Dynamic heat transfer modeling of a closed refrigerated display cabinet

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Heat properties of a hydrophilic carboxylate-based MOF for water adsorption applications

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Abstract

The development of new porous materials is expanding the boundaries of applications related to gas adsorption, including gas separation, catalysis, drying and energy storage. The specific heat capacity and thermal conductivity of the adsorbent materials are important parameters in the engineering process. For instance, in the adsorptive heat pump technology, the energy generation and transfer by the adsorbent during the adsorption and desorption process of the adsorbate directly determines the energy efficiency of the working cycle. However, the thermal properties' data for the novel types of adsorbent materials, metal-organic frameworks (MOF), is often lacking in the literature. This work followed a protocol particularly relevant for the measurement of MOFs' thermal properties under powder form. A very promising hybrid material for energy storage, separation and other applications, MIL-160, has been tested as a reference. The specific heat capacity of the material was measured at temperatures ranging from 20 °C to 75 °C with a heat flow type differential scanning calorimeter (DSC). The thermal conductivity was measured with a transient heating source technique within a similar temperature range. By fitting the experimental data to the Clausius-Clapeyron model, the performance of this material in the application of adsorptive heat pump was obtained.

Key words

Metal-organic frameworks, specific heat capacity, thermal conductivity, adsorption, thermodynamic efficiency

Introduction

The superior adsorption performance of modern porous solid materials incited the development of various technologies including gas storage and separation, dehumidification, cooling, and heating. In an adsorption process, the guest molecules attach to adsorption sites on the surface of the host molecules, creating a relatively stable phase by interactions of chemical bonds between the adsorbate and the adsorbent. The adsorbent can later release the adsorbate when receiving external energy input. The whole process involves a large amount of energy conversion under heat form, while porous solids often have high specific heat capacity and low thermal conductivity due to open pore structure and high pore volume, which often lead to a reduction in the sorption performance.

As a new class of porous solids, metal-organic frameworks have aroused a great interest for its potential in the immense possibilities of fine-tuned adsorptive properties [1]. Also, water has been considered as the best green sorbate due to its broad applicability, non-toxicity and large enthalpy during sorption. Since the discovery of water-stable MOFs, the adsorption applications based on water-MOFs pairs have promoted cross-border research between fundamental chemistry and thermal engineering [2][3][4]. The unique functions of MOFs in tuning the hydrophilicity and water uptake show prospects in the improvement of energy efficiency in specific working environment [5]. Variable concepts have made progress in the aforementioned applications, especially in cooling [6][7][8], water production[9][10][11][12] and drying[13][14][15].

The pore-filling step of water in MOF for the adsorption application in practice should be reversible. Water molecules interact with the polar sites in MOF's structure via hydrogen bonds, but not via strong coordination bonds within the frameworks. This pore-filling mechanism is different from a typical chemisorption and can have a smaller adsorption enthalpy close to the water evaporation heat. As a consequence, a strategy of developing novel sorbents is to create ordered large pores to enhance the cyclic adsorption capacity [16][17]. A higher fraction of void volume would result in undesirable heat properties that have a negative impact on the cycling sorption performance.

The charging and discharging of thermal energy accompanying the cyclic ad-desorption operations involves heat retention by the sorbents and thus a rapid temperature swing of the MOFs. Because a miniscule movement along the step-wise sorption isotherms of MOFs may engender a great amount of change in water uptake, precise measurement of specific heat capacity and thermal conductivity has a significant impact on the evaluation and prediction of the adsorption performance, especially in a dynamic modeling work. Yet very few values have been reported in the literature and most researchers adopt an average heat capacity of 1 J/(g. K). Huang et al.[18] have reported a thermal conductivity below 0.1 W/ m K of MOF-5 at room temperature after shaping, which is much lower than the single crystal. Purewal et al. [19] have showed that this value can increase by 5 times with 10wt% graphite additives. Ming et al. [20] measured the specific heat capacity of MOF-5 as 0.72 J/g K, similar to alumina and graphite. Erickson KJ et al.[21] found HKUST-1 composite with a thermal conductivity of 0.27 W/ m K. These results remain in the range of low heat transfer performance similar to conventional adsorbents such as zeolite type X, zeolite type CHA, carbon- or silica-based matrix encapsulating phase change materials (PCM), etc.[22][23][24][25][26][27]

The differential scanning calorimetry is a dominant technique in the direct measurement of heat properties for its simple operation and wide adaptability to variable working conditions [28]. Frazzica et al. [29] developed a methodology to directly measure the heat transfer properties of AQSOA Z02 in an adsorptive heat pump application with similar techniques. BASF and co-workers [30] carried out the room temperature thermal conductivity test of MOF-5 for gas storage by a DSC and a xenon thermal flash diffusivity instrument. Mu and Walton [31] measured the specific heat capacity of several MOFs by using DSC coupled with a thermal gravimetric analyzer covering 50 to 200 °C to verify their thermal stability.

