MICROPOROUS ALUMINOPHOSPHATES FOR HEAT REALLOCATION

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ABSTRACT

In this work we present the idea of heat reallocation with adsorption-driven heat pump (AdHP). In order to find an appropriate material for this application, we compared sorption properties of various microporous materials. Among them $AlPO_4$-LTA was the best. AdHP containing $AlPO_4$-LTA as adsorbent could in theory achieve very high pumping power (> 520 kWh per m^3 of adsorbent) with temperatures required for regeneration of the material that are 10-15 °C lower than in other promising materials (e.g. metal-organic frameworks MOF-801 and MIL-160).

Keywords: microporous aluminophosphates, metal-organic frameworks, heat storage, adsorption-driven heat pump.

INTRODUCTION

Heat reallocation can be performed by employing standard heat-pump system which requires electricity for operation, or alternatively by the adsorption-driven heat pump (AdHP) system powered by the solar energy. The latter system is larger in size since it requires the use of the solar collectors and an additional space for the adsorbent. However, the promise of operation almost independently of other energy sources successfully conceals such a drawback. The required area of solar collectors and the size of adsorbent tank depend on the type of the chosen adsorbent. An appropriate material should have a steep-like water sorption isotherm in a narrow relative pressure range, high coefficient of performance (COP) and high heat-storage capacity which often correlates with high water uptake. A material should withstand many hydration-dehydration cycles to ensure seamless operation of AdHP over several years. The COP is defined as the quotient between reallocated heat and the heat required for material's regeneration. It can be calculated directly from the obtained water sorption isotherms when the heat of adsorption versus water uptake dependency is known for a given material. COP is not as crucial as heat-storage capacity, since low value of COP can be compensated by expanding the area of solar collectors. On the contrary, if the material with low heat-storage capacity is used, additional space for storage of adsorbent has to be wasted in order to satisfy the heating requirements during the winter.

Among many different porous materials, metal-organic frameworks (MOFs) are emerging as very promising candidates for use in the heat-reallocation applications. Very recently Furukawa *et al*. presented MOF-801 framework and characterized it with a high heat-storage capacity and, compared to other MOFs, with a better hydrothermal stability.[1] In the review article of de Lange *et al*., the authors benchmarked different MOFs and also a few commercially available

zeolite-like materials and came up with a clear winner, MOF-801.[2] For AdHP cooling applications, low heat-pumping capacity of the adsorbent is tolerable, and consequentially the span of appropriate materials is greatly extended. In the literature most of the attention is paid to MIL-160, which shows great cycling stability and low production costs.[3,4] But none of the promising MOFs exhibits water sorption isotherm as steep as microporous aluminophosphates. Moreover, aluminophosphate frameworks are highly resistant to moisture and thermal treatments. In 2012, Ristić *et al*. examined the performance of $AlPO_4$-34 for heat-storage applications.[5] The authors revealed a high heat-storage capacity of about 480 kWh m^{-3}. Yet even more enhanced performance can be anticipated. For example, aluminophosphate with higher framework porosity should in principle outperform $AlPO_4$-34. A simple calculations of topological parameters with ZEOMICS software revealed that $AlPO_4$-LTA could have the highest porosity among all the successfully synthesized aluminophosphates.[6]

EXPERIMENTAL

The synthesis of $AlPO_4$-LTA was based on the procedure described by Schreyeck *et al*.[7] The as-synthesized product was calcined at 850 °C for 2 h in air. $AlPO_4$-34 was prepared according to the published procedure,[8] whereas synthesis of MOF-801 was performed by the modified procedure from Furukawa *et al.*,[1] with the same molar ratios of reaction components and synthesis condition as described in the literature, but using $ZrCl_4$ instead of $ZrOCl_2$.

