MOFs as Adsorbents for Low Temperature Heating and Cooling Applications

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The adsorption of vapor on the surface of a highly porous solid is well suited for low temperature heat transformation applications like thermally driven heat pumps or adsorption chillers (Figure 1).[1]
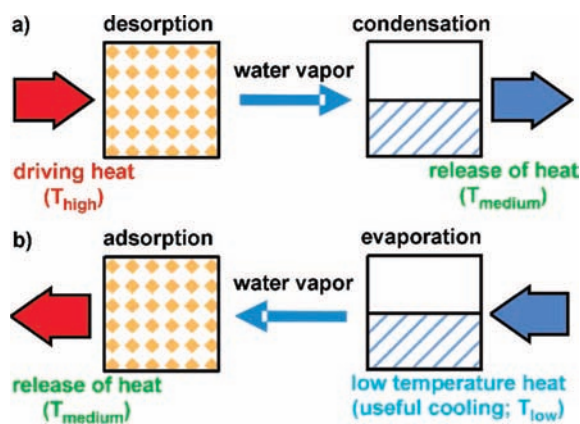

Figure 1. Principle process in an adsorption chiller. (a) During the regeneration or desorption cycle, heat from a high temperature source (e.g., solarthermal collector, gas burner) is used to desorb the porous solid. The released water vapor condenses at a medium temperature level (ambient temperature) with the heat of condensation released to the environment. (b) In the production or adsorption cycle, the working fluid is evaporated with heat at a low temperature level, thereby producing the useful cooling. When the vapor is adsorbed in the porous solid, it releases the adsorption heat at a medium temperature level which can be used as useful heat in the heat pump case or withdrawn to the environment in case of the cooling applications.[1]

In recent years, there has been significant research progress on micro- and mesoporous adsorbent materials for closed system heat transformation applications like thermally driven adsorption chillers or adsorption heat pumps.[2] For a cooling application, the choice of the adsorbent/adsorptive working pair is determined by the amount of heat that can be extracted from the evaporator per adsorption cycle. Unlike the use in heat pumping or storage applications, the heat of adsorption is only of secondary importance, since it is simply rejected to the environment. The heat extracted from the evaporator is proportional to the amount of vapor adsorbed and the evaporation enthalpy of the selected working fluid. Therefore, the loading spread ΔX (in g of adsorbed vapor/kg of adsorbent) of the adsorbent over a given cycle is a good first figure of merit. The present generation of adsorption chillers mostly uses silica gels as adsorbents. Finding improved silica gels for heat pumping and cooling applications has been a research priority for many years.[3] The key problem with silica gel adsorbents for these applications is that most of the water adsorption occurs at too high relative pressures. For a cooling application, this can mean that the loading difference ΔX over the cycle is only a small part of the

total adsorption capacity X_{max} of the silica gel.[4] The preferred working fluid for heat storage and transformation with a solid sorbent is water, as it has the highest mass-based evaporation enthalpy (2440 kJ/kg at 25 °C) and adsorption enthalpy of all known fluids.

