would allow for enhanced electrostatic interactions between the HUM and the CO₂ molecule.

IV. CONCLUSION

A theoretical study that utilized MC methods and periodic DFT calculations to investigate CO₂ sorption within all five current members of SIFSIX-3-M was presented. Even though these HUMs are isostructural, differing only in the saturated metal, they display distinct CO₂ sorption properties and energetics as shown through experimental measurements and theoretical calculations. The results from the experimental CO₂ sorption studies on SIFSIX-3-Fe in this work demonstrate that this analogue exhibits the lowest CO₂ uptake at low pressures (< 0.10 atm) and Qₐ within the series. This was due to the fact that this variant contains relatively larger pore sizes and has the longest a/b lattice constants compared to other members.

Experimental studies have shown the following trend for the Qₐ for CO₂ within SIFSIX-3-M: SIFSIX-3-Cu > SIFSIX-3-Ni > SIFSIX-3-Co > SIFSIX-3-Zn > SIFSIX-3-Fe. This trend was remarkably reproduced from the simulations executed herein, as our CMC-calculated Qₐ values are in outstanding agreement with experiment for the individual analogues. This trend was also further supported by periodic DFT calculations of the adsorption energy of a CO₂ molecule localized within the unit cell of the respective HUMs. Indeed, the magnitudes of the calculated ΔE values in this work are comparable to those for the experimental and theoretical Qₐ for the respective variants. We attribute the trend in the CO₂ Qₐ within the SIFSIX-3-M platform to their differences in pore size and a/b unit cell lengths. It can be deduced that the smaller the pore size and a/b lattice constant within this series, the greater Qₐ for CO₂.

Substitution of the M²⁺ ion within this platform results
in different crystal lattice parameters and pore sizes. We have therefore shown through theoretical calculations that minor variations in such quantities lead to different CO$_2$ $Q_{st}$ values. The CO$_2$ $Q_{st}$ within SIFSIX-3-M ranges from 42 to 54 kJ mol$^{-1}$. Indeed, the adsorption enthalpy within this family can be controlled by changing the metal ion. Further, the aforementioned $Q_{st}$ range lies within a “sweet spot” that is favorable for efficient and reversible adsorption-desorption of CO$_2$. As such, these SIFSIX-3-M materials are very promising for applications in CO$_2$ sorption and separation. In general, the results from this study suggest that altering the metal ion in HUMs and other MOM platforms could be a useful strategy for tuning the CO$_2$ uptake and $Q_{st}$ in these materials. This has also been demonstrated previously through CO$_2$ sorption studies in the M-MOF-74 series.$^{70}$

Overall, we have shown how changing the SMC within SIFSIX-3-M leads to different CO$_2$ sorption properties and energetics. We note that different “SIFSIX” materials have also been synthesized by changing the linear bifunctional ligand.$^{22,71}$ It was shown that utilizing shorter ligands resulted in variants with smaller pore sizes, which in turn led to higher $Q_{st}$ for CO$_2$. This finding was supported through previous simulation studies on various “SIFSIX” materials with different ligands.$^{41}$ Next, it is planned to study the effect of pillar substitution on CO$_2$ sorption in the SIFSIX-3-M platform through theoretical studies. Recent experimental studies have shown that the SIFSIX pillars in SIFSIX-3-Ni can be replaced with NbOF$_5$$^{2-}$ (“NbOFFIVE”) and TiF$_6$$^{2-}$ (“TIFSIX”) anions to afford NbOFFIVE-1-Ni$^{25}$ and TIFSIX-3-Ni,$^{72}$ respectively. Experimental CO$_2$ sorption studies on these HUMs have shown that both materials display greater low-pressure CO$_2$ uptake and $Q_{st}$ than SIFSIX-3-Ni. We plan to investigate this through theoretical calculations in future work. In general, different HUMs can be synthesized or envisioned by changing the saturated metal ion, organic ligand, and/or anionic pillar. Although SIFSIX-3-Cu has been shown to display remarkably high $Q_{st}$ for CO$_2$ according to experimental measurements and theoretical calculations, it is predicted that a variant of this HUM consisting of NbOFFIVE or TIFSIX as the pillar could exhibit even stronger interactions with CO$_2$. 

