New Water Adsorbent for Adsorption Driven Chillers

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Abstract

A new water adsorbent for thermally driven adsorption chillers was developed. A stable microporous aluminophosphate with ordered microporous 3-dimensional channel structure and high surface area (784 m^2g^{-1}) was prepared. The material adsorbs water in a very narrow relative-pressure range and can be charged at 65 ^oC. The material shows a very good thermal stability up to 850 ºC, hydrothermal stability and a water adsorption capacity up to 0.42 gg^{-1}. The cooling enthalpy of 730 $kJkg^{-1}$ and COP 0.7 is determined for the boundary conditions: evaporator temperature of 5 ^oC, cooling temperature of 30 ^oC and desorption temperature of 65 ^oC. As such, it exhibits exceptional properties for applications in cooling devices.

Keywords: adsorption chiller, water, APO-LTA, microporous aluminophosphate

1. Introduction

Heat transformation systems can reduce the carbon footprint of the building sector. Thermally stable porous adsorbents can be used in adsorption heat transformation (AHT) processes such as heat pumps, thermally driven adsorption chillers or dehumidification, where the main principle is based on the sequential adsorption and desorption processes. The efficiency and cost-effectiveness of such processes are critically governed by the performance of the applied adsorbents. Recently, it has been shown that the adsorbents which adsorption equilibrium with working fluid is characterized by S-shaped adsorption isotherms are advantageous for the adsorption heat transformation (Aristov, 2014). For most applications, the steep increase in the adsorption should take place in a relative pressure range of 0.05-0.3 (Henninger et al., 2017). Recent research activities are focused on the development of materials with high sorption capacity and low charging temperature for efficient utilization of low-temperature solar energy for heating and cooling applications. Adsorbents, which are currently considered for this sorption technology, are activated carbons, silica gels, zeolites, aluminophosphates, MOFs and composites, while as adsorbates water, ethanol, methanol and ammonia are usually used (Freni et al., 2016). A major trend in this field of research is the evaluation of MOFs (Lenzen et al., 2018) and aluminophosphates (Brancato and Frazzica, 2018) in adsorption driven chillers.

Among commercially available aluminophosphates mainly two adsorbents have been investigated, AQSOA® (FAM-Z02 and FAM-Z01), SAPO-34 and APO-5, respectively. Both materials present S-shaped isotherms, can adsorb amount of water up to 0.30 gg^{-1} and 0.20 gg^{-1} respectively, within narrow humidity ranges and can be charged at 90^oC (Kakiuchi et al., 2005a, 2005b).

In this study we present a new aluminophosphate with much higher water uptake (0.42 gg^{-1}) and low desorption temperature (65^oC). Cooling enthalpy for the air conditioning working conditions of APO-LTA, SAPO-34 and APO-5, APO-18 and FAPO-34 adsorbents are compared, showing higher cooling enthalpy for the APO-LTA.

2. Experimental

APO-LTA was hydrothermally synthesized from a fluoride medium using Kriptofix 222 (K222) as a structure-directing agent (Krajnc, 2017). The as-synthesized sample was calcined in air at 850 ^oC over night. The crystallinity of the APO-LTA was examined by High-temperature X-ray powder diffraction (HT-XRD) using PANalytical X'Pert PRO high-resolution diffractometer in the 2θ range from 5° to 60° using a step of 0.026° per 100 s. XRPD patterns were collected at constant temperatures between room temperature and 550 ^oC. Between the scans, the

