Supporting Information

Record Atmospheric Fresh Water Capture and Heat Transfer with a Material Operating at the Water Uptake Reversibility Limit

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Materials and Methods

MnCl\textsubscript{2}•4H\textsubscript{2}O (98%, Strem Chemicals), CoCl\textsubscript{2}•6H\textsubscript{2}O (99.9%, Alfa Aesar), NiCl\textsubscript{2}•6H\textsubscript{2}O (Strem Chemicals), HCl (32-35%, BDH – VWR Analytic) methanol (99.9%, VWR), N,N-dimethylformamide (99.8%, Millipore), ethanol (ACS grade, Mallinckrodt) were used as received.

Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker Advance II diffractometer equipped with a θ/2θ Bragg-Brentano geometry and Ni-filtered CuKα radiation (Kα\textsubscript{1} = 1.5406 Å, Kα\textsubscript{2} = 1.5444 Å, Kα\textsubscript{1}/Kα\textsubscript{2} = 0.5). The tube voltage and current were 40 kV and 40 mA, respectively. Samples for PXRD were prepared by placing a thin layer of the appropriate material on a zero-background silicon crystal plate.

Nitrogen adsorption isotherms were measured by a volumetric method using a Micromeritics ASAP 2020 gas sorption analyzer. A typical sample of ca. 40 mg of metal-organic framework, pre-activated at 100°C to remove all residual solvent, was transferred in an Ar filled glovebox to a pre-weighed analysis tube. The tube with sample inside was weighed again to determine the mass of the sample. The tube was capped with a Micromeritics TranSeal, brought out of the glovebox, and transferred to the analysis port of the gas sorption analyzer. Free space correction measurements were performed using ultra-high purity He gas (UHP grade 5, 99.999% pure). Nitrogen isotherms were measured using UHP grade nitrogen. All nitrogen analyses were performed using a liquid nitrogen bath at 77 K. Oil-free vacuum pumps were used to prevent contamination of sample or feed gases.

Water vapor adsorption isotherms were measured by a volumetric method using a Micromeritics ASAP 2020 gas sorption analyzer with a vapor dose option and a heated manifold. A typical sample of ca. 40 mg of metal-organic framework, pre-activated at 100°C to remove all residual solvent, was transferred in an Ar filled glovebox to a pre-weighed analysis tube. The tube with sample inside was weighed again to determine the mass of the sample. The tube was capped with a Micromeritics TranSeal, brought out of the glovebox, and transferred to the analysis port of the gas sorption analyzer. Free space correction measurements were performed using ultra-high purity He gas (UHP grade 5, 99.999% pure). Water vapor adsorption isotherms were measured using Milli-Q water. The water was degassed on the ASAP 2020 manifold prior to measurement. All water analyses were performed using water baths held at constant temperature with a recirculating chiller. The manifold was held 10 °C above the temperature of the sample water bath, and the vapor dosing tube was held 15 °C above the temperature of the sample water bath. Oil-free vacuum pumps were used to prevent contamination of sample or feed gases.

Water vapor adsorption cycling experiments under a flow of nitrogen were performed using a TA Instruments Q5000SA thermogravimetric vapor analyzer. A typical sample of ca. 5 mg of MOF, pre-activated at 100 °C, but later exposed to air, was loaded into the microbalance. The flow of nitrogen carrier gas was constant over the
sample at 10 ml min\(^{-1}\). Cycles were performed by holding 25 °C and 35% RH for 180 min followed by ramping 1 °C/min to 45 °C and holding 45 °C and 5% RH for 90 min.

Water vapor adsorption cycling experiments under partial vacuum were performed using a Surface Measurement Systems DVS Adventure dynamic gravimetric water sorption analyzer. A typical sample of ca. 5 mg of MOF, pre-activated at 100 °C, but later exposed to air, was loaded into the microbalance. The instrument was set to deliver a constant vapor pressure of 13 mmHg. The baseline mass of the sample was measured over 2 hours at the desorption temperature. The sample was then cycled between the adsorption temperature, normally 25 °C, and the desorption temperature 30 times. The sample mass was measured once per minute. Heating and cooling ramp rates were 1 °C per minute. The instrument switched to the next cycle when the change in mass per minute was less than 0.02%.

\(\text{M}_2\text{Cl}_2\text{BTDD}\) MOFs were synthesized and activated according to previously published procedures according to Scheme S1.\(^1\)

\[\text{bis(1H-1,2,3-triazolo[4',5'-i]dibenzo[1,4]dioxin)}\]

\[\text{“H}_2\text{BTDD”}\]

\[\text{M}_2\text{Cl}_2\text{BTDD}\]

**Scheme S1.** Synthesis of metal-organic frameworks \(\text{M}_2\text{Cl}_2\text{BTDD}\), where M may be Mn, Co, or Ni from the organic linker bis(1H-1,2,3-triazolo[4’,5’-i])dibenzo[1,4]dioxin), abbreviated as H\(_2\)BTDD, and a divalent metal chloride salt in dimethylformamide (DMF), methanol (MeOH), and hydrochloric acid at 70 °C.
Calculation of the Characteristic Curve for Co₂Cl₂BTDD (2).

