Supporting Information

CO₂ Capture by Hybrid Ultramicroporous TIFSIX-3-Ni under Humid Conditions Using Non-Equilibrium Cycling

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— Supporting Information —

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1. Methods

Synthesis: TIFSIX-3-Ni was synthesized by slurry method following the reported procedure.\(^1\) A solution of NiTiF\(_6\).6H\(_2\)O (2.27 mmol, 0.5 g) and pyrazine (31.2 mmol, 2.5 g) in 5 mL of deionized water was stirred at room temperature for 48 h to obtain the precursor of TIFSIX-3-Ni. The precursor was first air dried and then heated at 160 °C under high vacuum to obtain TIFSIX-3-Ni. SIFSIX-3-Ni was solvothermally synthesized following the reported procedure.\(^2\) A solution of NiSiF\(_6\).6H\(_2\)O (1 mmol, 0.30 g) and pyrazine (2 mmol, 0.16 g) in 20 mL of MeOH was reacted at 85 °C in a 100 ml Schott Duran\(^\text{®}\) bottle. Blue powder was collected after 2 days by filtration and washed by MeOH.

Dynamic Column Breakthrough (DCB) Experiments: DCB experiments were carried out using a Micromeritics SAA 8100 breakthrough system connected to a MKS Cirrus 3 mass spectrometer (see Scheme S1), using CP Grade He, N\(_2\), and CO\(_2\) purchased from BOC Gases Ireland Ltd. Dry and wet DCB experiments were conducted on pre-activated samples of TIFSIX-3-Ni, which was initially heated at 120 °C for two hours and cooled to 25 °C under a constant He flow of 20 sccm. Following this pre-treatment step, the sample was exposed to specified flows of dry CO\(_2\) and moisture-saturated CO\(_2\) in the dry and wet experiments respectively with the temperature maintained at 298 K for the adsorption branch of the experiment. Moisture saturated CO\(_2\) was produced by passing the CO\(_2\) stream through a bubbler containing HPLC grade H\(_2\)O \textit{en route} to the sample. Long and short adsorption branches were conducted at various specified flow rates and DCB plots were generated using the MS signals for outlet CO\(_2\) and H\(_2\)O signals.

Uptakes were determined from the adsorption branch of the experiments, assuming negligible pressure drop and following Eqn. S1. Dead volume correction was applied by adjusting \(t_0\) to account for time lag between inlet and outlet flows using blank experiments for each inlet mixture composition.

\[
q_i = \frac{V_i t_0 - \int_0^{t_0} V_e \, dt}{m}
\]  
(S1)

Here, \(V_i\) is the inlet flow rate of gas (cm\(^3\) min\(^{-1}\)), \(V_e\) is the effluent flow rate of gas (cm\(^3\) min\(^{-1}\)), \(t_0\) is the adsorption saturation time (min) and \(m\) is the mass of the sorbent (g).
Temperature-programmed desorption (TPD) experiments: TPD experiments were carried out using a Micromeritics SAA 8100 breakthrough system connected to a MKS Cirrus 3 mass spectrometer (see Scheme S1), using CP Grade He, N\textsubscript{2}, and CO\textsubscript{2} purchased from BOC Gases Ireland Ltd. Dry and wet TPD experiments were conducted on pre-activated samples of TIFSIX-3-Ni, which was initially heated at 120 °C for two hours and cooled to 25 °C under a constant He flow of 20 sccm. Following this pre-treatment step, the sample was exposed to specified flows of dry CO\textsubscript{2} and moisture-saturated CO\textsubscript{2} in the dry and wet experiments respectively. Moisture saturated CO\textsubscript{2} was produced by passing the CO\textsubscript{2} stream through a bubbler containing HPLC grade H\textsubscript{2}O 	extit{en route} to the sample. After exposing the sample to dry or wet CO\textsubscript{2} flow for the duration of the adsorption branch of the experiment, a temperature ramp of 5 °C per minute was begun until a maximum temperature of 120 °C while the inlet gas stream was changed to 20 sccm dry He. TPD plots were generated using the MS signals for desorbed CO\textsubscript{2} and H\textsubscript{2}O.

