Energy Conversion and Management 174 (2018) 356–363

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

MOF-801 as a promising material for adsorption cooling: Equilibrium and dynamics of water adsorption

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ARTICLE INFO

Keywords:
Adsorption cooling
Water
MOF-801
Adsorption equilibrium
Dynamics
Specific cooling power

ABSTRACT

With exhausting fossil fuels and increasing demand for heating and cooling, the effective utilization of renewable and waste energy sources becomes of increasing importance. Adsorption cooling driven by low temperature heat is an energy and environment saving alternative to the common compression systems. The performance of adsorption chillers strongly depends on the compliance of the adsorbent properties with the cycle operating conditions. In this paper, the comprehensive study of equilibrium and dynamics of water adsorption on a new efficient adsorbent of water vapour MOF-801 is performed to evaluate its feasibility for adsorption cooling. It was shown that at the adsorption temperature of 30 °C the MOF-801 provides the cooling effect at the evaporation temperature as low as 5 °C that indicates significant affinity to water vapour. On the other hand, it can be regenerated by low temperature heat at 80–85 °C. The uptake variation under the conditions of a typical adsorption cooling cycle reaches 0.21 g/g. Water adsorption on loose grains of MOF-801 occurs under grain-size insensitive mode when the adsorption rate is proportional to the (S/m)-ratio of the heat transfer surface S to the adsorbent mass m. The Specific Cooling Power equal to 2 kW/kg is measured at $S/m = 6\,\mathrm{m}^2/\mathrm{kg}$ and 80% of reaching the equilibrium conversion, which is of high practical interest. Thus, the results obtained demonstrate the high potential of the working pair "MOF-801 – water" for adsorption cooling.

1. Introduction

Adsorption Cooling (AC) is a field of power engineering fast developing during the last two decades [1]. The AC systems can efficiently exploit low-temperature heat as energy sources, e.g. solar thermal energy [2] or building waste heat [3]. Due to their high energy saving potential as well as the use of environmentally friendly working fluids (water, methanol, ethanol), AC systems are a promising alternative to conventional compression refrigerators and heat pumps. Despite significant progress achieved, more R&D, aimed to the enhancement of both efficiency [4] and specific power of AC units [5], are still necessary for a broader diffusion of this technology. Currently, a large number of different AC cycles have been implemented, the effectiveness of which is largely determined by the compliance of the properties of the used adsorbent with the operating conditions of the cycle [6]. Particularly, it was shown that the adsorbents with step-wise (or S-shaped) adsorption isotherms are profitable for AC cycles from both thermodynamic [7] and dynamic [8] points of view. Furthermore, the step position depends on the operating conditions of the specific AC application. Therefore, the study of the adsorbents with such step-wise isotherms and tunable sorption behaviour, which can be adopted to the specific AC cycles, provides promising avenues for further development of this emerging technology.

A class of microporous crystalline materials, known as metal–organic frameworks (MOFs), has aroused considerable interest in recent years [9]. These compounds are constructed from metal ions or metal–oxygen clusters and bridging organic linkers [10]. They possess unique features such as high porosity, large surface area, and tunable adsorption behaviour. All these properties lead to a broad range of applications of these compounds, namely, catalysis, gas storage and separation, etc. [11]. The adsorption equilibrium of water and methanol vapours on several MOFs is characterized by step-wise isotherms, which were shown [7] to be profitable for AC. For these reasons, MOFs are considered as promising adsorbents for AC systems as it was first suggested in [12] and afterwards confirmed in [13]. To date, a number of MOFs (MIL-101 [14], ISE-1 [15], NH_2-MIL-125 [16], MIL-100(Al, Fe) [17], UiO-66 [18], CAU-10 [19], etc.) have been studied as water, methanol and ethanol adsorbents for various AC cycles. Mesoporous MIL-100 and MIL-101 adsorb a huge amount of water (0.7–1.0 g/g) by a step-wise manner. However, the step of the uptake is

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https://doi.org/10.1016/j.enconman.2018.08.032
Received 15 May 2018; Received in revised form 8 August 2018; Accepted 9 August 2018

Nomenclature

c_p	specific heat, J/(g K)
d_{gr}	grain size, mm
ΔH	enthalpy, J/g
ΔL	latent heat, J/g
Q	specific heat, J/mol
m	mass, g
N	layers number
P	pressure, Pa
q	conversion
R_0	initial ad-/desorption rate, g/(g s)
S	heat transfer surface, m^2
S_{sp}	specific surface area, m^2/g
SCP	specific cooling power, kW/kg
COP	coefficient of performance
T	temperature, °C
t	time, s
V	pore volume, cm^3/g
w	uptake, g/g

Greek symbols

τ	characteristic time, s

Subscripts:

ads	adsorption
des	desorption
ev	evaporation
con	condensation
p	pore
μ	micropore
ist	isosteric
ads.in.	initial temperature adsorption
des.in.	initial temperature desorption

observed at the relative pressure $P/P_0 = 0.25–0.50$, which is higher than that required for typical AC cycles [20]. NH_2-MIL-125, UiO-66 and CaU-10 adsorb 0.25–0.4 (g of water)/g at $P/P_0 = 0.2–0.3$ and are promising for adsorption air conditioning, providing cooling effect at the evaporation temperature $T_{ev} = 10–20\,°C$. To get the stronger cooling effect (lower temperature in evaporator) the adsorbents with higher affinity to water vapour are required.