In this work, a simple method and protocol is presented for the measurement of heat transfer properties of MOF bulk materials for adsorption applications. The specific heat capacity and thermal conductivity are key parameters in the design of adsorptive based energy transformation devices. A hydrophilic Al furane dicarboxylic based MOF, MIL-160(Al), which is one of the most promising adsorbents to date in the storage and transformation of low-grade energy is taken as an example [32]. The thermal efficiency of an adsorptive heat pump employing the adsorbent is also derived.

1. Experiments

1.1 Material preparation

MIL-160(Al) was synthesized via an up-scale version of the process reported in a previous study [32]. In short, $Al(OH)(CH_3COO)_2$ (0.6 mol, 93.7 g; Aldrich, 90%) and

2,5-furandicarboxylicacid (0.6 mol, 97.3 g) were mixed in distilled water (600 mL) and stirred under reflux condition for 24 h. The mixture was filtered and washed with ethanol at room temperature. The resulting white solid in powder form was dried under 100°C, yielding 111.5g activated MIL-160(Al) (90%).

The Brunauer-Emmett-Teller (BET) surface calculations were carried out from N2 adsorption-desorption isotherms measured at liquid nitrogen temperature (77 K) after dehydration under vacuum at 423 K for 12 h using Micromeritics Tristar 3020. The pore volume was taken by a single point method at relative pressure (p/p_0) = 0.99. The high-resolution X-ray powder diffraction-pattern of MIL-160 was recorded in two hours within the 4-60 ° 2θ range, with a step of 0.002° and a λ equal to 1.540598 Å.

Water-sorption isotherms were measured by an intelligent dynamic vapor sorption instrument (DVS Vacuum, SurfaceMesurementSystems Ltd.) connected to a humidity generator. The experiments were carried out in the temperature range of 20-60 °C at the relative vapour pressure precisely (RH=0-95%). The humidity was controlled by using two mass-flow controllers with dry air and pure vapour, respectively. The precise humidified airflow passed through two thermogravimetric balances with the sample in one and blank for another. Prior to the adsorption experiment, the samples were dehydrated at 150°C for 12 h under high vacuum ($< 10^{-6}$ torr).

1.2 Specific heat capacity

The specific heat capacity is directly linked to the thermal loss in an adsorption process [33]. The DSC used in the experiment is μSC, a Tian-Calvet type microcalorimeter manufactured by Setaram Instrumentation, France. With this instrument, measurements can be realized under isothermal conditions or with a constant heating rate ranging between

0.001 and 1.2 K/min. A schematic representation of the DSC is shown in Fig. 1. It has a RMS noise level of 0.2 µW typically. The temperature ranges from -20°C to 170°C, controlled precisely by a Peltier element based thermostat, that surround the sample on all sides. It is equipped with four calorimetric wells that enable two simultaneous tests for two samples and two references. The measurement cell is made of Hastelloy C276 with an internal volume of 850 µL and is able to measure solid, liquid samples or blends. A bunch of Peltier elements are positioned around the cell to measure the temperature difference between the sample and the environment in 3D. This arrangement allows for measuring thicker samples on larger volume closer to real conditions.