In order to make the loading dependent on only one free variable ("energy") rather than two (P,T), we constructed a characteristic curve. The energy parameter used is the adsorption potential (A), which is the Gibbs free energy of adsorption with inverse sign:

\[ A = RT \ln \left( \frac{p_o(T)}{p} \right) \]

\( p_o \) is the saturation vapor pressure of the working fluid at the temperature of analysis, \( p \) is the pressure at each loading value, \( R \) is the ideal gas constant, and \( T \) is the analysis temperature.

Isotherms measured at different temperatures should collapse onto a single characteristic curve. Water isotherms for 2 were measured at 283 K, 293 K, and 298 K (Figure S8). After calculating the characteristic curve using each of these isotherms, it is evident that they all collapse into a single characteristic curve (Figure S9) confirming the validity of the characteristic curve model.

Calculation of the Heat Transferred per cycle as a Function of Temperature Lift for the Water-2 working pair (Figure 4A).

To determine temperature lift, the evaporator temperature, which determines the RH of the vapor being adsorbed by the MOF, was varied while the condenser temperature (set equal to the temperature of the MOF bed) was held constant at 303 K and the desorption temperature was held constant at 373 K. The adsorption potential was then calculated for the empty state, using the vapor pressure and temperature at desorption conditions (373 K). The adsorption potential was also calculated for the full state, using a bed temperature of 303 K and with the water vapor pressure allowed to vary with the condenser temperature from 275 K (28 ° lift) to 303 K (0 ° lift). The adsorption potential values were then converted to loadings of water in 2 by using the previously determined characteristic curve. The desorption loading was then subtracted from the adsorption loading to determine the net capacity. Loading values of water per gram MOF were then converted into energy values using the enthalpy of evaporation of water. Gravimetric values were converted into volumetric values using the crystal density of the MOF (0.69 g cm⁻³).

Calculation of the Coefficient of Performance for the Water-2 working pair.

The COP for cooling with a 20 °C temperature lift (Refrigeration 1 conditions as defined by De Lange, et. al) was calculated as described in the literature. Briefly, the COP for cooling is defined as:

\[ \frac{Q_{ev}}{Q_{regen}} \]

The COP for cooling may vary between 0 and 1. \( Q_{ev} \) is the heat energy removed from the evaporator through evaporation of the working fluid, and \( Q_{regen} \) is the heat energy required to regenerate the adsorbent, including isosteric heating, of both the adsorbent and the working fluid, and isobaric desorption steps. The enthalpy of adsorption of water
in 2 was assumed to be 45.8 kJ mol\(^{-1}\) throughout the working range. This is the enthalpy of adsorption at the pore filling step (Figure S7). The heat capacity of the sorbent was assumed constant at 1 J g\(^{-1}\) K\(^{-1}\), in accordance with the literature.\(^d\) The relevant temperatures for the calculation are \(T_{\text{cond}} = 303\) K, \(T_{\text{ev}} = 283\) K. The desorption temperature was allowed to vary. The COP for cooling applications with a 20 °C temperature lift for water in 2 at varied desorption temperature is shown in Figure 3B.
Figure S1. Powder X-ray diffraction patterns of activated 1 (red), 1 after a single water isotherm at 298 K (pink), and a simulated pattern for the structure (black). Inset shows magnification after 10 degrees.
Figure S2. N$_2$ adsorption isotherms of activated 1 (red), and 1 reactivated at 150°C after a single water isotherm at 298 K (pink).
Figure S3. Powder X-ray diffraction patterns of activated 3 (green), 3 after a single water isotherm at 298 K (light green), and a simulated pattern for the structure (black). Inset shows magnification after 10 degrees.
Figure S4. $N_2$ adsorption isotherms of activated 3 (green), and 3 reactivated at 150 °C after a single water isotherm at 298 K (light green).
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Figure S7. The enthalpy of adsorption for water in 2 versus coverage.
Figure S8. Characteristic curves for water vapor adsorption in 2 calculated using the isotherms at 298 K (orange squares), 293 K (green circles), and 283 K (blue triangles). The characteristic curve is temperature invariant, justifying its usage to calculate isotherms at other temperatures relevant for AHP.
Figure S9. Water adsorption isotherms for 2 at 298 K (orange squares), 293 K (green circles), and 283 K (blue triangles). Closed symbols represent adsorption and open symbols represent desorption. Data are symbols, lines are meant only as guides for the eye.
Figure S10. Water vapor adsorption isotherms for 2 calculated from the characteristic curve at a range of temperatures relevant for AHP applications.
Figure S11. Water vapor desorption isotherms for 2 calculated from the desorption characteristic curve at a range of temperatures relevant for AHP and AWG applications.
Figure S12. Estimation of the deliverable capacity of water in 2 volumetrically (left axis) and gravimetrically (right axis) versus the desorption temperature for AHP applications, using an evaporation temperature of 283 K and a condenser temperature of 303 K. Capacities were determined from isotherms calculated from the characteristic curve.
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