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# Characterisation and comparative analysis of zeotype water adsorbents for heat transformation applications

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ABSTRACT

This paper presents the experimental characterisation of three zeotype materials, namely, AlPO-18, FAPO-34 and SAPO-34, suitable for adsorption heat transformation applications, employing water as refrigerant. Morphological and thermo-physical analyses were performed on each sample. In particular, the adsorption capacity of each material was evaluated by measuring a complete set of water vapour adsorption/desorption isotherms, in order to investigate the hysteresis effect. The obtained equilibrium data were fitted by means of Dubinin-Astakhov equation, both for adsorption and desorption branches. Finally, a thermodynamic analysis of the achievable performance of these three working pairs was performed under three main operating conditions, namely, thermal energy storage, air conditioning and heat pumping. The achieved results confirmed the potentiality of these adsorbents, showing promising cooling and thermal COP, up to 0.80 and 1.60 respectively, and heat storage capacities both for daily and seasonal operation.

## 1. Introduction

The ever-increasing worldwide energy demand is still mainly satisfied by employing fossil fuels as primary energy source. This is causing a sharp reduction of fossil fuels reserves as well as concerns related to the increasing emissions of polluting agents and greenhouse gases [1]. In such a background the exploitation of alternative and renewable energy sources, such as solar, geothermal, wind and biomass is recognized as one of the crucial point for a more sustainable development. For instance, a recent analysis [2] demonstrated that the increasing in the share of non-fossil fuels in electricity generation sector can significantly reduce the $CO_2$ emissions from this sector. It was estimated that an increasing of a one percent of the share of non-fossil fuel can reduce $CO_2$ emissions by about 0.82%. Nevertheless, the benefits deriving from the employment of renewable energy sources are not limited to the electricity generation sector. Indeed renewable heating and cooling technologies have been recently defined as the "sleeping giants" [3] among the possible fields of application of renewables, since so far these sources were mainly investigated and developed for electricity production and transportation. In this regards, adsorption technology for heat storage [4] and transformation [5] is currently gaining a lot of attention in the scientific community. Indeed, these systems can be driven by low-grade thermal energy sources (e.g. solar energy from non-concentrating solar collectors) to provide heating and cooling as well as to store the thermal energy. The working principle of this technology can be found elsewhere [6]. It is based on the ability of some classes of porous materials to reversibly adsorb and desorb a working fluid (e.g. water, methanol, ethanol, ammonia) according to the temperature levels of the heat source and sink. In such a way, a thermo-activated compressor substitutes the mechanical compressor of a common vapour compression machine, thus extremely lowering the needs for electrical energy.

Despite the good level of development already reached by this technology, which is confirmed by the first machines on the market, especially for heating [7] and cooling [8,9] applications, there is still room for improvement of their achievable performance. Particularly, a lot of attention is paid towards the development and characterisation of advanced adsorbent materials, with enhanced adsorption capacity and hydrothermal stability [10,11]. As reported in [12], the current trends for adsorption materials optimization are focused on different adsorbents, namely, modified zeolites, silico-alumino-phosphates and other zeotype materials, composite sorbents and metal-organic frameworks (MOFs). In [13] the surface modification of classical zeolites like A, X and Y by means of organosilane compounds was reported. The main aim was to reduce the strong hydrophilic behaviour of these materials, allowing for a reduction of the regeneration temperature needed [14]. First results demonstrated the possibility to obtain this behaviour, nevertheless it is still necessary improving the preparation

*Abbreviation:* COP, coefficient of performance; DS, daily storage; HSC, heat storage capacity; SCE, specific cooling energy; SHE, specific heating energy; SS, seasonal thermal storage

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**Nomenclature**

| | |
|---|---|
| A | adsorption potential [J/g] |
| $c_{peq,max}$ | equivalent specific heat calculated for the maximum uptake [J/g K] |
| $c_{peq,ave}$ | equivalent specific heat calculated for the average uptake [J/g K] |
| E | characteristic energy [J/g] |
| L | heat of evaporation of the working fluid (i.e. water) [J/g] |
| $L(T_{ev})$ | enthalpy of evaporation of water at the evaporator temperature [J/g] |
| $L(T_{cond})$ | enthalpy of condensation of water at the condenser temperature [J/g] |
| $p_s$ | saturated vapour pressure at T [kPa] |
| p | pressure of the working fluid vapour [kPa] |
| T | adsorption/desorption temperature [K] |
| $T_{ads}$ | adsorption temperature [dimensionless] |
| $T_{ev}$ | evaporation temperature [dimensionless] |
| $T_{des}$ | desorption temperature [dimensionless] |
| $T_c$ | condensation temperature [dimensionless] |
| $T_2$ | ending temperature of the isosteric desorption phase [K] |
| W | water vapour adsorbed [g/g] |
| $W_0$ | maximum water vapour uptake [g/g] |
| $\alpha$ | coefficient of thermal expansion of water [1/K] |
| $\Delta w$ | exchanged water vapour at working conditions [g/g] |
| $\Delta H_{des}$ | differential enthalpy of desorption [J/g] |