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sample was heated at a rate of 10 ^{o}C min^{-1} in air. To confirm the phase purity, the powder patterns were compared with literature data. The morphology of the material was examined using a scanning electron microscope Zeiss Supra 35VP. Thermogravimetric investigation of the as-synthesised sample was performed with a Q5000IR (TA Instruments). The sample was heated in a stream of argon with a heating rate of 10 K min^{-1}. The specific surface area was evaluated by analysis of nitrogen adsorption isotherms measured on a Micromeritics ASAP 2020 instrument. The isotherm was recorded at 77 K. The sample was outgassed at 473 K for 2 h in the port of the adsorption analyzer. The BET specific surface area was calculated from adsorption data in the relative pressure range from 0.05 to 0.25. In addition, water sorption analysis was performed by an IGA-100 gravimetric analyzer (Hiden Isochema Ltd.). Water sorption isotherms were performed at different temperatures at 25 to 40 °C in the relative pressure range from 0 to 0.9 in order to elucidate sorption enthalpies. Prior to measurements, the samples were degassed at 150 °C to a constant weight overnight. Hydration/dehydration cycling performance was carried out with the sequential procedure of isothermal measurements at 25 °C and relative humidity of 0.3 until equilibrium, followed by drying at 150 °C for 2 h in vacuum. The sequence was repeated 40 times. The Coefficient of Performance for cooling is defined as:

$$\mathrm{COP} = \frac{Qev}{Qreg}, \quad \text{(eq.1)}$$

where Q_{ev} is the heat transferred from the evaporator and Q_{reg} is the heat needed for regeneration of the adsorbent, i.e. the heat consumed in the desorption part of the cycle. Q_{reg} includes the heat consumed or released during sorption itself and the sensible heat required to cool the adsorbent. To calculate the cooling enthalpy (Q_{ev} per mass of the adsorbent) and the COP, one needs to know the loading function $W(p,T)$ and the differential heat of adsorption of the material $\Delta_{\mathrm{ads}}H(W)$. For APO-LTA, the latter was calculated from the isotherms measured at 25 °C and 40 °C using a finite difference approximation to the isosteric formula,

$$\Delta_{\mathrm{ads}}H(W) = R\left(\frac{\partial \ln(p)}{\partial\left(\frac{1}{T}\right)}\right)_{W}. \quad \text{(eq.2)}$$

Because we were unable to measure isotherms at high temperatures, two approximations were made: (i) the enthalpy of adsorption was assumed to be temperature-independent in a temperature range between 25 °C and 65 °C, (ii) $W(p,T)$ was determined by reformulating water sorption isotherm measured at 40 °C as a function of adsorption potential,

$$A = RT\ln\left(\frac{p_0(T)}{p}\right), \quad \text{(eq. 3)}$$

where p_0 is saturation vapour pressure of water. $W(A)$ is assumed to be temperature-independent and thus the loading can be calculated for any given temperature.

3. Results

The structure (Fig. 1.) of the new water adsorbent APO-LTA is built of double-four ring, sodalite and LTA cages, which form pore openings of 0.41 nm. The accessible pore volume is 21 % according to the database of zeolite structure types. The BET specific surface area was determined to be 784 m^{2}g^{-1}.

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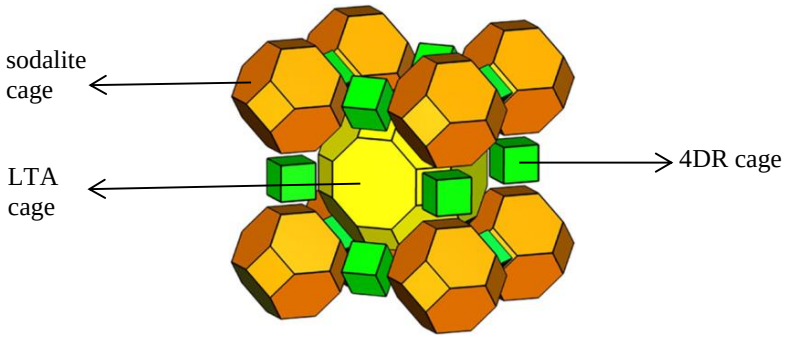

Fig. 1: Scheme of the water adsorbent APO-LTA structure

SEM picture in Fig. 2 shows pure crystalline as-synthesised product composed of cubes with the size from 5 to 20 μm.