ASSOCIATED CONTENT

Supporting Information. Details of parametrization, electronic structure calculations and Monte Carlo methods, pictures of HUM fragments, tables of properties, and additional simulated CO$_2$ sorption results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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Bae, Y.-S.; Yazaydin, A. O.; Suur, R. Q. Evaluation of the BET Method for Determining Surface Areas of MOFs and


Figure 1. (a) Perspective c-axis view and (b) a/b axis-view of the $3 \times 3 \times 3$ system cell of SIFSIX-3-M ($M = \text{Fe, Co, Ni, Cu, Zn}$). Atom colors: C = gray, H = white, N = blue, F = cyan, Si = yellow, M = lavender.

Figure 2. Orthographic c-axis view of the pillaring square grid in SIFSIX-3-M ($M = \text{Fe, Co, Ni, Cu, Zn}$) illustrating the pore size in these HUMs. Pore size is defined as the diagonal F···F distance ($d$) across the channel minus 2.94 Å corresponding to the sum of the van der Waals radius of each F atom. Atom colors: C = gray, H = white, N = blue, F = cyan, Si = yellow, M = lavender.

Table 1. Comparison of the lattice parameters and unit cell volumes for the single X-ray crystal structures of SIFSIX-3-M ($M = \text{Fe, Co, Ni, Cu, Zn}$).

<table>
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<tr>
<th>Lattice Parameter</th>
<th>SIFSIX-3-Fe</th>
<th>SIFSIX-3-Co</th>
<th>SIFSIX-3-Ni</th>
<th>SIFSIX-3-Cu</th>
<th>SIFSIX-3-Zn</th>
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<tr>
<td>$a$ (Å)</td>
<td>7.1831</td>
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<td>6.9807</td>
<td>6.9186</td>
<td>7.1409</td>
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<tr>
<td>$b$ (Å)</td>
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<td>6.9807</td>
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<td>$c$ (Å)</td>
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<td>$\alpha$ (°)</td>
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<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>90</td>
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<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>$\gamma$ (°)</td>
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<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
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<td>366.23</td>
<td>378.44</td>
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<td>Reference</td>
<td>28</td>
<td>27</td>
<td>27</td>
<td>24</td>
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Figure 3. CO$_2$ sorption isotherms in SIFSIX-3-Fe (orange), SIFSIX-3-Co (red), SIFSIX-3-Ni (green), SIFSIX-3-Cu (blue), and SIFSIX-3-Zn (violet) for experiment (solid lines) and simulation (circles with dashed lines) at 298 K. The experimental data for SIFSIX-3-Co, SIFSIX-3-Ni, SIFSIX-3-Cu, SIFSIX-3-Zn were estimated/taken from references 27, 27, 24, and 22, respectively. CO$_2$ uptakes are plotted against (a) the actual pressures and (b) the logarithm of the pressures.

Figure 4. Isosteric heat of adsorption ($Q_{st}$) for CO$_2$ as a function of loading in SIFSIX-3-Fe (orange), SIFSIX-3-Co (red), SIFSIX-3-Ni (green), SIFSIX-3-Cu (blue), and SIFSIX-3-Zn (violet) for experiment (circles) and simulation (squares). The experimental data for SIFSIX-3-Co, SIFSIX-3-Ni, SIFSIX-3-Cu, SIFSIX-3-Zn were estimated/taken from references 27, 27, 24, and 22, respectively.

Table 2. Comparison of the pore size (in Å) within the crystal structures of SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn). Pore size in these HUMs is defined as the diagonal F···F distance ($d$) across the channel (see Figure 2) minus 2.94 Å corresponding to the sum of the van der Waals radius of each F atom.

<table>
<thead>
<tr>
<th>HUM</th>
<th>Pore Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-3-Fe</td>
<td>3.84</td>
</tr>
<tr>
<td>SIFSIX-3-Co</td>
<td>3.77</td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>3.55</td>
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<tr>
<td>SIFSIX-3-Cu</td>
<td>3.54</td>
</tr>
<tr>
<td>SIFSIX-3-Zn</td>
<td>3.84</td>
</tr>
</tbody>
</table>
Figure 5. (a) Perspective c-axis view and (b) a/b axis-view of a portion of the crystal structure of SIFSIX-3-Ni showing the optimized position of a CO$_2$ molecule in the HUM as determined through periodic DFT calculations using VASP. The CO$_2$ molecule position in other variants is graphically similar. The F(HUM)--C(CO$_2$) interaction distances for all SIFSIX-3-M analogues are summarized in Table 6. Atom colors: C = gray, H = white, N = blue, F = cyan, Si = yellow, Ni = lavender.

