DOI: 10.1002/ejic.201001156

Water Adsorption Characteristics of MIL-101 for Heat-Transformation Applications of MOFs

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Dedicated to Prof. Dr. Peter Klüfers on the occasion of his 60th birthday

Keywords: Metal-organic frameworks / Mesoporous materials / Adsorption / Adsorption chilling / Heat transformation

The adsorption of water vapor in the highly porous metal-organic framework (MOF) of 3D-[$Cr_3F(H_2O)_2O(bdc)_3$·~25H_2O] (MIL-101) (bdc = benzene-1,4-dicarboxylate, terephthalate) of up to 1 g of water per gram of sorbent material (between 140 °C and 40 °C under a water vapor pressure of 5.6 kPa) together with the stability over several cycles makes MIL-101 the most promising material, so far, for heat transformation applications like thermally driven heat pumps or adsorption chillers.

Introduction

In recent years, tremendous research progress has been made in the study of micro- and mesoporous adsorbent materials suitable for heat-transformation applications.[1] Thermally driven chillers and heat pumps based on the reversible adsorption/desorption of water in micro- and mesoporous materials, in particular, provide a promising approach towards a more rational use of energy, a sustainable energy policy as well as an effective climate protection through the reduction of the environmental impact of conventional heating and cooling devices.[2]

The principle cycle of an adsorption heat-pump process or chiller is illustrated as an ideal cycle in Figure 1. The process is determined by the minimum adsorption (point B), the maximum desorption temperature (point D) as well as by the evaporator and condenser pressure. In the production phase (A → B) the working fluid is evaporated thereby producing the useful cold (cooling case) whereby the heat of adsorption is released to the environment. In case of a heat-pump application this is the useful heat. The evaporator pressure is defined either by the temperature for the useful cold (cooling case) or by the available low-temperature heat source (heat-pump case). After an isosteric heating (B → C), thus lifting the pressure level to the condenser pressure level, the regeneration phase (C → D) takes place. In the regeneration phase heat from a high-tempera-

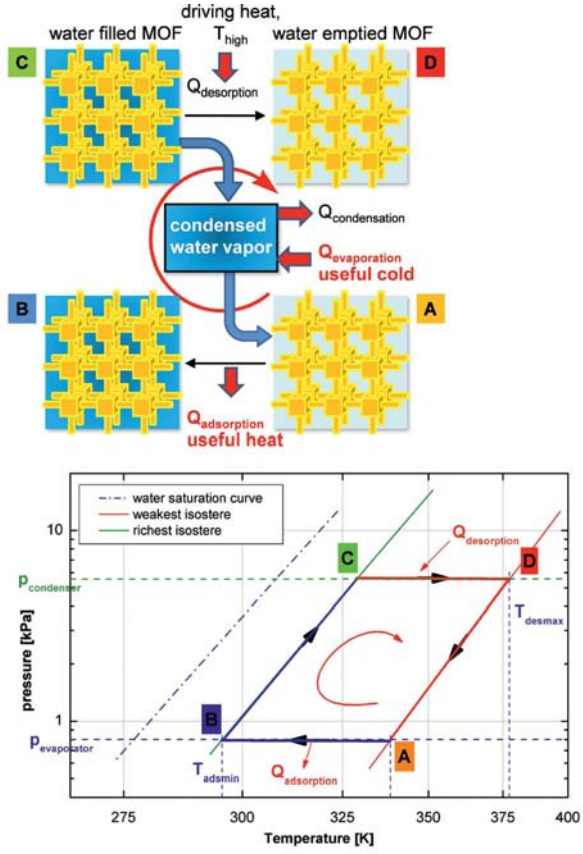

Figure 1. Principle process in an adsorption heat-pump or chiller process. A → B: production or adsorption cycle. C → D: regeneration or desorption cycle.

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ture source (e.g. solar-thermal collector, waste heat) is used to desorb the water from the porous solid. Finally, the cycle is closed by an isosteric cooling (D → A). The working-fluid exchange within this cycle (loading lift between the weakest and richest isostere) is the most important figure of merit.

Due to their high porosity, large surface area and tuneable pore sizes, MOFs have attracted a still increasing attention over the past years.[3–6] The possibilities for the syntheses of MOFs allow to specifically tailor materials for different applications[5,7,8] such as gas adsorption[9] or catalysis.[10] Although many possible applications are being envisioned, none has – to the best of our knowledge – yet been actually realized.[8] Hence, we present a dehydratable-hydratable water-stable MOF as a promising solid adsorbent material in heat-transformation cycles for refrigeration, heat pumping, and heat storage.[11,12] The sample shows the largest water-loading spread for typical application conditions for any material reported so far.