Dynamic calorimetric measurements were performed on a Q2000 DSC apparatus (TA Instruments) in the temperature range from 25 to 200 °C with the heating ramp of 1 °C min^{-1}. Water sorption analysis was performed by an IGA-100 gravimetric analyzer (Hiden Isochema) at different temperatures from 25 to 40 °C. The definition of the thermodynamic heat cycle and the calculation of the amount of heat involved are given by De Lange *et al*.[2]

RESULTS AND DISCUSSION

Calcination of $AlPO_4$-LTA is known to be problematic, as all the researchers reported partial loss of crystallinity and/or collapse of the microporous structure upon thermal treatment.[7,9,10] But their assumptions and statements were incorrect. We found out that the framework is in fact very stable with a special uniqueness – its deformation in the presence of the moisture does not exhibit long-range order.[11] This is the reason for the broadening of X-ray diffraction (XRD) peaks, and not the degradation of the framework as the others assumed. After the successful calcination we employed calorimetric measurements on $AlPO_4$-LTA, $AlPO_4$-34 and MOF-801 samples. The synthesis of MIL-160 was not successful, so for the comparison we relied on the data of MIL-160 obtained from the literature.[3] Figure 1a and Table 1 compare the differential scanning calorimetry (DSC) profiles and the values of the energies that were

Table 1. Crystal densities of dry materials, water uptakes, and energy-storage capacities of the benchmarked microporous materials.

Sample	Cryst. density	Water uptake (0.05-0.30)		Water uptake (0-0.9)		Stored heat	
	[g cm^{-3}]	[g g^{-1}]	[g cm^{-3}]	[g g^{-1}]	[g cm^{-3}]	[Wh kg^{-1}]	[kWh m^{-3}]
$AlPO_4$-LTA	1.412	0.37	0.52	0.42	0.59	373	527
$AlPO_4$-34	1.474	0.29	0.42	0.35	0.49	320	472
MOF-801	1.592	0.24	0.39	0.36	0.57	323	514
MIL-160	1.068	0.30	0.32	0.38	0.41	-	-

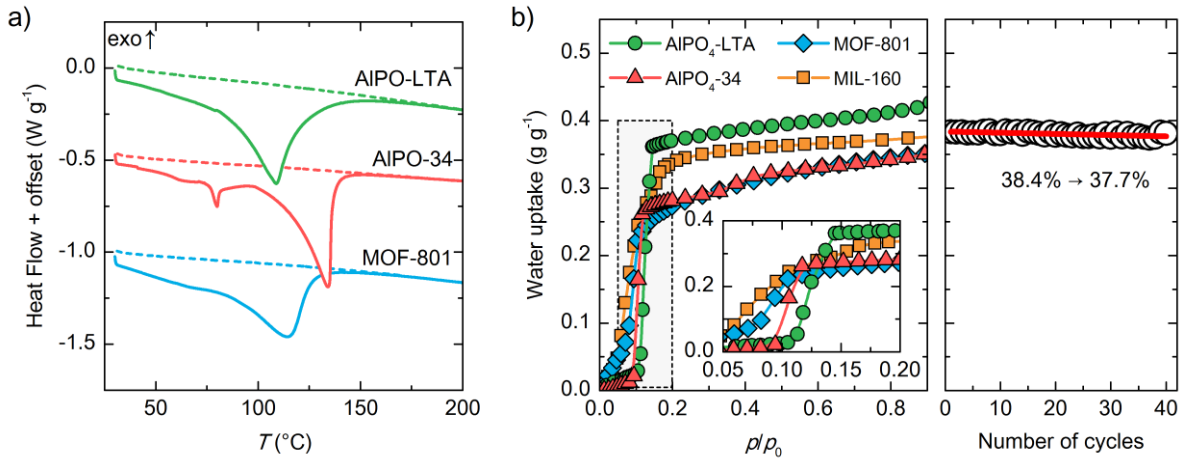

Figure 1. (a) Calorimetric measurements obtained on a set of hydrated (solid lines) and dried samples (dotted lines) of $AlPO_4$-LTA (green), $AlPO_4$-34 (red), MOF-801 (blue), and MIL-160 (orange). (b) Water sorption isotherms for all the samples (left) and hydration/dehydration cycling performance of $AlPO_4$-LTA (right).