Figure 6. (a) Orthographic c-axis view and (b) a/b axis-view of the truncated 3 × 3 × 3 system cell of SIFSIX-3-Ni showing the sites of occupancy for the CO$_2$ carbon atoms (orange) in the HUM as determined through GCMC simulations at 298 K and 1.0 atm. A similar distribution of sites was observed in the other variants at this state point. Atom colors: C = gray, H = white, N = blue, F = cyan, Si = yellow, Ni = lavender.

Table 3. Summary of the experimental BET$^{31}$ and calculated accessible surface areas$^{34}$ (in m$^2$ g$^{-1}$) and theoretical pore volumes (in cm$^3$ g$^{-1}$), as calculated using PLATON$^{35}$ for SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn). The reference for the experimental BET area is given in parentheses.

<table>
<thead>
<tr>
<th>HUM</th>
<th>BET Surface Area (m$^2$ g$^{-1}$)</th>
<th>Accessible Surface Area (m$^2$ g$^{-1}$)</th>
<th>Pore Volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-3-Fe</td>
<td>358 (ref. 28)</td>
<td>166</td>
<td>0.197</td>
</tr>
<tr>
<td>SIFSIX-3-Co</td>
<td>223 (ref. 27)</td>
<td>129</td>
<td>0.186</td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>368 (ref. 27)</td>
<td>62</td>
<td>0.167</td>
</tr>
<tr>
<td>SIFSIX-3-Cu</td>
<td>300 (ref. 24)</td>
<td>63</td>
<td>0.178</td>
</tr>
<tr>
<td>SIFSIX-3-Zn</td>
<td>250 (ref. 22)</td>
<td>156</td>
<td>0.188</td>
</tr>
</tbody>
</table>
Figure 7. Radial distribution function ($g(r)$) of CO$_2$ carbon atoms about the Si atom of the SIFSIX pillars in SIFSIX-3-Fe (orange), SIFSIX-3-Co (red), SIFSIX-3-Ni (green), SIFSIX-3-Cu (blue), and SIFSIX-3-Zn (violet) at 298 K and 1.0 atm.

Figure 8. Normalized distribution of induced dipoles for CO$_2$ molecules in SIFSIX-3-Fe (orange), SIFSIX-3-Co (red), SIFSIX-3-Ni (green), SIFSIX-3-Cu (blue), and SIFSIX-3-Zn (violet) at 298 K and 1.0 atm.

Figure 9. Averaged percent contribution of energy components in SIFSIX-3-Fe (orange), SIFSIX-3-Co (red), SIFSIX-3-Ni (green), SIFSIX-3-Cu (blue), and SIFSIX-3-Zn (violet) at 298 K and pressures up to 1.0 atm, with solid lines corresponding to repulsion/dispersion (R/D) contributions, dashed lines corresponding to electrostatic (Elec) contributions, and squares corresponding to polarization (Pol) contributions.
Table 4. Summary of the experimental and simulated CO\textsubscript{2} uptakes in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn) at 298 K and 0.10/1.0 atm. The reference for the experimental values is given in parentheses.

<table>
<thead>
<tr>
<th>HUM</th>
<th>Exp. CO\textsubscript{2} Uptake (mmol g\textsuperscript{-1})</th>
<th>Sim. CO\textsubscript{2} Uptake (mmol g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-3-Fe</td>
<td>2.43/2.83 (This work)</td>
<td>2.65/2.78</td>
</tr>
<tr>
<td>SIFSIX-3-Co</td>
<td>2.51/2.79 (ref. 27)</td>
<td>2.75/2.77</td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>2.68/2.88 (ref. 27)</td>
<td>2.75/2.77</td>
</tr>
<tr>
<td>SIFSIX-3-Cu</td>
<td>2.46/2.58 (ref. 24)</td>
<td>2.73/2.73</td>
</tr>
<tr>
<td>SIFSIX-3-Zn</td>
<td>2.43/2.64 (ref. 22)</td>
<td>2.67/2.72</td>
</tr>
</tbody>
</table>

Table 5. Summary of the experimental and theoretical CO\textsubscript{2} Q\textsubscript{st} and calculated \(\Delta E\) values (in kJ mol\textsuperscript{-1}) for CO\textsubscript{2} in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn). *Reported value at low loading (experimental reference given in parentheses). \(^b\)Calculated from CMC simulations where \(N = 1\). \(^c\)Calculated for the optimized CO\textsubscript{2} molecule position using VASP.