Results and Discussion

The crystalline mesoporous material 3D-[$Cr_3F(H_2O)_2O$-$(bdc)_3$•~$25H_2O$] (MIL-101), which was discovered by Férey et al.,[13] is a Cr terephthalate with inner free-cage diameters of up to 34 Å, resembles an augmented MZN zeolite topology.[13] The water adsorption behavior and water stability have been investigated here.

As has already been mentioned by Akiyama, Matsuda and Kitagawa,[12] the MIL-100 samples show an already highly interesting water adsorption behavior in a temperature range that is predestinated for heat-transformation applications. However, the MIL-101 sample surpasses its predecessor in its reversible water adsorption characteristics.

To examine the water adsorption characteristics of MIL-101,[14] adsorption/desorption isobars and isotherms have been performed with thermogravimetric (TG) and volumetric (Vol) methods. As illustrated in Figure 1, the cycle is more or less an isobaric process. Therefore, measurements of adsorption and desorption isobars (instead of isotherms[15]) are most important, especially with regard to possible framework structure changes during the adsorption process.[16] This gate effect may result in different behavior of the materials in isothermal and isobaric adsorption. For MIL-101 the isobar and isotherm measurements in Figure 2 show a very good agreement, hence no gate effects are evident. It can be seen in Figure 2 that the material MIL-101 shows a high water uptake of 1.01 g of water per gram of sorbent with an S-shaped form of the isotherm. This shape is advantageous for the application, as a large loading lift can be reached within a narrow range of relative pressure. The main amount of the water exchange is within a relative pressure of 0.3 and 0.6, which means that this material can be desorbed at 363 K or even lower temperatures. Unfortunately, the usable loading lift in the application is slightly reduced due to the hysteresis between adsorption and desorption. However, the water loading lift for isobar desorption and adsorption at 5.6 kPa for a desorption temperature of 90 °C (363 K) and an adsorption temperature of 40 °C is 0.939 g of water per gram of sorbent.

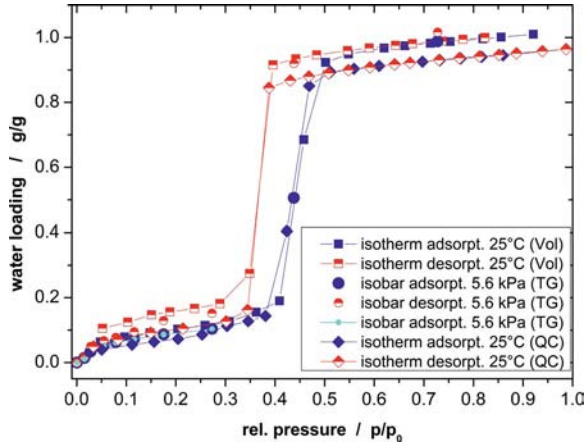

Figure 2. Water adsorption and desorption isotherms of the MIL-101 sample. The isotherms at 298 K were measured by a volumetric method (Vol), while the isobars at 5.6 kPa were measured thermogravimetrically (TG). As can be seen, the material shows a high water uptake of up to 1.01 g of water per gram of sorbent. Furthermore, there is a hysteresis between the adsorption and desorption path. In addition, adsorption measurements have been performed independently at Quantachrome (QC).

Furthermore, for an estimation of the possible thermal coefficient of performance (COP) the heat of adsorption and the thermal masses including the adsorbent must be known. Consequently, the integral heat of adsorption and the heat capacity have been measured with the simultaneous Setaram TG/DSC 111. The setup is described in detail in ref.[2] The integral heat has been measured for three adsorption/desorption cycles in order to avoid any (single) structural effects. For the first adsorption cycle starting at 140 °C down to 40 °C the integral heat including the sensible heat (heat capacity of the material and the adsorbed water) has been determined to 2.557 kJ/g. For the reverse step the integral heat has been determined to 2.620 kJ/g. As the accuracy of the 3D-DSC sensor in vertical operation is limited to ±5%, these values are in good agreement. As these values are near the evaporation enthalpy of water, the interaction energies with the framework are very low compared to other materials used so far, like e.g. zeolites. Moreover, the influence of the heat capacity is marginal as can be seen by the calorimetric measurements. The measured heat capacity has been determined to 1–1.5 J/(g K) for temperatures between 40 and 140 °C.