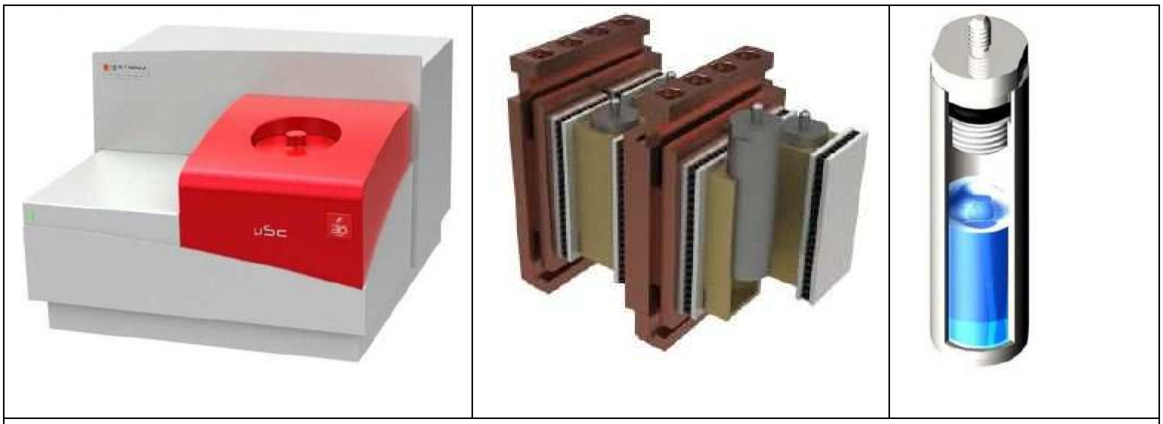


Figure 1. µSC experimental platform. Left: Setaram µSC Type Tian-Calvet. Middle: 4 calorimetric wells. Right: measurement cell

The determination of the specific heat capacity of MIL-160(Al) using the continuous temperature programming method requires the realization of two different and successive tests:

-a test with two empty cells (which will be called "blank");

-a test with the sample in the measurement cell and the reference cell remaining empty.

It is imperative to use the same "measurement" cell for both tests as well as an identical temperature program.

To compare the impact of water sorption, both dry and fully loaded samples were measured.

For the loaded sample, before the test, the powder of MIL-160(Al) was saturated under an air-vapor mixing flow of 30% RH at 20°C for 2 hours to ensure it achieved the uptake equilibrium at this state. The sample was weighed and inserted into a batch cell. The powder was carefully packed into the cell to ensure the homogeneity of the measured sample. The initial mass was 400.85 mg.

The following experimental profile has been employed:

- stabilization at 20 °C during 1800s
- heating from 20 ° C to 75 °C to 0.2 ° C / min
- stabilization at 75 °C during 1800s

2.3 Thermal conductivity

Thermal conductivity is measured with a C-ThermTCi sensor from C-Therm, Canada. The C-Therm TCi employs a modified Transient Plane Source technique. Instead of a common used laser light heating source, a known current is applied to the sensor's spiral heating element, providing a small amount of heat (Fig 2.). A guard ring around the sensor is simultaneously charged to support a one-dimensional heat exchange between the primary sensor coil and the sample. The current applied to the spiral element results in a rise in temperature at the interface between the sensor and sample, which induces a change in the voltage drop of the coil. The thermal diffusivity and conductivity is derived from the temperature increasing curves versus heating time. The temperature increasing thus the voltage rise is steeper for materials with lower thermal conductivity and flatter for higher thermal conductivity.

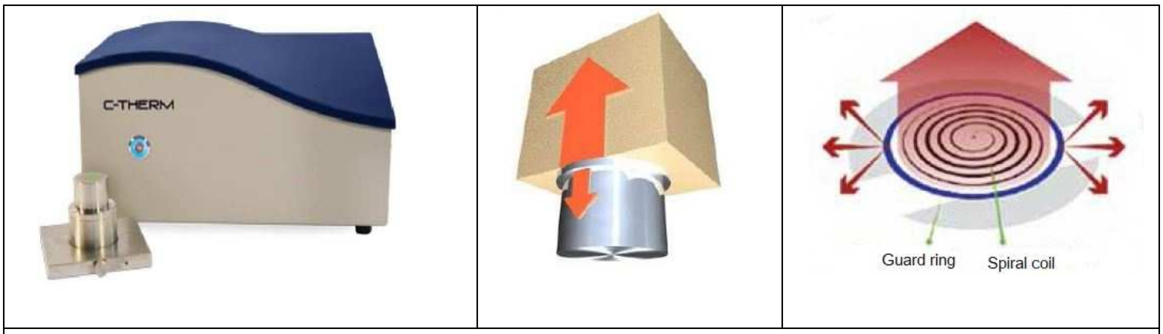


Figure 2. Thermal conductivity experimental platform.

The thermal conductivity is linked to the density of the sample. Powders of MIL-160(Al) have been compressed in to bloc under pressure. Again, a humid sample was obtained by saturating the packed powder under an air-vapor mixing flow of 30%RH at a lower temperature for 2 hours to ensure it achieved the loading equilibrium at this state. The whole analysis instrument was placed in a small climate chamber to regulate the RH. A dry sample for comparison was obtained by heating the humid sample under 90°C for 2 hours.

