

MIL-100(Al, Fe) as water adsorbents for heat transformation purposes—
a promising application†Felix Jeremias,^{ab} Anupam Khutia,^b Stefan K. Henninger^{*a} and Christoph Janiak^{*b}

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The adsorption/desorption of up to 0.75 g of water vapour per g of the porous MOFs 3D- $\{M_3O(X)(H_2O)_2[btc]_2 \cdot nH_2O\}$, MIL-100 (M = Al, Fe; X = OH, F, btc = benzene-1,3,5-tricarboxylate, trimesate), occurs at small relative pressures of $p/p_0 < 0.4$ and a comparatively small hysteresis. Together with very good cycle stability, these properties render both MIL-100(Al and Fe) very suitable candidates for thermally driven heat pumps or adsorption chillers.

More than 50% of the energy consumption and, simultaneously, the CO₂ emissions of modern buildings originate from air conditioning processes. These are traditionally based on electrically driven, mechanical compression chillers and heat pumps or classical burner systems, respectively. This demand is expected to rise in the future because of increased living standards and global climate change.¹ However, with alternative technologies, less exergetic (that is, closer to equilibrium) forms of energy, even low-temperature waste heat from industrial processes, can be employed for both heating and cooling. Solar heat as driving energy is especially interesting due to the high coincidence of cooling demand and solar irradiation. While multiple working principles for thermally driven heat-pumps can be realised, the evaporation–adsorption method has proven most feasible for this purpose and is briefly described in Fig. 1 and Table 1.

The presented process renders cooling applications independent of precious electrical energy. If it is used for heating, the incorporation of environmental heat allows for considerable fuel savings. The coefficient of performance (*i.e.* the relation between useful and driving heat), power density, cost and operating lifetime of the complete machine are governed by the sorption material and its figures of merit, *i.e.* porosity, water sorption capacity, hydrophilicity and hydrothermal stability.^{2,3} The achievable loading lift and also the required desorption temperature directly depend on the hydrophilicity of the material, *i.e.*, the p/p_0 value at which adsorption occurs

(ideally at $0.05 < p/p_0 < 0.4$ for realistic performance characteristics), and hence the shape of the adsorption isotherm (*cf.* Fig. 3). Apart from stability issues, this is the main reason why silica gel and zeolites are currently used in commercial systems although several MOFs have already shown a higher water sorption capacity.^{4–7} Due to the outperforming microporosities of MOF materials,^{8,9} the discovery or development of a long-term water stable MOF with sufficient hydrophilicity could help to establish sorption cooling in general applications.

MIL-100 has the empirical formula 3D- $\{M_3O(X)(H_2O)_2[btc]_2 \cdot nH_2O\}$ (M = Cr,¹⁰ Fe¹¹ and, lately, Al,¹² X = OH, F, btc = benzene-1,3,5-tricarboxylate, trimesate) and has received attention

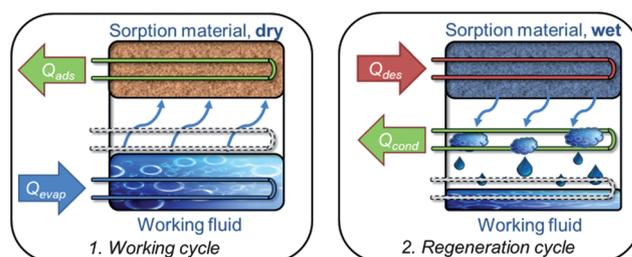


Fig. 1 A liquid (preferably water, as it has the highest evaporation enthalpy of all known fluids and is non-hazardous) is vaporized at a low pressure, taking up evaporation heat Q_{evap} . The water molecules are then incorporated into a sorption material, generating adsorption heat Q_{ads} . When the material is completely loaded with water molecules, it is regenerated by applying driving heat Q_{des} for desorption. The water desorbs, condenses at a medium temperature level releasing the condensation heat Q_{cond} , and is consequently available for the next cycle. Depending on the operation direction and therewith the heat sources and sinks, the same machine can be used as the chiller or heat pump (see Table 1).

