Electronic Supplementary Material (ESI)

Water and methanol adsorption on MOFs for cycling heat transformation processes

Felix Jeremias,[a,b] Dominik Fröhlich,[a,b] Christoph Janiak[b]* and Stefan K. Henninger[a]*

[a] Dept. Thermally Active Materials and Solar Cooling, Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstr. 2, 79110 Freiburg, Germany. Fax: +49 761 4588 9000; Tel: +49 761 4588 5104; E-mail: stefan.henninger@ise.fraunhofer.de

[b] Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, 40204 Düsseldorf, Germany. Fax: +49 211 8112287; E-mail: janiak@uni-duesseldorf.de

Thermodynamic boundaries for heat transformation cycles[1]

For the heat transformation cycles with sorption materials the first figure of merit is the achievable *water loading lift*. This is the working fluid exchange between the production cycle (adsorption) and the regeneration cycle (desorption). This exchange is the difference between the richest (**B-C**) and the weakest (**A-D**) isostere of the cycle in an Arrhenius diagram in Fig. S1. The thermodynamic term *isosteric* denotes a process which occurs at a constant water loading, i.e., without ad- or desorption. In case of the cooling application, the cooling enthalpy produced in one cycle can simply be calculated as evaporation enthalpy multiplied by the working fluid exchange. The cycle is defined by the highest desorption temperature (driving temperature, Point **D**), the minimum adsorption temperature (Point **B**), the condenser and evaporator pressure. The selection of the two pressure levels is motivated with respect to the possible applications. The pressure level of 1.2 kPa corresponds to an evaporation temperature of 10 °C, which is a useful temperature level for cooling applications. The second pressure level of 5.6 kPa corresponds to 35 °C which either marks the temperature where heat can be rejected (cooling application) or can be used for low temperature heating (heat pump application).

In the production phase (A➔B) the working fluid is evaporated - producing the useful cold (cooling case) with the heat of adsorption is released to the environment or utilizted as useful heat in a heat pump application.

An isosteric heating (B➔C) then lifts the pressure level to the condenser pressure level.

---

[1] This section is adapted from
S. K. Henninger, F. Jeremias, H. Kummer and C. Janiak, *Eur. J. Inorg. Chem.*, 2012, 2625-2634, and J. Ehrenmann, S. K. Henninger and C. Janiak, *Eur. J. Inorg. Chem.*, 2011, 471-474.

Then, the regeneration phase (C➔D) takes place by applying heat from a high temperature source (e.g. solarthermal collector, waste heat) to desorb the porous solid.

The cycle is closed by an isosteric cooling (D➔A).

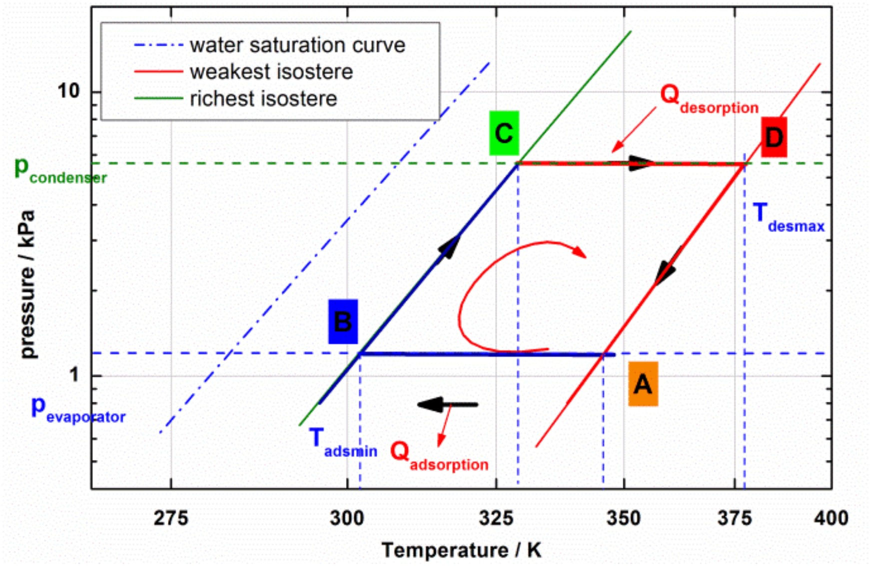


Figure S1 Arrhenius diagram of the ideal cycle in an adsorption heat pump or chiller process. A➔B: Production or adsorption cycle. C➔D: Regeneration or desorption cycle. See text for further explanation. Diagram is reprinted with permissions from the authors from S. K. Henninger, F. Jeremias, H. Kummer and C. Janiak, *Eur. J. Inorg. Chem.*, 2012, 2625-2634; © Wiley-VCH, 2012.