We describe here a metal−organic framework (MOF)[5] as an adsorbent for heat transformations in comparison to other materials. The 3D MOF $^3_\infty\{[Ni_3(\mu_3\text{-btc})_2(\mu_4\text{-btre})_2(\mu\text{-H}_2\text{O})_2] \cdot \sim 22\text{H}_2\text{O}\}$ (ISE-1) is constructed with benzene-1,3,5-tricarboxylate (btc) and 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) (Figure 2) and filled with ~22
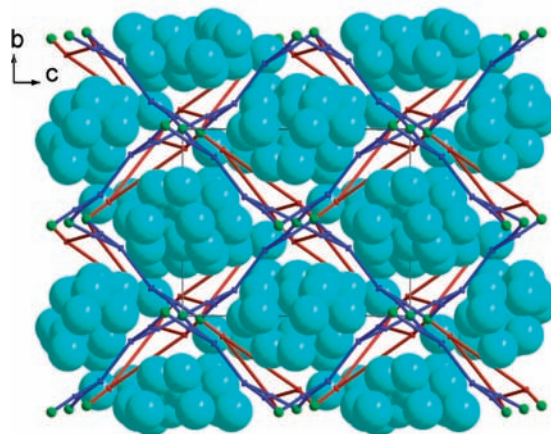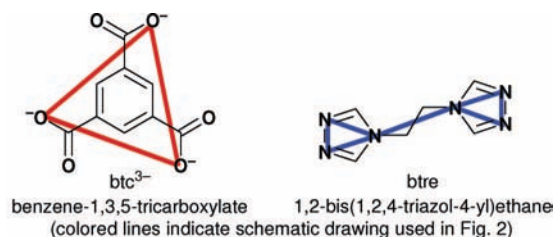

btc[3−]
benzene-1,3,5-tricarboxylate

btre
1,2-bis(1,2,4-triazol-4-yl)ethane

(colored lines indicate schematic drawing used in Fig. 2)

Figure 2. Schematic drawing of the ISE-1 framework (btc ligand in red, btre ligand in dark blue, nickel atoms in green) with the oxygen atoms (light blue) of the water of crystallization in space-filling mode.

water molecules per formula unit to a potential solvent volume of 1621 Å³ (52%) of the unit cell volume.[6] ISE-1 is water-stable, unlike many zinc- or copper-based MOFs.

For a measurement of candidate adsorbents, the adsorption equilibrium data points corresponding to common cycle conditions (at the end of the adsorption and desorption half-cycle) are recorded.[7] Figure 3 shows the results of these measurements on ISE-1 in comparison to a silica gel and several zeolites.

It can be seen in Figure 3 that, at the higher desorption temperature of 140 °C against the lower condensator pressure of 12 hPa (total height of the bars), the loading spread achieved with the new material ISE-1 is ~210 g/kg and therefore larger than that

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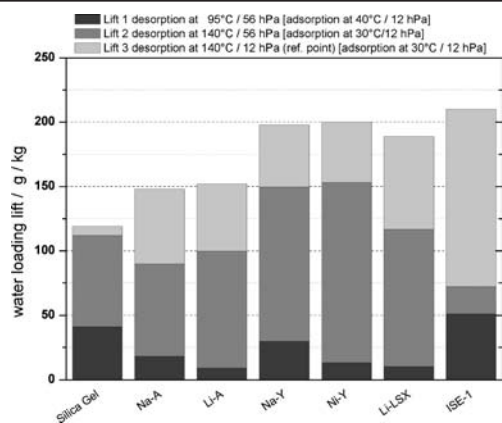[‡] Universität Freiburg.

Figure 3. Loading spread over cooling cycle for various adsorbents. Evaporator at 10 °C (= 12 hPa) for all data points. Cycle conditions for Lift 1 (black part of the bar): Max. desorption temp. 95 °C, condenser at 35 °C (= 56 hPa), lowest adsorption temp. 40 °C. Conditions for Lift 2 (black + gray part of the bar): Desorption at 140 °C, condenser at 35 °C, lowest adsorption temp. 30 °C. Conditions for Lift 3 (whole bar): Max. desorption temp. 140 °C, condenser at 10 °C, lowest adsorption temp. 30 °C. Na–A, Li–A = commercial zeolite A, primarily used as an ion exchanger in washing agents, for water treatment or as desiccant. Na–Y, Ni–Y, and Li–LSX = commercial zeolites X and Y (faujasite structure type) have since the 1980s been considered for adsorptive heat pumping and cooling cycles.[8] LSX = Low Silica X. For the released adsorption heat of ISE-1, 40 °C adsorption isotherm, pore volumes, and additonal information, see the Supporting Information.