Table 1 Heat sources and sinks, depending on the direction of operation

Kind of heat	Cooling application	Heating application
Input: evaporation heat Q_{evap}	Useful cold	Environment
Output: adsorption heat Q_{ads}	Environment	Useful heat
Input: desorption heat Q_{des}	Both cases: solar or waste heat, gas burner	
Output: condens. heat Q_{cond}	Environment	Useful heat

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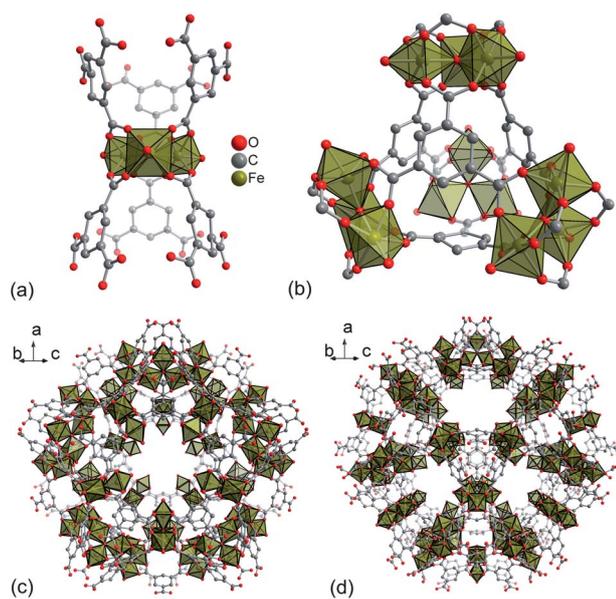


Fig. 2 (a) SBU, (b) supertetrahedra, (c) small S cage and (d) large L cage in MIL-100(Fe) (different objects are not drawn to scale). Hydrogen atoms and solvent molecules of crystallization are not shown. MIL-100 (Al) is isostructural with Al instead of Fe.

in the literature with respect to its catalytic, gas separation and gas storage properties.^{11–16} The porosity of MIL-100 originates from both 25 Å and 29 Å mesopores, which are accessible *via* 5.5 Å and 8.6 Å windows, respectively (Fig. 2).¹¹ As both MIL-100(Al) and MIL-100(Fe) form under quite harsh synthesis conditions (pH = 0.6, $T = 210\text{ }^{\circ}\text{C}$, and pH < 1, $T = 150\text{ }^{\circ}\text{C}$, respectively), a fundamental water stability can be anticipated. Together with the already published data for the water sorption behaviour of MIL-100(Fe and Cr),^{6,17} this suggested that it is worth making a more profound examination of this compound.

As chromium compounds are potentially harmful even in the trivalent oxidation state, we focused our studies on MIL-100(Fe) and MIL-100(Al) with regard to the intended application in a “green” technology.

Synthesis, activation and porosity characterization

MIL-100(Fe) was synthesized and activated according to the reported procedure,¹¹ and obtained as the single crystalline phase (*cf.* Fig. 6) ($S_{\text{BET}} = 1917\text{ m}^2\text{ g}^{-1}$, $V_{\text{pore}} = 1.00\text{ cm}^3\text{ g}^{-1}$). For the synthesis of MIL-100(Al), a literature method published together with the synthesis of MIL-110(Al) was used ($S_{\text{BET}} = 1814\text{ m}^2\text{ g}^{-1}$, $V_{\text{pore}} = 1.14\text{ cm}^3\text{ g}^{-1}$).¹⁸ The activation procedure was carried out by washing the samples with DMF and ethanol (see ESI† for details).

Water sorption isotherms

Water sorption isotherms (Fig. 3) give a valuable first estimation of the sorption behaviour and therefore the suitability of the materials for the intended application.

For MIL-100(Fe), the water adsorption isotherm is in very good agreement with results previously published by Küsgens *et al.*, and can be explained as follows:⁶ at small relative pressures ($p/p_0 < 0.25$), adsorption and cluster formation at the hydrophilic metal sites of the