Uptakes of H\textsubscript{2}O and CO\textsubscript{2} were determined using Eqn. S2.

\[ q_i = \frac{\int_{t_1}^{t_2} V \, e \, dt}{m} \]  

S2

Where \( t_1 \) and \( t_2 \) correspond to the start and end times of the period of temperature-programmed desorption and other terms are as in Eqn. S1.

In situ infrared (IR) spectroscopy: In situ IR measurements were performed on a Nicolet 6700 FTIR spectrometer using a liquid N\textsubscript{2}-cooled mercury cadmium telluride (MCT-A) detector. A vacuum cell was placed in the sample compartment of the infrared spectrometer with the sample at the focal point of the beam. The samples (~5 mg) were gently pressed onto KBr pellet and placed into a cell that is connected to a vacuum line for evacuation. A sample of TIFSIX-3-Ni was activated by evacuation overnight at 180 °C and then cooled back to room temperature for CO\textsubscript{2} and H\textsubscript{2}O vapor exposure measurements.

Simulations: First-principles density functional theory (DFT\textsuperscript{[3,4]} calculations were performed with VASP\textsuperscript{[5,6]} Non-covalent interactions were incorporated using the non-local vdW-DF1 exchange-correlation functional.\textsuperscript{[7–12]} Projected augmented wave (PAW) pseudopotentials were used with a kinetic energy cutoff of 600 eV.\textsuperscript{[13]} We utilize a \( 2 \times 2 \times 2 \) supercell for which \( \Gamma \) –point sampling
is sufficient. All calculations were done using spin polarization, selecting anti-ferromagnetic (AFM) ordering for Ni. The open-shell 3d localized electrons were additionally treated using the Hubbard U corrections\textsuperscript{[14]} with a U value of 6.4 and 2.0 eV for Ni and Ti, respectively.\textsuperscript{[15,16]} Despite the absence of open-metal sites in the structure, we found that the inclusion of both AFM ordering and U is critical to obtaining the correct energetics. Systems were optimized with tight criteria for energy ($10^{-6}$ eV) and forces (0.005 eV/Å).
2. Experimental Figures

Scheme S1. A schematic of the experimental setup used for dry and wet DCB and TPD experiments.

Figure S1. Single component breakthrough of dry CO$_2$ on TIFSIX-3-Ni at an inlet flow rate of 10 sccm.
Figure S2. Full cycling plots of adsorption-desorption cycles of dry (left) and wet (right) CO$_2$ with an inlet flow of 3 sccm with shortened adsorption times. MS Signals are shown without normalization, and the unbroken x-axis is presented in units of absolute time in minutes. Red traces represent the CO$_2$ MS signal, black traces represent the H$_2$O MS signal, and blue lines represent the temperature.