needed to dry the samples. As one can see, $AlPO_4$-LTA has the largest capacity among them, closely followed by MOF-801 and $AlPO_4$-34. Water sorption analysis revealed the differences between the slopes of the isotherms in the relative pressure region of 0.05-0.30 (Figure 1b). It is clear that $AlPO_4$-LTA features much steeper isotherm in comparison with MOF-801 and MIL-160. The steep isotherm in aluminophosphates can be explained with the change of the framework hydrophilicity just after the first water molecules coordinate to the aluminum atoms and deform the framework.[11] Afterwards, hydrogen-bonded water clusters are suddenly formed inside the deformed cages. In case of MOFs, there are usually hydrophilic OH groups present in the framework; hence it is more likely that water molecules coordinate primarily to all OH groups and only thereafter, when the chemical potential is increased, hydrogen-bonded clusters start to form inside the pores. Moreover, the framework of $AlPO_4$-LTA is hydrothermally extremely stable. After 40 consequent cycles of hydration and dehydration water uptake dropped by less than 1 % (Figure 1b).

Effectiveness of the materials used in a typical sorption heat-pump cycle was examined by calculating COPs for heating and cooling. The details of thermodynamic efficiency calculations

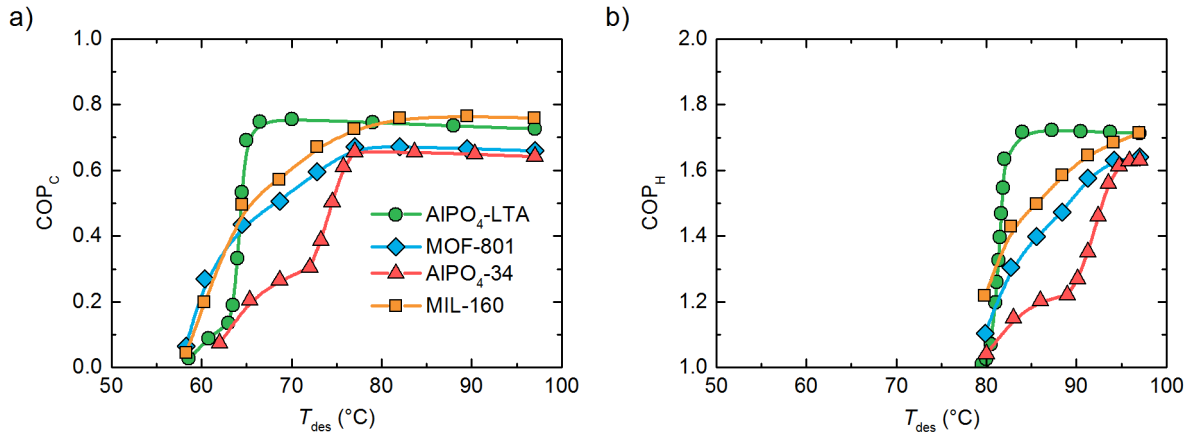

Figure 2. Coefficients of performance of AdHP for (a) cooling (T_{ev} = 5 °C, T_{ads} = 30 °C) and (b) heating (T_{ev} = 15 °C, T_{ads} = 45 °C) as a function of desorption temperature (T_{des}) for $AlPO_4$-LTA (green), MOF-801 (blue), $AlPO_4$-34 (red), and MIL-160 (orange).

are described elsewhere.[2] In our examination, all the materials achieved very similar maximal COPs, but $AlPO_4$-LTA retained high COP even at 10-15 °C lower desorption temperatures (Figure 2).

CONCLUSION

$AlPO_4$-LTA is an excellent material for sorption-based solar-energy allocation and storage. It exhibits unprecedented water uptake and heat-storage capacity and shows a remarkable cycling stability. Water molecules that are firstly adsorbed in $AlPO_4$-LTA deform the framework and trigger sudden pore filling and formation of water clusters. This, so called one-step adsorption mechanism, is the main reason for steep-like water sorption isotherm that is desired in AdHP heating or cooling applications. The temperatures required for regeneration are 10-15 °C lower compared to MOF-801 and MIL-160, making it the most appropriate material for heating and cooling applications also in regions without extended periods of intense solar irradiation.

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