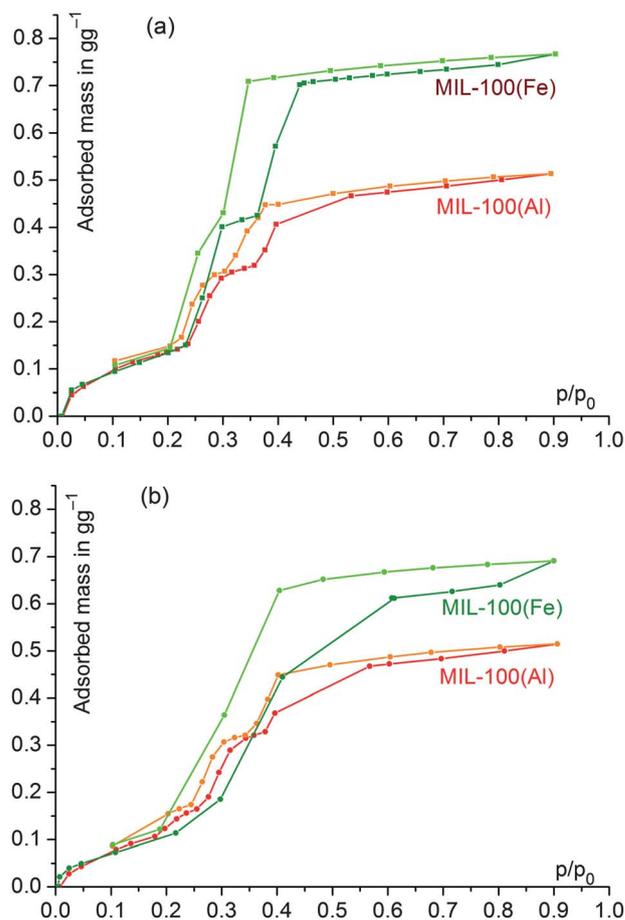


Fig. 3 Water sorption isotherms for MIL-100(Fe and Al) at 25 °C (a) and 40 °C (b). Adsorption in dark and desorption in light green/red.

compound occur. The steep rise at $0.25 < p/p_0 < 0.45$ has been soundly explained with the consecutive filling of first the 25 Å mesopores, then the 29 Å mesopores. The desorption branch of MIL-100(Fe) shows a distinct hysteresis especially for the big mesopores. This phenomenon is widely known for mesoporous materials, yet undesired for the intended application, as it considerably decreases the usable part of the loading lift.

As MIL-100(Al) is isostructural to MIL-100(Fe), it features basically the same shape of the isotherm. Obviously, the exchange of Fe^{3+} with Al^{3+} bond has no influence on the position of the shape of the isotherm or the position of the main lift. The hysteresis, however, is considerably about 30% smaller than that of MIL-100(Fe), which is beneficial for the intended application.

The main difference between the two adsorption isotherms in Fig. 3 is the considerably smaller water uptake of MIL-100(Al) compared to MIL-100(Fe). In the $p/p_0 < 0.2$ region, the adsorption isotherms are similar, but strongly differ in the pore filling region. The total micropore volumes of MIL-100(Al) ($0.65\text{ cm}^3\text{ g}^{-1}$) and MIL-100(Fe) ($0.87\text{ cm}^3\text{ g}^{-1}$) are also different, as determined by N_2 sorption. This explains the smaller water capacity of MIL-100(Al). Additionally, the differences in water uptake can be explained by incomplete H_2O filling of the MIL-100(Al) pores, and may be caused by the presence of additional hydrophobic sites, *e.g.* small amounts of unremoved H_3btc , which inhibit complete wetting of the pore walls.

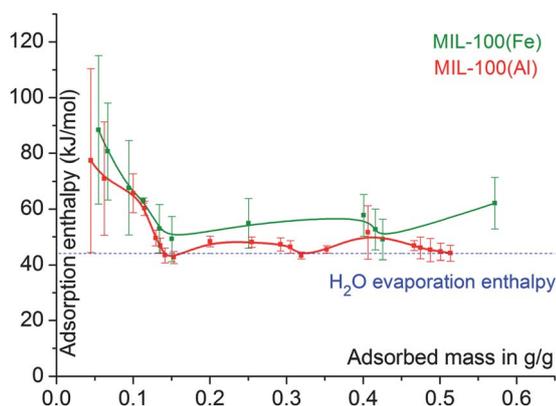


Fig. 4 Heats of adsorption for MIL-100(Al) and MIL-100(Fe) (with error bars, see ESI†), calculated from the adsorption branches of the 25 °C/40 °C isotherms.

The relatively small hysteresis can also be explained by this effect: if there are still water clusters present within the pores at $p/p_0 > 0.4$, the desorption mechanism is more similar to the adsorption mechanism, which results in a better compliance of the two isotherms.