Figure S3. An overlay of CO$_2$ concentrations over three successive wet adsorption desorption cycles with shortened adsorption times.
Figure S4. Time evolution of the vibrational band $\nu_{as}(\text{CO}_2)$ in TIFSIX-3-Ni (black diamond) upon loading and subsequent evacuation of ~760 Torr gas phase CO$_2$, monitored by recording the band integrated areas shown in panel (b). The error bars were calculated from the variations in the measured integrated areas and do not exceed 0.2. The spectra were reproduced from reference$^{[17]}$. 
Figure S5. Time evolution of the vibrational band $v_{as}(CO_2)$ in TIFSIX-3-Ni before (lime circle) and after loading H$_2$O with increasing vapor pressure (red circles). The spectra were shown in the middle panel of Figure 1. The error bars were calculated from the variations in the measured integrated areas and do not exceed 0.2.
**Figure S6.** Differential spectra showing the perturbation of the $v_{as}(\text{CO}_2)$ bands with loading of H$_2$O, referenced to the spectrum of pre-loaded CO$_2$ in TIFSIX-3-Ni (the bottom lime line in the middle panel of Figure 2). The full spectra are shown in the top panel of Figure 2.
Figure S7. IR spectra of the $\beta$(H$_2$O) band upon exposure of empty TIFSIX-3-Ni and TIFSIX-3-Ni with pre-loaded CO$_2$ to ~14 Torr H$_2$O. The intensity of the $\beta$(H$_2$O) band exhibits a decrease by ~20% in TIFSIX-3-Ni with pre-loaded CO$_2$ compared with that in empty TIFSIX-3-Ni, which corresponds to 4 water molecules per unit cell (see Figure S11).
Figure S8. IR spectra showing the loading of H₂O at ~10 Torr for ~3 min (top line) into SIFSIX-3-Ni with pre-loaded CO₂ (bottom line), which was achieved by exposing the sample to ~80 Torr CO₂ for ~5 min and subsequent evacuation of the gas phase for ~0.5 min under vacuum. The adsorbed H₂O is characterized by stretching ν(OH) and bending bands β(H₂O) at 3578 and 1662 cm⁻¹, respectively. Each spectrum was referenced to the activated SIFSIX-3-Ni under vacuum. No significant loss of the CO₂ band is noted upon H₂O exposure and the results are quite similar to those of TIFSIX-3-Ni. Further details can be found in the main text. In addition, our results match well with our ab initio calculations.
Figure S9. IR spectra showing the loading of CO$_2$ at ~80 Torr as a function of time into SIFSIX-3-Ni with pre-adsorbed H$_2$O (top four lines), referenced to the bottom spectrum that displays the $\beta$(H$_2$O) and $\nu$(OH)$_{\text{H}_2\text{O}}$ bands after exposure of empty SIFSIX-3-Ni to H$_2$O at ~10 Torr, which is further referenced to the spectrum of the activated sample under vacuum. We see a clear decrease of water bands upon CO$_2$ loading as observed in TIFSIX-3-Ni (see main text for details).
Figure S10. Left panel: PXRD pattern of TIFSIX-3-Ni. Right panel: dynamic vapor sorption isotherm measurements on TIFSIX-3-Ni showing H2O occupancy at full loading to ~4 molecules per unit cell at ~14 Torr (0.018 bar). The negative adsorption feature in the water sorption isotherm occurs due to the reversible conversion of TIFSIX-3-Ni to its hydrated, less-porous phase at RH between 80 and 90%. This has already been described in ref. [19].
Figure S11. CO₂ adsorption isotherm in TIFSix-3-Ni as measured at 298 K.
Figure S12. Calculated BET surface area for TIFSIX-3-Ni (based on 298 K CO₂ adsorption isotherm) is 218 m²g⁻¹[20].
Figure S13. PXRD patterns of TIFSIX-3-Ni as synthesized and after dry and wet DCB-TPD cycles.
Figure S14. The ground state TIFSIX-3-Ni structure has rotated pyz rings and is 1.26 eV more stable than the structure with unrotated pyz rings. Both geometries are shown in the inset. Due to the pyz rotation, the F–F distance is different in alternating pores. For example, the equatorial F–F diagonal distance can either be 6.28 Å or 6.33 Å depending on the pore.
Figure S15. The ground state SIFSIX-3-Ni structure has rotated pyz rings (the same way as found in TIFSIX-3-Ni) and is 1.16 eV more stable than the structure with unrotated pyz rings. The inset shows both these rotated/unrotated geometries. Due to the pyz rotation, the F··F distance is different in alternating pores. As found in TIFSIX-3-Ni, the equatorial F··F diagonal distance can either be 6.628 Å or 6.639 Å depending on the pore.