With regard to the application, a typical cycle time for the adsorption process is in the range of 10 min. Therefore, the cycle stability under humid condition is another important figure. In order to evaluate the hydrothermal cycle stability the sample has been exposed to a short cycle test consisting of a continuous cycling between 140 and 40 °C for 40 full cycles under a water vapor pressure of 5.6 kPa. Before, after the first half, and at the end the water uptake capacity for the temperature step 140 °C/40 °C has been

measured. There is a slight degradation visible with a water uptake capacity of 98.1% after 20 cycles and 96.8% after 40 cycles compared to the initial load (Table 1).

Table 1. Mass-variation results before cycling, after the first 20 cycles and after 40 cycles.

No. of cycles	0	20	40
Initial mass [mg]	11.58	11.56	11.56
Final mass [mg]	22.84	22.61	22.46
Δm [mg]	11.26	11.05	10.9
% of initial load	100%	98.1%	96.8%

In addition, nitrogen adsorption measurements have been performed before and after the hydrothermal treatment. As can be seen in Figure 3, neither significant modifications on the shape of the isotherm nor on the pore volume have been observed. Furthermore, the BET surface and total pore volume before and after the hydrothermal treatment has been determined (see Table 2). The difference in the surface area and pore volume is within the reproducibility of the measurement. For the DFT calculation a silica-kernel assuming a cylindrical pore shape has been used.

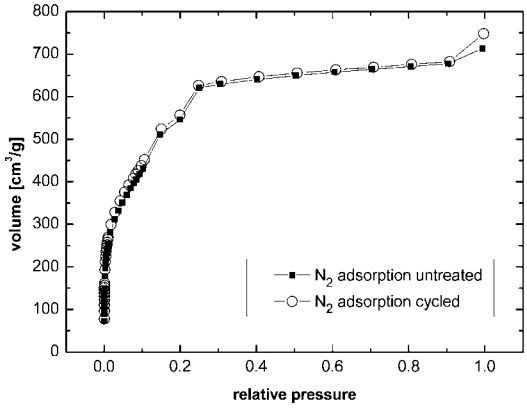

Figure 3. Nitrogen adsorption isotherms on the MIL-101 sample before and after the hydrothermal treatment.

Table 2. Nitrogen and water adsorption measurements results.

	Untreated	Cycled sample
BET surface area	2059 m^2/g	2047 m^2/g
DR surface area	2455 m^2/g	2504 m^2/g
N_2 pore volume	1.103 cm^3/g (p/p_0 = 0.99365)	1.156 cm^3/g (p/p_0 = 0.9972)
N_2 pore volume (DFT)	0.986 cm^3/g	0.996 cm^3/g
H_2O pore volume (p/p_0 = 0.9212)	1.013 cm^3/g	

Conclusions

It may be concluded that MIL-101 is one of the most promising MOF sorbent materials for heat-transformation applications known so far, as it adsorbs up to 1 g of water per gram of sorbent and is stable even over several cycles. Furthermore, the incorporation of affordable reagents in the synthesis of this compound as well as an easily feasible synthetic route approves this material as a highly interesting candidate for a thoroughly effective heat transformation application.

Experimental Section

The synthesis of MIL-101 samples was executed according to the literature.[13] The material could be obtained reproducibly in the described octahedral crystal morphology. The isobars have been measured with a Setaram combined TG/DSC thermobalance, whereas the volumetric isotherms have been measured with a Quantachrome Autosorp. In addition to the analysis at Fraunhofer ISE, water and nitrogen adsorption measurements have been performed at Quantachrome GmbH Odelzhausen with a Hydrosorb water sorption analyzer and an Autosorp iQ. The water adsorption isotherm measured by Quantachrome is in good agreement with the measurements performed at Fraunhofer ISE. The slightly lower adsorption capacity can be explained by a lower desorption temperature of 110 °C compared to 120 °C at ISE. In addition, 12 mg have been analyzed at Quantachrome, therefore the reference dry mass has a relative error of approximately 6%. The determination of surface areas and pore volumes are currently under critical discussion and have been recently discussed in context with MOFs where extremely high surface areas have been reported.[17,18] Therefore, the total pore volume has been measured for different pressures and different adsorbates.

Acknowledgments

Funding by the Federal German Ministry of Economics (BMWi) under grant 0327851 and by the Deutsche Forschungsgemeinschaft (DFG) through grant Ja466/14-1 is gratefully acknowledged. The authors would like to thank Quantachrome GmbH & Co. KG for independent additional water and nitrogen adsorption control measurements.

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Received: October 29, 2010
Published Online: December 23, 2010