Heats of adsorption

Depending on the direction of operation (chiller or heat pump), the heat of adsorption is either useful heat or must be dissipated to the

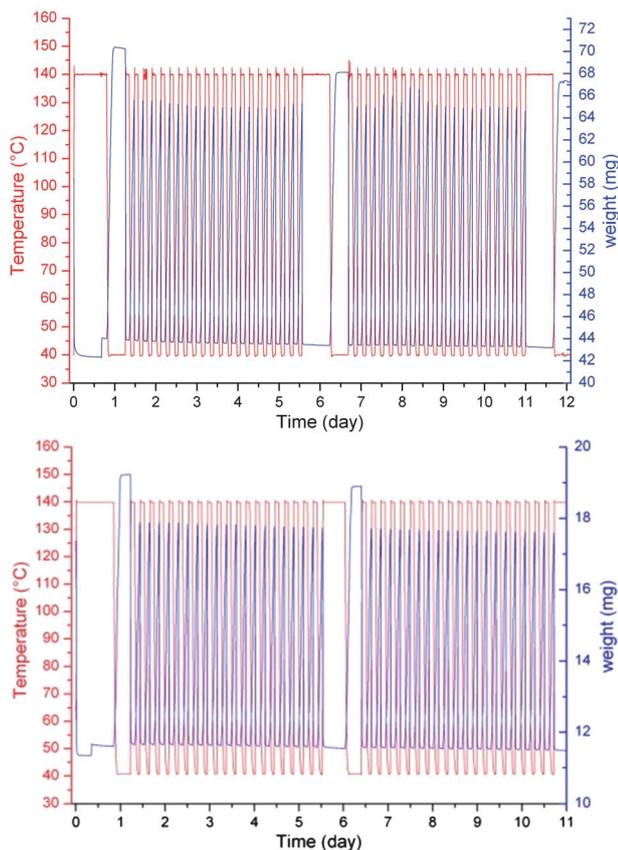


Fig. 5 Temperature profile and load signal of the MIL-100(Al, upper, and Fe, lower graph) cycling experiment, acquired at $p_{\text{H}_2\text{O}} = 5.6$ kPa.

environment. In both cases, it is an important parameter for the design of the apparatus.

From two adsorption isotherms acquired at different temperatures T_1 and T_2 (Fig. 3a and b), the differential heat of adsorption $\Delta H_{\text{ads,diff}}$ can be calculated for any amount of adsorbed substance after determining the required relative pressures p_1 and p_2 . A modified form of the Clausius–Clapeyron equation is used (eqn (1)).¹⁹ $\Delta H_{\text{ads,diff}}$ was calculated over the whole adsorption range from the 25 °C and 40 °C isotherms (Fig. 4).

$$\Delta H_{\text{ads,diff}} = -R \ln \left(\frac{p_2}{p_1} \right) \frac{T_1 T_2}{T_2 - T_1} \quad (1)$$

For both MIL-100(Fe and Al), one can see in Fig. 4 that the evaporation enthalpy is high for small adsorbed amounts, but steeply drops and then approximates a constant value close to the molar evaporation enthalpy of water (44 kJ mol⁻¹ at 25 °C). This supports the theory that adsorption first takes place at the very hydrophilic metal sites and subsequently by formation of water clusters around the already adsorbed molecules.

Additionally, direct calorimetric measurements for MIL-100(Fe/Al) have been conducted for $0.02 < p/p_0 < 0.7$ and yielded an average adsorption enthalpy of $\Delta H_{\text{ads,direct}} = 44.4/43.3$ kJ mol⁻¹, which is very close to the molar evaporation enthalpy of H₂O. This is sound because the largest share of water adsorption is achieved by capillary condensation, as evident *e.g.* from Fig. 3.

Hydrothermal cycle stabilities

Water stabilities of both MIL-100(Fe and Al) have been quantified in this work through a cycling experiment (Fig. 5). Samples were exposed to a humidified gas flow, with a partial water vapour pressure of 5.6 kPa using argon as a carrier, with sample temperatures varying between 40 and 140 °C for 40 cycles and 5 h per cycle. As the heat of adsorption is poorly dissipated in the cycling experiments, kinetics is slow and absolute equilibrium is reached only in the long analytic cycles at the beginning, in the middle and at the end of the experiment (Fig. 5). Additionally, BET (Fig. S1 and S2 in ESI†) and powder X-ray diffraction (PXRD, Fig. 6) measurements were performed in order to investigate the change of porosity (Table 2) and crystallinity, respectively.