In an ideal cycle, the adsorption and desorption is an isobaric process.

The study of porous materials for this type of application is carried out by measuring the two isobars corresponding to the condenser (C➔D) and evaporator (A➔B) pressure.

The ideal cycle in Fig. S1 is shown with the corresponding points as two isosters with load (in $g_{H2O}/g_{adsorbent}$) 0.1 (weakest) and 0.4 (richest) (cf. Fig. S2). The difference is the reachable loading lift within the cycle of 0.3 gg^{-1}, which is the lower limit for a commercial application. The maximum desorption temperature (104 °C, Point **D**) and the minimum adsorption temperature (28 °C, Point **B**) are defining the relative pressure window between $p/p_0 = 0.05$ and 0.32 (cf. Fig. S2) in which a maximum load has to be reached. This is illustrated in Fig. S2 for an isobaric adsorption measurement at 5.6 kPa of a MIL-100Fe sample. As can be seen, the MIL-100Fe fits quite well the requirements for the desorption step, with a lower loading compared to the model material. If the minimal adsorption temperature can be lowered to 20 °C (Point **B'**), the water exchange or loading lift within this cycle is approximately 0.4 gg^{-1}.

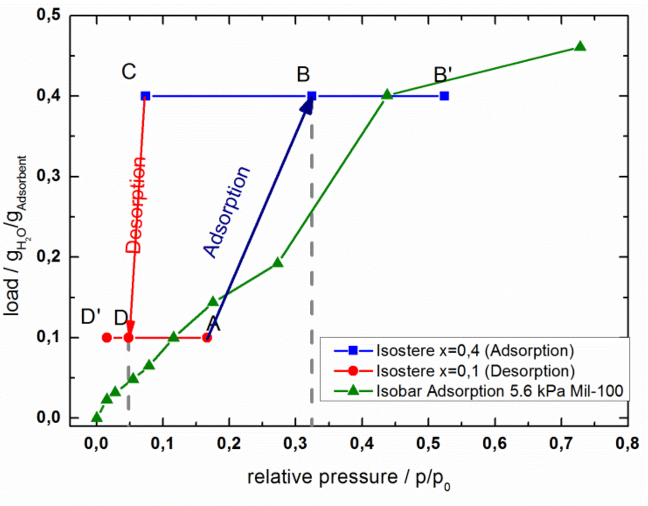


Figure S2 Illustration of a chiller cycle with the data of MIL-100(Fe). Diagram is reprinted with permissions from the authors from S. K. Henninger, F. Jeremias, H. Kummer and C. Janiak, *Eur. J. Inorg. Chem.*, 2012, 2625-2634; © Wiley-VCH, 2012.

It is evident that MIL-100Fe realizes only part of its possible water uptake in the applicable relative pressure window between p/p_0 = 0.05 and 0.32. In this respect the load-pressure behavior for MIL-100Fe is typical for a MOF. The major uptake change often takes place at too high relative pressure of p/p_0 between 0.3-0.5 (see Fig. 3 in article for MIL-101Cr (◆) and MIL-100Fe (⬟)). Yet, even this loading lift of approximately 0.2 gg^{-1} between p/p_0 = 0.05 and 0.32 for MIL-100Fe is already higher in this pressure range than for SAPO-34 which can be considered as a benchmark material.

Adsorption in MOFs takes place at a comparatively high relative vapor pressure, which corresponds to a comparatively high evaporator temperature and a comparatively low achievable temperature lift. Heat pumping applications intended, e.g., for domestic heating will consequently favor inorganic, highly hydrophilic materials. However, as stated in the introduction, the application also aims towards thermally driven room chillers, where a higher evaporator temperature is perfectly acceptable. Given that the desorption process of a thermally driven chiller is supposed to be fueled by low temperature heat from district or solar heating, a comparatively low affinity towards the adsorbent is in fact desirable.