Among a large number of metal-organic frameworks, MOF-801 is expected to be promising for such adsorption chillers. MOF-801 is a microporous crystalline compound, which consists of basic units of $Zr_6O_4(OH)_4(-O_2C-CH{=}CH-CO_2-)_6$ [21]. Furukawa et al. showed that adsorption of water vapour on MOF-801 is characterized by step-wise isotherms [21]. Furthermore, the affinity of MOF-801 to water vapour is higher, than that of NH_2-MIL-125, UiO-66 and CAU-10 as the abrupt rise of adsorption occurs at a relative pressure of about 0.1 that allows getting lower evaporation temperature.

In this paper, the data on the equilibrium and dynamics of water vapour adsorption on MOF-801 under operating conditions of a typical AC cycle are presented. Based on the data obtained, the coefficient of performance (COP) and the specific cooling power (SCP) achievable in a chiller with the "MOF-801 – water" working pair are assessed and the potential of MOF-801 for AC is evaluated.

2. Experimental

MOF-801 was synthesized by a solvothermal method according to a modified procedure described in [21]. $ZrOCl_2{\cdot}8H_2O$ (3.2 g, 10 mmol) and fumaric acid (1.2 g, 10 mmol) were dissolved in a solution of dimethylformamide (DMF)/formic acid (40 ml/14 ml), then the mixture was placed into 100-ml Teflon-line autoclave and heated at 130 °C for 6 h. After cooling to room temperature, the mixture was filtered and washed with DMF and methanol. Then the white solid precipitate obtained was dried at 150 °C for 24 h at continuous evacuation, yielding activated sample of MOF-801.

2.1. Characterization

The structure of the MOF-801 was confirmed by X-ray powder diffraction (XRD) using a Bruker D8 diffractometer with an XRK-900 reactor chamber. The diffraction patterns were recorded using CuK_α radiation in the range of 2θ from 5° to 60°. Measurements were carried out in the scan mode with 0.02° increments and an accumulation time of 10 s at each point.

Characterization of dry and water saturated samples was carried out by infrared spectra ($400–4000\,cm^{-1}$) recorded in attenuated total reflection (ATR) mode on a Varian 660 FT-IR spectrometer with 025-2018 MIRacle ZnSe Perf Crystal Plate.

The porous structure of synthesized MOF-801 was studied by low-temperature N_2 adsorption at 77 K on a Quantachrome Nova 1200 gas sorption analyzer. The samples were degassed at 150 °C for 3 h before N_2 adsorption measurement. The specific surface area S_{sp} was calculated using BET analysis of the adsorption branch of the isotherm in the relative pressure range of 0.01–0.02. The total pore volume V_p was calculated from the amount of N_2 adsorbed at a relative pressure $P/P_0 = 0.99$. The micropore volume V_μ was calculated using the statistical thickness analysis of the isotherm adsorption branch and de Boer's t-method.

2.2. Water adsorption equilibrium

Sorption equilibrium of MOF-801 with water vapour was studied by a thermogravimetric method using a Rubotherm thermal balance (accuracy ± 0.00002 g). Water adsorption isobars were measured in the temperature range of 20–100 °C at the vapour pressure $P = 0.9$, 1.2, 2.4 and 4.3 kPa. Before the measurements, the sample (ca 100 mg) was heated at 150 °C under continuous evacuation until reaching the stable weight. To initiate adsorption, the measuring cell was connected to an evaporator filled with degassed water, whose temperature was controlled with the accuracy ± 0.1 °C. The sample weight was recorded continuously during the adsorption. The uptake was calculated as

$$w = m(P, T)/m_0, \tag{1}$$

where $m(P, T)$ is the weight of water adsorbed and m_0 is the dry weight of the adsorbent. The temperature of the sample was controlled with the accuracy ± 0.1 °C. The accumulative uncertainty of uptake measurements was ± 0.01 g/g.

2.3. Water sorption dynamics

The water adsorption dynamics was studied by a Large Temperature Jump method [22]. According to this approach, the sorption process was induced by a fast change of the temperature of a metal plate on which the adsorbent is placed, while the water vapour pressure remains about constant, as it occurs at isobaric stages of AC cycles. The experimental rig and measurement procedure are described in more detail elsewhere [23].

The adsorption dynamics was measured for the loose MOF-801 grains. At first, the MOF-801 powder was shaped as pellets by pressing without binder. Then the pellets were ground and sieved to get the following fractions of grains: $d_{gr} = 0.20–0.25$, 0.4–0.5, and 0.8–0.9 mm.