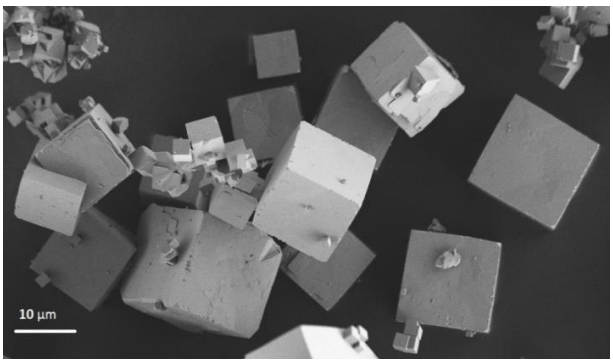

Fig. 2: SEM picture of the as-synthesised APO-LTA

The structure directing agent was removed by calcination in air. The calcined sample was thermally stable up to 850 ^{o}C. XRD pattern (Fig. 3) of the sample at 550 ^{o}C still shows full crystalline porous material. The structure does not change after cooling to room temperature and exposing to the humidity.

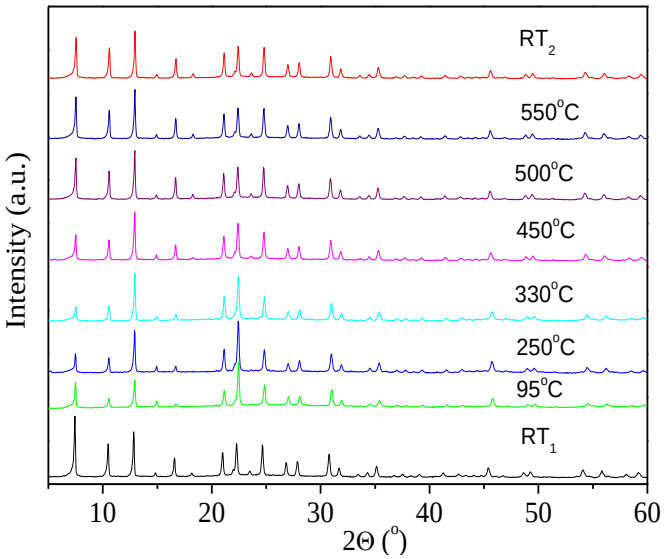

Fig. 3: High temperature XRD patterns of the APO-LTA

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Figure 4 shows water adsorption isotherm gravimetrically determined at 25 ^{o}C. The water adsorption capacity of this materials is the highest (0.42 gg^{-1}) among aluminophosphate adsorbents due to the structure and high specific surface area (784 m^2g^{-1}).

The hydrothermal stability was tested by 40 hydration/dehydration cycles between 25 and 150 ^{o}C. The minor reduction (~ 1 %) of the water adsorption capacity was observed. The characteristic curve of APO-LTA is shown in Fig. 5.

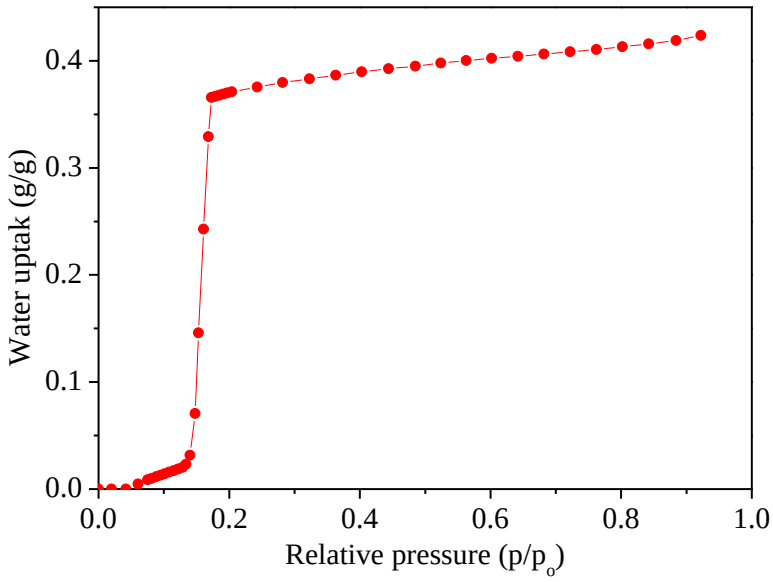

Fig. 4: Water adsorption isotherm of aluminophosphate at 25°C.