of all five zeolites and of the reference silica gel. In the case of a condensor pressure of 56 hPa, ISE-1 shows the lowest loading lift of all materials. However, at the lower desorption temperature (black part of the bar in Figure 3), ISE-1 again outperforms all other materials with a loading lift of ∼51 g/kg. The poor performance of the zeolites is due to their strong hydrophilicity (insufficient temperature for desorption), and the reason for the lower silica gel performance is the high temperature lift of 30 °C required by this cycle. In comparison ISE-1 shows quite interesting adsorption characteristics with a better performance at low desorption temperatures but lower lift in the intermediate section. The metal–organic network is less hydrophilic than silica gel or zeolites; thus, it releases the water at lower temperature and lower partial pressure.

A cycle test of ISE-1 in Figure 4 demonstrates good stability under the test conditions (the loading spread decreases only very
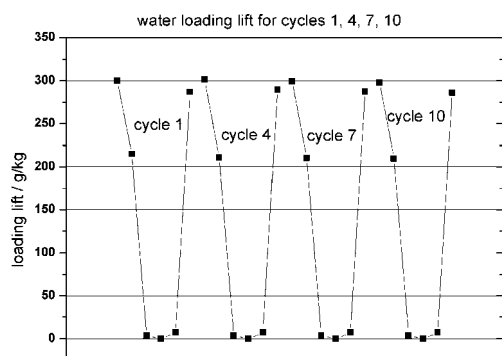

Figure 4. Loading spread over different cycles for stability tests. Test points are from left to right sample temperature/water vapor pressure: 40 °C/56 hPa; 40 °C/12 hPa; 140 °C/12 hPa; 150 °C/12 hPa; 150 °C/56 hPa; 40 °C/56 hPa for all cycles.

slightly over 10 cycles) and a remarkable loading spread of 280 g/kg for a higher desorption temperature of 150 °C. This impressively demonstrates the potential of MOF materials for use in heat transformation processes.

In summary, we present here a dehydratable–hydratable water-stable MOF material with a large loading spread of 210 g/kg for typical application temperatures as a candidate for solid adsorbents in heat transformation cycles for refrigeration, heat pumping, and heat storage.

Supporting Information Available: Released adsorption heat of ISE-1, 40 °C adsorption isotherm, pore volumes, and additonal information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Experimental: All measurements of sorption loading lift and cycle stability tests have been performed on a SETARAM TG-DSC 111 coupled to the humidity generator Wetsys. Between 7 and 15 mg of the material has been analyzed within a platinum crucible. Argon has been used as the carrier gas for the humidification. Prior to the measurement, adsorbent samples are stored at ambient conditions. First, a desorption isobar starting at ambient temperature up to 140°C at 56 hPa is recorded, corresponding to the regeneration cycle with a condensator temperature of 35 °C in the application case. While keeping the sample temperature at 140°C, the pressure is lowered to 12.3 hPa, which gives the lowest loading within the measurement cycle. Therefore the equilibrium at this point is taken to be the reference mass (for calculating the loading values). Subsequently, adsorption equilibria are taken along the 12.3 hPa water vapor isobar, corresponding to an evaporator temperature of 10 °C, at 140 °C down to 30 °C. The choice of data points was made to cover a range of typical operating conditions in heat pumping, cooling, and heat storage applications. The maximum desorption temperature point is motivated by the available heat source. A temperature of 95 °C accounts for, e.g., mobile applications or applications where water is used in the fluid cycle, whereas a driving temperature of 140 °C is related to stationary systems. The minimal adsorption point is correlated to the minimum usable temperature level. In the case of a heat pumping application, this may be the temperature level where floor heating can occur (∼40°C). In the cooling case, the minimum adsorption temperature is restricted to the heat rejection temperature level. The adsorption enthalpy has to be rejected to the recooling cycle (actually the environment) to maintain the adsorption process, which is possible for temperatures down to 30°C in the case of a coupling to a cooling tower.

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