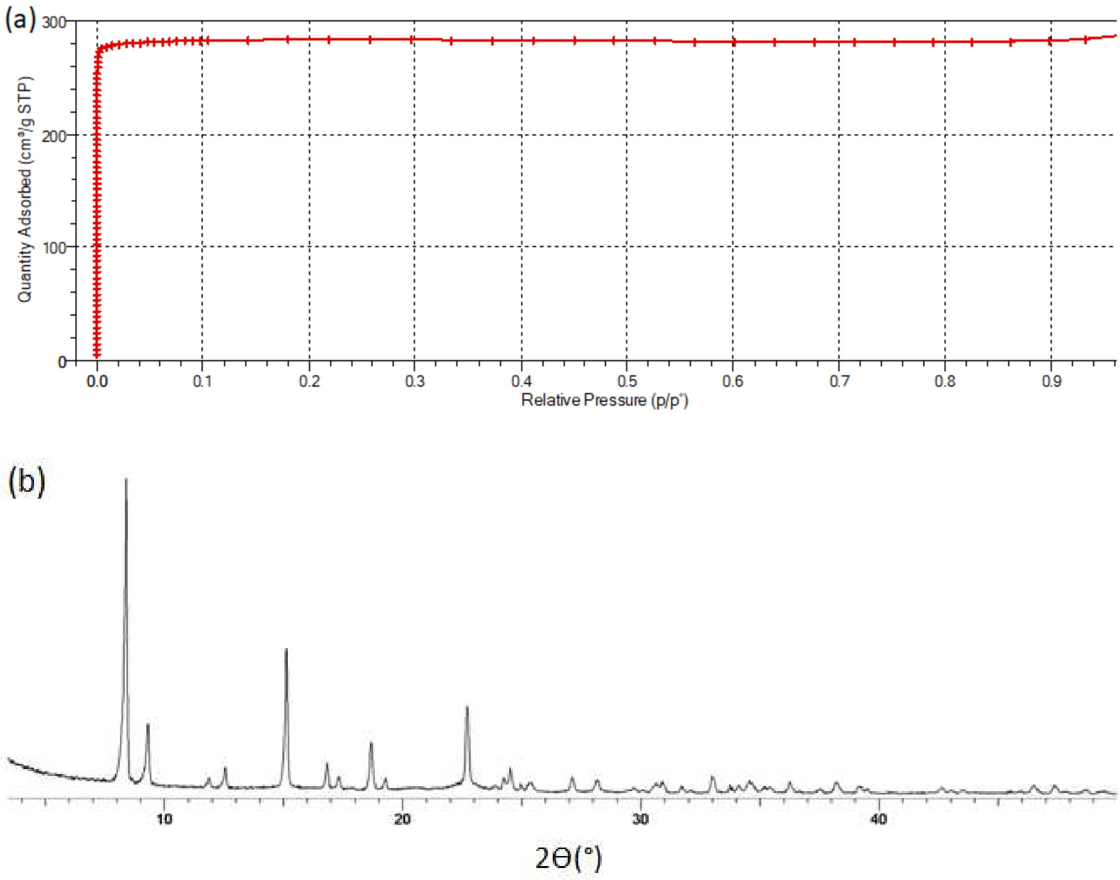
2. Results and discussion

2.1 Characterization of MIL-160(Al)

After purification and activation, the BET specific surface area and pore volume of the sample were found to be 1200 m^2/g and 0.398 cm^3/g respectively (Fig 3a).The PXRD pattern and thermalgravimetric of the MIL-160(Al) powder (Fig 3b,c) are consistent with previously synthesized with small scale process reported in [32]. Water adsorption isotherms for MIL-160 are step-wise curves with reflection point at around 8% P/P_0 and the majority uptake (>90%) is complete at 20% P/P_0 (Fig 3d). The position of adsorption stage varies very little under different temperature and can be neglected as we only focused on the full uptake conditions. The maximum uptake at $P/P_0=0.9$ reaches around 0.4 g/g dry mass. There is barely sorption hysteresis at all temperatures so that the adsorption and desorption routines almost coincide with each other which is an advantage to be integrated into an active mechanic system. The isosteric heat ΔH_{ads} of water adsorption can be calculated from the adsorption isosteres according to the Clausius-Clapeyron relation, given by [35]:

$$\Delta H_{ads}(T) = \mathrm{R}\left(\frac{\mathrm{d}(\ln \mathrm{P})}{\mathrm{d}\ \left(-\frac{1}{\mathrm{T}}\right)}\right)_{w} \qquad (2)$$