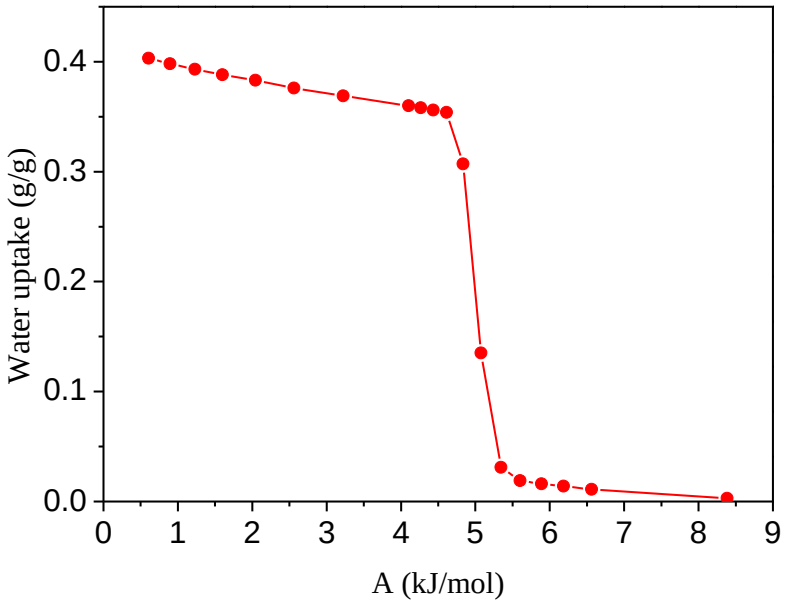

Fig. 5: The characteristic curve of APO-LTA.

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Cooling COP and cooling enthalpy of APO-LTA for air conditioning with desorption (regeneration) temperature of 65 ^{o}C (T_{ev}=5 ^{o}C, T_{con}=30 ^{o}C) were compared to cooling COP and cooling enthalpy of APO-5 and SAPO-34 (Freni et al., 2016). APO-5 and SAPO-34 are known as AQSOA® Z01 and Z02 adsorbents, respectively. Adsorption characteristics of these aluminophosphate adsorbents have been investigated by several research groups (Kayal et al., 2016). Among these water adsorbents considered, APO-LTA appeared to be the best candidate for application in air conditioning cycles due to the highest cooling enthalpy, which can be directly translated to higher power density (Freni et al., 2016). APO-5 and APO-LTA achieve similar COPs, but the latter yields much higher cooling enthalpy than APO-5 and SAPO-34 (Fig. 6).