From the cycling experiments, it can be seen that both materials are relatively water-stable, with small consequential losses of water capacities and porosities (Table 2), and no detectable loss of crystallinity, as indicated in the PXRD measurements (Fig. 6). For MIL-100(Al) the degree of crystallinity seems even to improve, as can be seen from the sharper peaks after cycling. This may be explained with an additional activation/washing of the pores by the repeated condensation of the adsorbate.

Regarding MIL-100(Al), this water stability could be expected, as the aluminium carboxylates MIL-53 and MIL-110, which have been examined so far, have proven water stable, too.²⁰ With respect to MIL-100(Fe), this is even more interesting, as iron(III) carboxylates have generally shown low stabilities in aqueous media.^{21,22}

The measured losses of water capacity and porosities for MIL-100s as inversely proportional “stability values” are in the same order of magnitude than for the very interesting MIL-101(Cr), which has been classified as highly steam-stable, but is more hydrophobic and contains a potentially critical heavy metal.²⁰

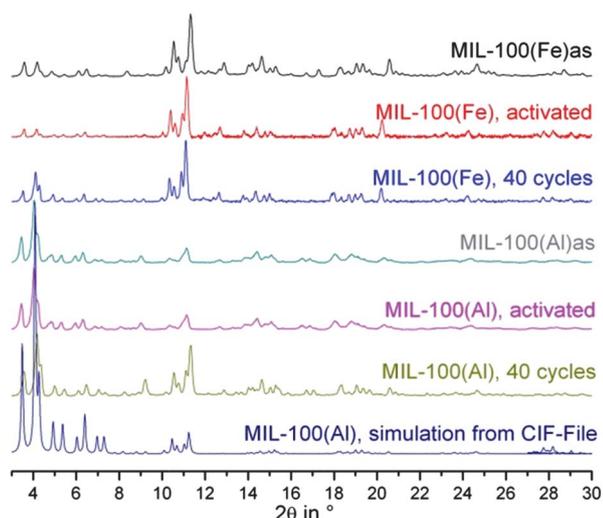


Fig. 6 PXRD comparisons of MIL-100(Fe and Al)—as synthesized (as), activated and after cycling. Diffractograms were obtained with Cu-K α radiation on flat layer probes where at low angle the beam spot is strongly broadened so that only a fraction of the reflected radiation reaches the detector, hence, the low relative intensities measured at $2\theta < 10^\circ$.

Table 2 Influence of cycling onto MIL-100(Fe and Al)

Compound	$\Delta_{\text{water load}}$ (20 cyc.) (%)	$\Delta_{\text{water load}}$ (40 cyc.) (%)	$\Delta_{\text{dry mass}}$ (20 cyc.) (%)	$\Delta_{\text{dry mass}}$ (40 cyc.) (%)	Δ_{SBET} (40 cyc.) (%)
MIL-100 (Fe)	-2.97	-6.37	-0.56	-1.13	-1.3
MIL-100 (Al)	-4.51	-6.56	-1.38	-1.84	-5.9

The decomposition of both MIL-100(Fe and Al) is small in comparison with hydrophilic MOFs like HKUST-1 (Cu–btc) or DUT-4 which degrade much more,⁴ and even with conventional sorption materials like silica gel or zeolites which also show some degree of initial degradation.^{6,23} Long-time measurements will have to prove whether the decomposition of MIL-100(Fe) and MIL-100(Al) continues during further use, or the water capacity stabilizes after a certain number of cycles.

Overall, the water sorption properties of MIL-100(Fe and Al) are very promising, once again made possible by the chemical variability and tailorability of metal–organic frameworks: the combination of high water capacities, very good cycle stabilities, suitable hydrophilicities and little hysteresis considerably enlarges the boundary conditions, under which a sorption chiller or heat pump can be operated. MIL-100 is a valuable extension to the pool of heat pump sorption materials examined so far, like silica gel, activated carbons and MOFs like MIL-101(Cr). Both MIL-100(Fe and Al) are built up from environmentally benign and inexpensive building blocks, which improve the usability on a technical scale.

These results render MIL-100s very interesting candidates for thermally driven, sorption-based chilling or heat pump systems, and

investigations regarding further hydrophilization, long-term stability and optimization of synthesis shall be conducted.

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