Where ΔH_{ads}, R, P, T and w represent the isosteric enthalpy of adsorption, universal gas constant, pressure, temperature, and water uptake. The isosteric enthalpy of adsorption is obtained as a function of water uptake and adsorption isotherms measured across a wide temperature range with a linear interpolation method. The ΔH_{ads} drops very quickly to 50 kJ/mol at the water uptake w=0.02 g/g dry mass, maintains this value until 0.3 g/g dry mass and varies a little thereafter. This plateau of the ΔH_{ads} indicates reversible adsorption-desorption phenomena.



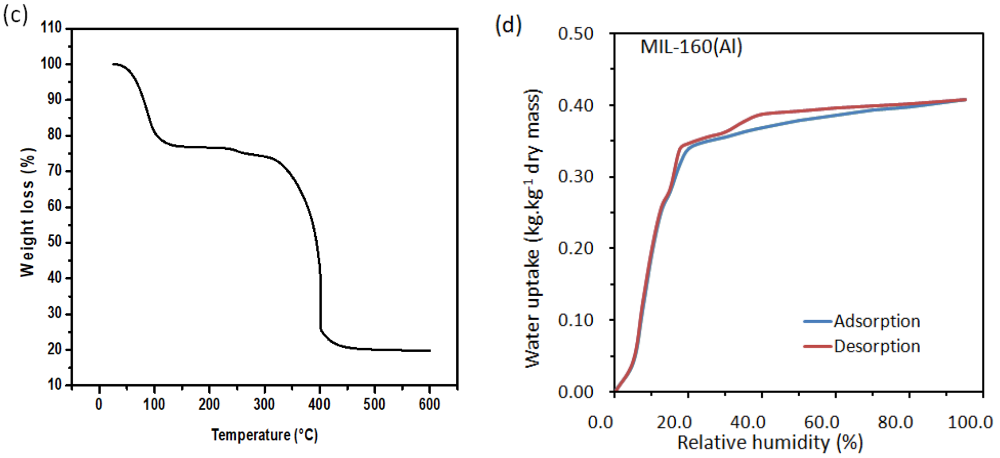


Figure 3. Characterization of MIL-160(Al). (a) Nitrogen gas sorption isotherm. (b) Powder X-Ray diffraction pattern (λ_{Cu}≈1.5406 Å) (c) Thermogravimetric analysis under air atmosphere (heating rate of 3°C/min) (d) Water vapor sorption isotherm at 298K

2.2 Specific heat capacity

The following idealized thermogram (Fig 4.) is obtained with the amplitudes of the Heat Flow signal A_s and A_b (µV) at temperature T of the sample and blank, respectively.

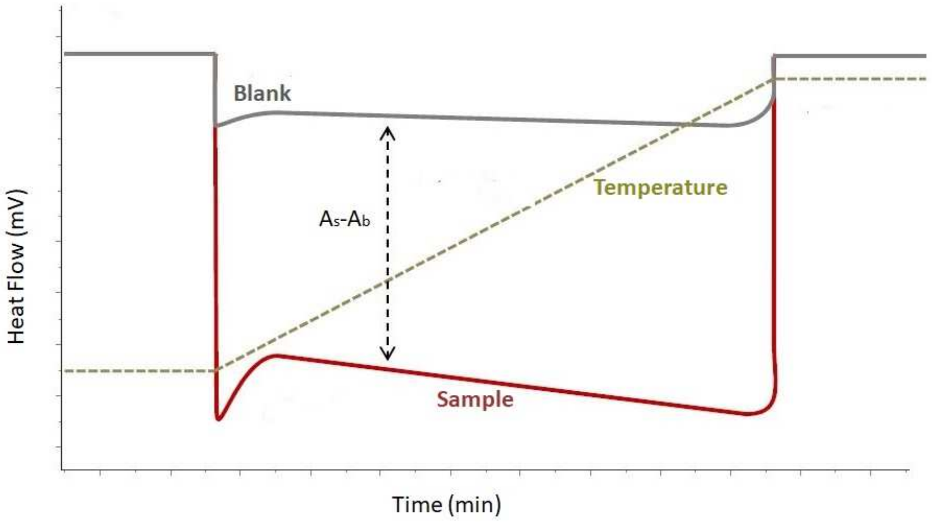


Figure 4. Thermograms superposition of blank and sample

The heat capacity of the sample can be calculated as the following equation:

$$C_p(T) = \frac{\mathrm{A_s} - \mathrm{A_b}}{\mathrm{m_s}\frac{\mathrm{dT}}{\mathrm{dt}}} \tag{1}$$

where C_p (T) is the heat capacity of the sample in J/(g. K) at a temperature T; A_s and A_b are sample and blank output signals in μV; m_s is mass of the sample in mg; $\frac{\mathrm{dT}}{\mathrm{dt}}$ is the heating rate in K/s.

The experimental conditions were adopted to measure a representative sample of 400 mg on macroscopic level and minimize the impact of the heating rate. The calculation of C_p was carried out from 20 to 75°C that is the operational temperature range of MIL-160(Al) for an adsorption heat pump system. The measured result of the highly loaded sample on each point of this temperature range is shown in Fig 5. The measured specific heat capacity remains almost constant with a slight increase by 3% over the temperature range.

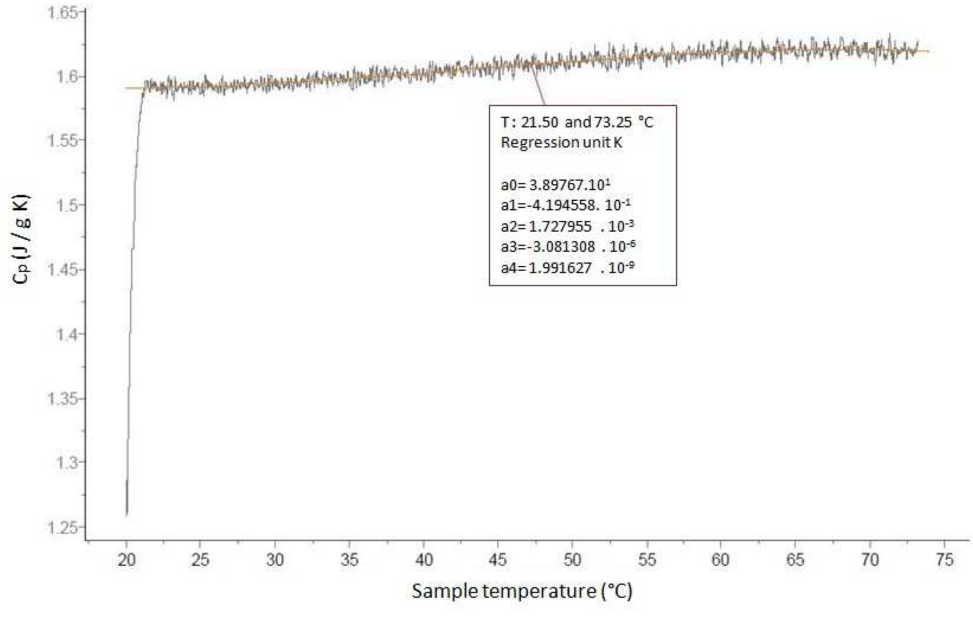


Figure 5. Evolution of the C_p of the sample between 20 °C and 75 °C

We listed the heat capacity of the dry material at a set of temperatures in Table 1 for the comparison.

Table 1. Comparison of the heat capacity between dry and highly loaded samples, measured C_p in J/(g.K)

Sample	24.8 °C	45.0 °C	70.0 °C
Highly loaded	1.588	1.605	1.617
Dry	1.117	1.125	1.160

The more water the MOF contains, the higher its specific heat capacity. A reduction of 30% on the C_p can be observed when the desorption is complete on the loaded sample. In a typical thermodynamic cycle of the adsorption heat pump, the sorbents with higher water uptake is often heated to desorption temperatures with external energy input and the released heat during temperature decreasing is to be evacuated. The necessary energy cost to power the cycling operation would be higher when using the heat capacity measured at different uptake state than in a calculation based only on the value of dry materials.

2.3 Thermal conductivity

The thermal conductivity of the sample can be calculated from the following equation:

$$e = \sqrt{k\rho C_p} \tag{1}$$

where e is the thermal effusively in W.s$^{1/2}$/(m^2.K), k is thermal conductivity in W/(m.K), ρ is the density in kg/m^3.