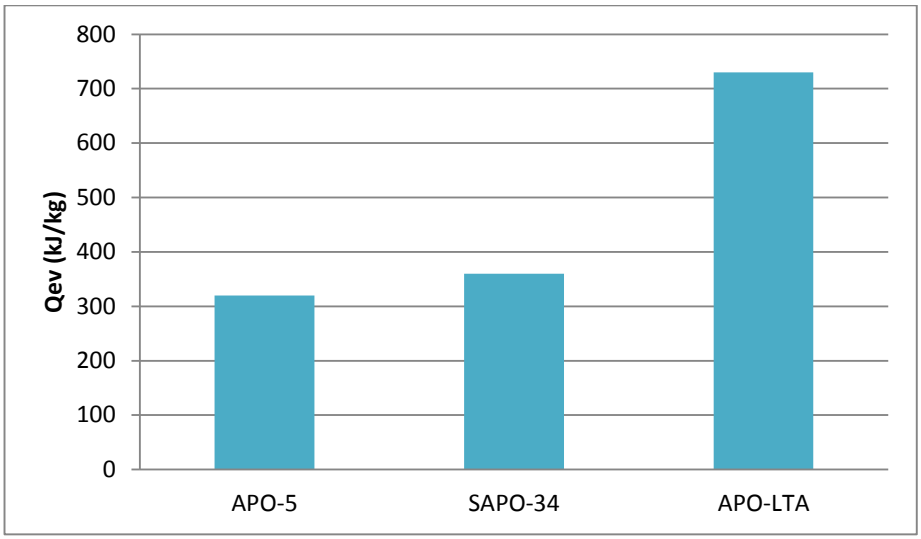

Fig. 6: Comparison of the cooling enthalpy Q_{ev} for APO-5, SAPO-34 and APO-LTA for boundary conditions (T_{ev}=5 ^{o}C, T_{con}=30 ^{o}C, T_{des}=65 ^{o}C)

Recently, APO-18, SAPO-34 and FAPO-34 were evaluated under boundary conditions T_{ev}=7 ^{o}C, T_{con}=30 ^{o}C, T_{des}=80 ^{o}C, showing the highest cooling enthalpy for APO-18 (Brancato and Frazzica, 2018). APO-18 can achieve the cooling enthalpy of 430 kJkg^{-1}. Under the same boundary conditions the cooling enthalpy of APO-LTA is determined to be two times higher (Fig. 7).

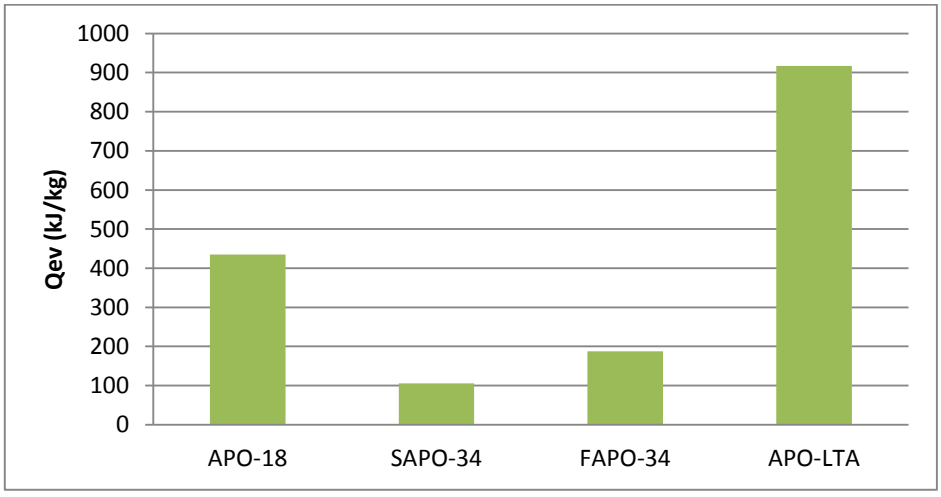

Fig. 7: Comparison of the cooling enthalpy Q_{ev} for APO-18, SAPO-34, FAPO-34 and APO-LTA for boundary conditions (T_{ev}=7 ^{o}C, T_{con}=30 ^{o}C, T_{des}=80 ^{o}C)

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4. Conclusions

New aluminophosphate adsorbent full fills requirements for the ideal performance in the low-temperature (solar energy) heat transformation applications because it performs in the proper relative pressure range with S-shaped water adsorption isotherm. The charging or regeneration temperature is 65 ^{o}C. COP and cooling enthalpy for cooling application at boundary conditions: evaporator temperature T_{ev}=5 ^{o}C, cooling temperature T_{con}=30 ^{o}C and desorption temperature T_{des}=65 ^{o}C is determined to be 0.70 and 730 kJkg^{-1}, respectively.

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