For related applications like dehumidification and open circuit cooling, e.g., by a desiccant wheel, these considerations also apply.

MOFs offer the possibility to shift the adsorptions isobars or isotherms into the required pressure window through linker modification. A nice example was illustrated by Zhang et al.[2]

with the replacement of hydrophobic 2-methylimidazolate in MAF-4 (ZIF-8) by more hydrophilic 3-methyl-1,2,4-triazolate in MAF-7 and mixed MAF-47 of different 2-methylimidazolate /3-methyl-1,2,4-triazolate content (Fig. S3).

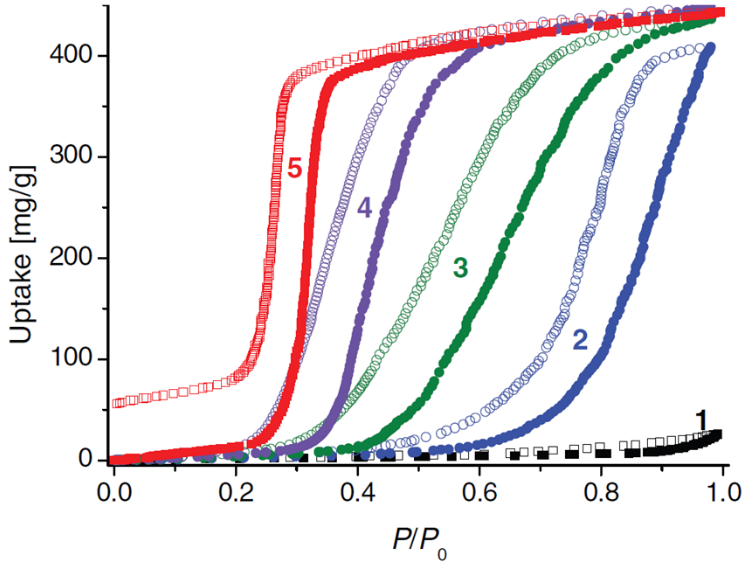
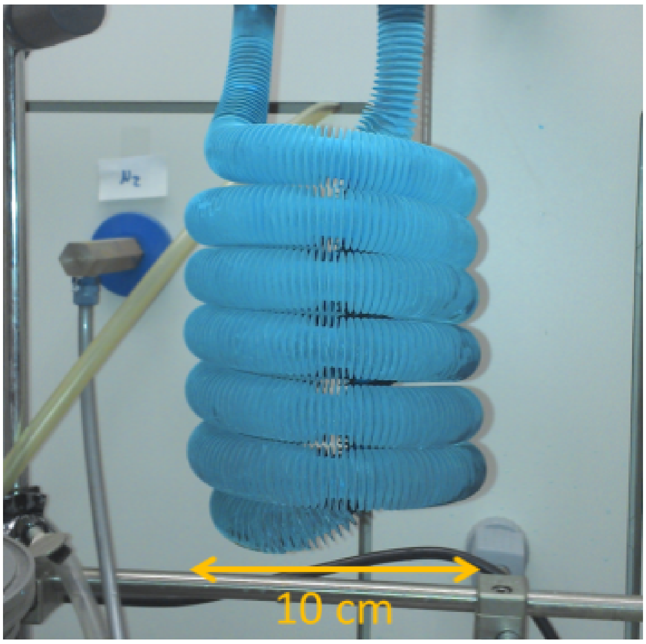


Figure S3 H_2O vapor sorption isotherms of MAF-4 (1), MAF-47-0.76 (2), MAF-47-0.49 (3), MAF-47-0.23 (4), and MAF-7 (5) at 298 K. Filled and open symbols represent absorption and desorption, respectively. Diagram is reprinted with permission from the publisher of *Adv. Mater.*, 2011, **23**, 1268-1271; © Wiley-VCH, 2011.



---

2 J.-P. Zhang, A.-X. Zhu, R.-B. Lin, X.-L. Qi and X.-M. Chen, *Adv. Mater.*, 2011, **23**, 1268-1271.

Figure S4 Representative image of a finned coil heat exchanger prototype, coated with 150 μm of copper trimesate, HKUST-1 (Cu-BTC) using the thermal gradient method.