methodology and investigating the chemistry of zeolite silanation. Concerning composite sorbent materials, recently an innovative material employing different inorganic salts inside multi-wall carbon nanotubes was proposed [15]. The developed materials were primarily meant for thermal storage applications, both exploiting water and methanol as working fluids. The reported results confirmed the possibility of achieving a high thermal energy storage density, under different climatic conditions. Different activities are also under development for MOFs to be applied in adsorption heat pumps and chillers. In [16] both thermodynamic and dynamic characterisation of MIL-101Cr with ethanol as working fluid was reported. The huge adsorption capacity showed by this working pair, up to 1.1 kg of ethanol per kg of dry adsorbent, confirmed that this material is promising for this application. Further investigations should be performed on its cycling stability. Recently, in [17] the $NH_2$-MIL-125 MOF, was characterised as water adsorbent for adsorptive heat transformation cycles. It is considered as a promising material, since it is characterised by high water adsorption ability, up to 0.42 g/g, with a favourable "s-shaped" isobar, which allows getting a huge water vapour exchange in a narrow temperature range. First cycling tests demonstrated, also for this material, a slight adsorption capacity reduction coupled to a reduction in specific surface area and specific pore volume, thus confirming the needs of further investigating the stability of this class of materials. The same material was investigated also to analyse the achievable dynamic performance under typical adsorption chiller working conditions in [18]. As expected, the achievable specific cooling power (SCP) is satisfactory, ranging between 0.4 and 2.8 kW/kg, but still lower than SCP achievable by other working pairs like AQSOA FAM-Z02/water.

In such a context, alumino-phosphates (AlPOs), silico-alumino-phosphates (SAPOs) and other materials often referred as zeotypes [19,20] are considered very promising, since they are characterised by high sorption capacities, limited regeneration temperature and good stability. A regular structure and pore networks, comparable with the one of classical zeolites, characterise these materials. Differently from zeolites, the AlPOs framework is electrically neutral, thus they do not hold any kind of cations to balance the structure. This reflects in a different sorption behaviour, indeed, the presence of cations in classical zeolites causes a strong hydrophilicity, which reflects in the typical isotherm I according to IUPAC. For AlPOs, the interaction between water vapour molecules and adsorbent is dominated by hydrogen bonding, occurring mainly between the water molecules and hydroxyl groups. This justifies the partially hydrophobic/hydrophilic behaviour of these materials, which are characterised by a type V isotherm evolution, according to IUPAC, considered more favourable for adsorptive heat transformation cycles [21]. When other metal atoms are introduced inside the AlPO structure (e.g. Si, Fe, Cr), further enhancement in the adsorption capacity of these materials is observed. This can be justified by the introduction of structural defects induced by the hetero-metals as well as by the creation of new -OH groups on the material surface [19].

In the literature, some experimental activities for the characterisation of advanced materials belonging to the zeotype class were reported so far. Henninger et al. [22] presented an experimental comparison of water adsorption properties of several materials for heat transformation applications, by selecting two typical working boundary conditions for heat pumping and chilling applications. Different samples of SAPO-34 and AlPO-18 were included in the comparison. The obtained results confirmed the potentiality of both materials for low driving temperature applications, with water uptake of SAPO-34 and AlPO-18 up to 0.2 g/g and 0.254 g/g respectively, almost 5 times and 6 times higher than the reference silica gel.

Frazzica et al. [23] presented a new experimental methodology to directly measure both water adsorption equilibrium curves and adsorption enthalpy by means of a modified TG/DSC apparatus. The approach was applied to the commercial material AQSOA Z02, which presents a CHA structure, typical of SAPO-34 material. The experimental results showed that this material could get COP up to 0.60 for cooling application and up to 1.62 for heat pumping applications.

Zheng et al. [24] presented the characterisation of coated heat exchangers employing both SAPO-34 and FAPO-34 as adsorbent materials for desiccant applications. Thanks to the S-shaped adsorption isotherms, they represent a good option also for dehumidification applications. Nevertheless, FAPO-34 showed higher performance compared to SAPO-34 at fixed regeneration temperature, due to the higher hydrophobic behaviour. Furthermore, the adsorption equilibrium between adsorbents and water vapour were investigated by means of a volumetric technique and, due to the isotherm shape, the experimental data were fitted applying the Polanyi theory but dividing the isotherms in three different sections. Nothing was reported about hysteresis effect between adsorption and desorption branches.

The present paper reports for the first time an experimental comparison among the most promising zeotypes, namely, AlPO-18, SAPO-34 and FAPO-34 for adsorption heat transformation applications. The morphological, structural and thermo-physical properties were characterised by means of scanning electron microscopy (SEM), x-ray diffraction (XRD), nitrogen physisorption and TG-DSC (thermo-gravimetric and differential scanning calorimetry). Furthermore, the complete water vapour adsorption capacities were measured isothermally by means of a gravimetric apparatus, with temperature ranging from 30 °C up to 60 °C and relative pressure up to 0.9. Both adsorption and desorption branches were measured for each isotherm. The equilibrium data were then reduced according to the Dubinin-Astakhov approach, differentiating between adsorption and desorption, in order to take into account the hysteresis effect. Finally, achievable performance under different operating conditions (i.e. air conditioning, heat pumping, thermal storage) were calculated for the investigated materials.