The calculated thermal conductivity of one sample was shown in Table 2, which slightly decreased with temperature increasing for each state of water uptake. The average values are similar to conventional sorbents. The case of Loaded sample was saturated at 25°C and 30%RH. The relative humidity in the environment maintained at 30% when increasing the temperature so that water uptake would not have an evident change. The case of Dry sample was for dried adsorbent with less than 5%RH at different temperature. The case of

Open system was the saturated sample undergoing the increase of temperature in an open environment so that the RH decreased accordingly. As the saturated MIL-160(Al) can be completely regenerated below 90 °C in either open or closed mechanic systems, results at three typical temperatures were listed to demonstrate the measurement of its thermal conductivity: 25 °C, the hydrophilic MIL-160(Al) is easily saturated; 40°C, the vapour starts to be released in an open system; 70°C, desorption is complete in an open system A drop of thermal conductivity by 15% in average was obtained when vapour is completely desorbed from the saturated sample.

Table 2. Comparison of the thermal conductivity between dry and highly loaded samples,

Sample 1	25.4 °C		43.6 °C		72.3 °C	
	Effusivity (Ws$^{1/2}$/m^2.K)	k (W/m. K)	Effusivity (Ws$^{1/2}$/m^2.K)	k (W/m. K)	Effusivity (Ws$^{1/2}$/m^2.K)	k (W/m. K)
Loaded	172..173	0.071	160.732	0.069	157.723	0.068
Dry	131.356	0.061	129.141	0.061	127.240	0.060
open system	171.189	0.071	160.617	0.068	127.206	0.060

The packed density also impacts the thermal conductivity. The measured thermal conductivity of differently packed powder is shown in Table 3. The packed density and thickness was closed to the operational conditions where the effect due to macroscopic void volume was also taken into consideration.

Table 3. Impact of the compression force on the thermal conductivity

	Temperature	Packed pressure	Test condition	k (W/m. K)
Loaded 1	25.4 °C	3.5 kPa	loosely	0.071
Loaded 2	25.3°C	3.5 kPa	3.5 kPa	0.078
Loaded 3	25.3°C	3.5 kPa	12.95 kPa	0.108
Loaded 4	26.1°C	3.5 kPa	25.91 kPa	0.117
bead$_{0.4\text{-}0.6\text{mm}}$	26.5°C	-	loosely	0.065

The packed pressure of the powder layer was 3.5 kPa and the samples were tested with different level of external compression. A shaped sample under bead form with size of 0.4 to 0.6 mm was shown to represent the realistic condition in the application of adsorption heat pump. The effective thermal conductivity of the beads is close to the loosely compacted powder which is a quite low value.

Since a low conductivity has a negative impact in the dynamic performance of the sorption cycle, different strategies could be followed to improve the thermal efficiency, such as packing the powder with higher bulk density, shaping the powder with variable binders (e.g. silicate), and mixing in highly conductive additives (e.g. graphite, thermal conductivity 1400 w/(m. K), heat capacity 0.7 J/(g. K) in the same temperature range). However, the additives will sacrifice the power density and energy storage density of the MOF in a mechanic system, thus requiring further optimization in different working environment. The pursuing in very high packed density is not recommended because of the drawback that the mass transfer becomes weaker which lowers the specific power. In practice, it is advised to coat the powder on the highly conductive surface to improve heat transfer.

2.4 Thermodynamic efficiency for adsorption cooler based on MIL-160(Al)

The above-measured values of adsorptive and thermal properties allow the accurate calculation of the coefficient of performance (COP) for an adsorption cooler device based on MIL-160(Al). The operational temperatures were chosen as 5°C for the evaporator, 30°C for the condenser and 85°C for the desorption process. The water adsorption isosteres derived from the isotherms were mapped in to a Clausius – Clapeyron diagram as shown in Fig. 5. The adsorbent exchanged water Δw by more than 30 wt% dry mass via a cyclic sorption process. The hydrophilic nature enables a typical evaporation temperature of 5-7°C. The desorption temperature below 90°C allows the use of low-grade heat source. MIL-160(Al) is approved as one of the most promising adsorbents for this application in the literature.