Figure S16. Top (along the pore channel) and side (across the pore channel) views of the calculated structure for TIFSIX-3-Ni. Our theoretical calculated average pore size of 3.365 Å (3.34–3.39 Å) is in agreement with the value reported in the main text (3.25 Å), which is calculated from the experimentally obtained PXRD for CO₂ loaded TIFSIX-3-Ni (CO₂<TIFSIX-3-Ni).[21] Since this PXRD pattern is quite similar to the activated sample, we believe that both these structures bear similar pore sizes. The structure-based pore size is calculated as the difference between the equatorial F⋅⋅⋅F diagonal distance and the sum of the vdW radius of each F atom (2.94 Å). Distances shown are inclusive of vdW radii.
Figure S17. Top (along the pore channel) and side (across the pore channel) views of the calculated structure for SIFSIX-3-Ni. Our theoretical calculated average pore size of 3.694 Å (3.688–3.699 Å) is in good agreement with the experimental value of 3.69 Å\textsuperscript{[22]} or 3.5 Å\textsuperscript{[17,23]}. Si is represented by cantaloup colored spheres. Distances shown are inclusive of vdW radii.
Figure S18. Changes induced in pyz rings in TIFSIX-3-Ni upon CO₂ loading, in agreement with the perturbations of phenyl ring modes including ν(CH), coupled ν(CC)/δ(CH)₁₆ and δ(CH)₁₆/ν(CC)/δ(ring) vibrations observed in our in situ IR spectra in Figure 2 of the main text. The equatorial F separation from M (Ti, Si) is also shown. Further details are given in Figures 4 and 5 in the main text. Distances shown are inclusive of vdW radii.
Figure S19. Top (along the pore channel) and side (across the pore channel) views of binding configuration with 2 H$_2$O and 1 CO$_2$. We can see a significant distortion of the equatorial F atoms on the CO$_2$ side, evidence of a strong interaction of C$_{CO2}$ with the F atoms. The O$_{H2O}$···O$_{CO2}$ separation is 3.255 Å, while the C$_{CO2}$···F distance is 2.71 Å. Moreover, O$_{CO2}$ is 2.88 Å away from the H$_{pyz}$. As such, CO$_2$ is clearly held in place by two of the equatorial F atoms, complimented by weaker interactions of O$_{H2O}$···H$_{pyz}$. Distances shown are inclusive of vdW radii.
Figure S20. Binding configuration with 3 H$_2$O and 1 CO$_2$ (top (along the pore channel) and side (across the pore channel) views). Increasing the concentration of H$_2$O starts the formation of a water cluster framework. Interestingly, O$_{CO2}$ is just 2.483 Å from H$_{H2O}$. Nevertheless, the H$_2$O⋯H$_2$O (H⋯O) separation is 1.826 Å. Further details are given in the main text and Table 1. Distances shown are inclusive of vdw radii.
Figure S21. Induced charge density configurations with 2 H2O and 1 CO2 (left) and 3 H2O and 1 CO2 (right). A strong interaction between C(CO2) with the equatorial F is evident, which is in perfect agreement with our *in situ* IR measurements. In the 3 H2O case (right panel), we also see the interaction between H$_{H2O}$ and O$_{CO2}$. Further information can be found in the main text.
Figure S22. High water loading (3 H₂O) in the ultramicropore of TIFSIX-3-Ni results in water cluster formation. Binding energy information is given in Table 1 of the main text.
Figure S23. Maximum water loading (4 H₂O) in the ultramicropore of TIFSIX-3-Ni based on dynamic vapor sorption measurements as given in Figure S10. Water molecules form a cluster inside the pore. Distances shown are inclusive of vdW radii.
Figure S24. Top (along the pore channel) and side (across the pore channel) views of the binding locations for H$_2$O (left) and CO$_2$ (right) adsorbed in SIFSIX-3-Ni. These binding patterns are quite similar as found in TIFSIX-3-Ni except for the larger H$_{H2O}$···F and C$_{CO2}$···F distances in SIFSIX-3-Ni due to the larger pore size. These larger host-guest separations explain the weaker binding energies of H$_2$O and CO$_2$ in SIFSIX-3-Ni in comparison with TIFSIX-3-Ni. The binding energy for H$_2$O and CO$_2$ in SIFSIX-3-Ni is 0.623 and 0.79 eV, respectively, slightly weaker than in TIFSIX-3-Ni.
Figure S25. The left and right panels show the top (along the pore channel) and side (across the pore channel) views of the H$_2$O and CO$_2$ co-adsorbed in SIFIX-3-Ni, respectively.
Figure S26. Front and side views of 2 CO$_2$ molecules per pore of TIFSIX-3-Ni. Due to the small size of the pore, the binding energy quickly becomes repulsive suggesting that it is energetically very unfavorable to be occupied by two CO$_2$. 
Figure S27. Binding energy per molecule per pore for H$_2$O and CO$_2$. Positive binding energies indicate favorable binding, while negative binding energies mean no favorable interaction, i.e., repulsion. The formation of similar water frameworks has already been reported by us in several other MOFs.$^{[24,25]}$
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