<table>
<thead>
<tr>
<th>HUM</th>
<th>Exp. (Q_{st}) (kJ mol\textsuperscript{-1})(^a)</th>
<th>Sim. (Q_{st}) (kJ mol\textsuperscript{-1})(^b)</th>
<th>(\Delta E) (kJ mol\textsuperscript{-1})(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-3-Fe</td>
<td>42 (This work)</td>
<td>40.7</td>
<td>41.44</td>
</tr>
<tr>
<td>SIFSIX-3-Co</td>
<td>47 (ref. 27)</td>
<td>48.1</td>
<td>47.23</td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>51 (ref. 27)</td>
<td>51.9</td>
<td>48.08</td>
</tr>
<tr>
<td>SIFSIX-3-Cu</td>
<td>54 (ref. 24)</td>
<td>55.4</td>
<td>54.94</td>
</tr>
<tr>
<td>SIFSIX-3-Zn</td>
<td>45 (ref. 22)</td>
<td>45.2</td>
<td>44.75</td>
</tr>
</tbody>
</table>

Table 6. Summary of the F(HUM)--C(CO\textsubscript{2}) interaction distances in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn) based on the optimized CO\textsubscript{2} molecule position in the unit cell of the respective HUMs as calculated using VASP. The F(HUM)--C(CO\textsubscript{2}) distances are the same on all four sides.

<table>
<thead>
<tr>
<th>HUM</th>
<th>F(HUM)--C(CO\textsubscript{2}) Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-3-Fe</td>
<td>3.37</td>
</tr>
<tr>
<td>SIFSIX-3-Co</td>
<td>3.33</td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>3.23</td>
</tr>
<tr>
<td>SIFSIX-3-Cu</td>
<td>3.18</td>
</tr>
<tr>
<td>SIFSIX-3-Zn</td>
<td>3.34</td>
</tr>
</tbody>
</table>

Table 7. Summary of the location of the nearest-neighbor peaks in the g(\(r\)) of CO\textsubscript{2} molecules about the Si atom in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn) at 298 K and 1.0 atm as shown in Figure 7.

<table>
<thead>
<tr>
<th>HUM</th>
<th>Location of Peak 1 (Å)</th>
<th>Location of Peak 2 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-3-Fe</td>
<td>4.6</td>
<td>5.6</td>
</tr>
<tr>
<td>SIFSIX-3-Co</td>
<td>4.6</td>
<td>5.6</td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>4.6</td>
<td>5.3</td>
</tr>
<tr>
<td>SIFSIX-3-Cu</td>
<td>4.4</td>
<td>5.4</td>
</tr>
<tr>
<td>SIFSIX-3-Zn</td>
<td>4.6</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Table 8. Summary of the averaged percent contributions of the total energy from GCMC simulations of CO\textsubscript{2} sorption in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn) at 298 K and 0.10 atm. \(U_{rd}\), \(U_{es}\), and \(U_{pot}\) represent the repulsion/dispersion, stationary electrostatic, and many-body polarization energy, respectively.

<table>
<thead>
<tr>
<th>HUM</th>
<th>(U_{rd}) (%)</th>
<th>(U_{es}) (%)</th>
<th>(U_{pot}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-3-Fe</td>
<td>51.5</td>
<td>42.7</td>
<td>5.8</td>
</tr>
<tr>
<td>SIFSIX-3-Co</td>
<td>49.5</td>
<td>44.0</td>
<td>6.5</td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>49.4</td>
<td>44.2</td>
<td>6.4</td>
</tr>
<tr>
<td>SIFSIX-3-Cu</td>
<td>40.8</td>
<td>49.2</td>
<td>10.0</td>
</tr>
<tr>
<td>SIFSIX-3-Zn</td>
<td>54.9</td>
<td>39.5</td>
<td>5.6</td>
</tr>
</tbody>
</table>
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Investigating CO$_2$ Sorption in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn) Through Computational Studies

Katherine A. Forrest, Tony Pham, Sameh K. Elsaidi, Mona H. Mohamed, Praveen K. Thallapally, Michael J. Zaworotko, and Brian Space

Theoretical investigations of CO$_2$ sorption were performed in SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn), a family of hybrid ultramicroporous materials with the formula [M(pyz)$_2$SiF$_6$]$_n$ (pyz = pyrazine). It was observed that the smaller the pore size and $a/b$ lattice constants within this series, the greater the isosteric heat of adsorption ($Q_{st}$) for CO$_2$. 