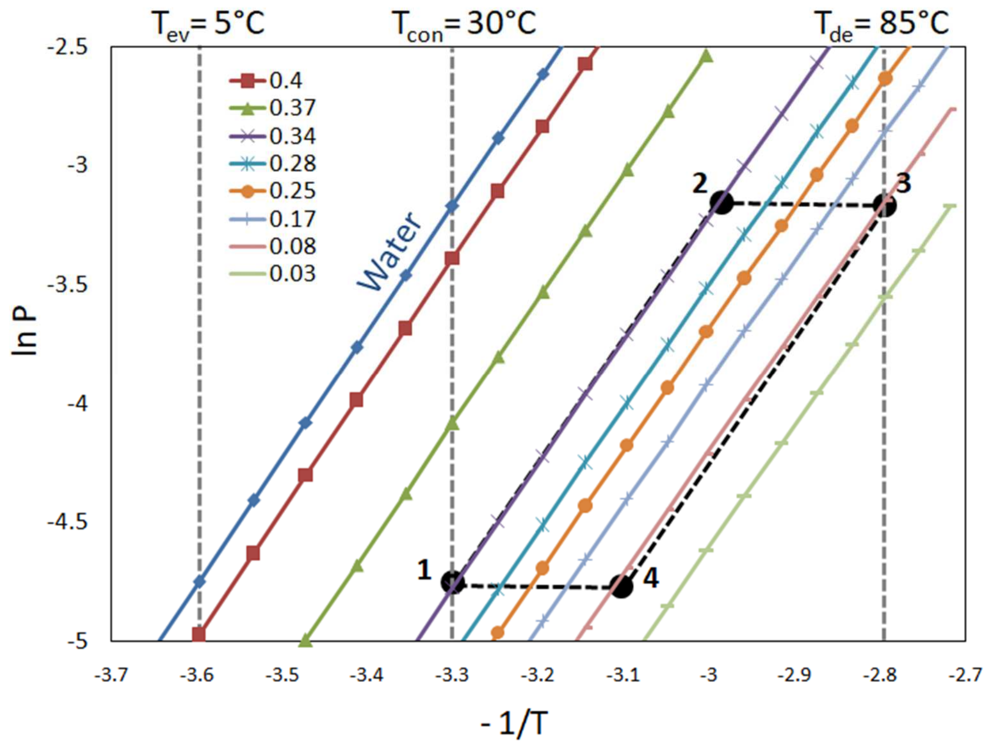


Figure 5. Water sorption isosteres of MIL-160(Al). Black dashed frameworks: adsorption cooling cycle at evaporation temperature (T_{ev}), condensation temperature (T_{con}) and desorption temperature (T_{de}) of 5/30/85°C. Water uptake *w* from 0.03 to 0.4.

The COP of the adsorption cooling cycle is calculated as the ratio of cold energy produced to the heat consumed during the isosteric heating and isobaric desorption [7].

$$\mathrm{COP} = \frac{Q_{ev}}{Q_{ist} + Q_{de}} \qquad (3)$$

This equation can be expressed as the refrigerant (water) evaporation heat over the sum of the specific heating process (Q_{ist}) and the latent heat of desorption process (Q_{de}). Assuming in adsorption and desorption, the adsorbent reaches thermodynamic equilibrium state at given temperature and pressure, the COP of the operational cycles of 5/30/85°C is 0.76. On the contrary, if the values of the heat properties were taken for the dry MOF, the corresponding calculation on the COP would render 0.79, with a positive deviation of 4%. The COP value makes MIL-160(Al) highly competitive to most conventional and innovative sorbents in the application of water adsorption cooling such as SAPO-34, TAPSO and AIPO-18 [36].

3. Conclusions

In this work, a simple method that measures the heat properties of bulk porous materials is applied on MIL-160(Al), an hydrophilic MOF highly performant in water vapor adsorption processes. Both the thermal capacity and conductivity of the MOF was measured with high resolution and accuracy in the common working range of an adsorption cooler. The specific heat capacity of MIL-160(Al) demonstrated a slightly incremental tendency with temperature. The heat capacity is undesirably higher than the commonly used zeolites such as SAPO-34, TAPSO, and their thermal conductivity is quite close. However, this difference has little impact on the COP of a thermal driven adsorption process given the fact that the adsorption enthalpy is two orders of magnitude larger.

Since water adsorption was proven to become a more and more important subject in both fundamental research and technology development thanks to the rapid development of innovative sorbents, the method and protocol presented here will serve as a reference technique to characterize the key thermal properties of the adsorbents in various sorption systems.

Acknowledgements

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