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Research Paper

Development and characterization of silane-zeolite adsorbent coatings for adsorption heat pump applications

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HIGHLIGHTS

- We studied water vapour adsorption for adsorption cooling systems.
- Silane/SAPO 34 coatings have been tested by a complete thermo-physical and mechanical characterization.
- Silane binders have been investigated to verify if they affect the open porosity of the adsorbent material.

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ABSTRACT

The enhancement of the efficiency of adsorption heat pumps depends on the adsorption capacity of the adsorbent materials as well as on heat transfer efficiency between the adsorbent material in contact with the heat exchanger and the heat transfer fluid. The heat transfer efficiency can be improved by coating the heat exchangers with a thin layer of adsorbent material consolidated by means of a proper binder. In the present paper, three innovative silane-based adsorbent coating compositions, employing a commercial SAPO 34 as adsorbent material, are presented. Their physico-chemical and the mechanical features have been deeply studied, demonstrating promising characteristics which make them as an attractive solution to enhance achievable power density of adsorption machines.

1. Introduction

Adsorption heat transformers (AHTs), are an attractive alternative to conventional electrically driven systems for a wide range of applications such as automotive air conditioning, solar air conditioning, waste heat recovery, domestic heat pumping and adsorption desalination. In the past decades, small size closed cycle prototypes have been developed in order to demonstrate the feasibility of this technology [1–4].

Aristov in his study [5] has considered the role of adsorbent in AHT technology, analysing which adsorbent is optimal for a specific cycle and discussing which COP and SCHP can be achieved depending only on the properties of the adsorbent. Indeed, the most important disadvantage of adsorption cycles is the poor heat transfer capacity of the solid adsorbent material, that restrict the achievable specific power. The adsorbent materials commonly employed (i.e. zeolite, zeotype, silica gel) are characterized by poor thermal conductivity, usually around 0.2 W/(m K) [6], and often embedded in loose grains configuration, leading to limited contact with the heat exchanger surface [7]. Accordingly, heat transfer efficiency can be improved by means of heat exchangers characterized by a large surface area coated with adsorbent material rather than packed adsorbent beds [8–10]. In-situ zeolite crystallization [11–13] and the dip coating processes [14] can be considered promising coating deposition technique.

The dip coating process presents various potential benefits, such as: mild reaction conditions, easily adjustable coating thickness (up to 0.5 mm), easy implementation both in serial production lines and for covering heat exchangers with different and complex shapes. On the other hand, possible issues are: poor mechanical strength, the occlusion of the pores of the adsorbent material by the binder, the production of volatile compounds from organic binders and the increase of the mass transfer resistance through the adsorbent layer.

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Nomenclature

AHT	adsorption heat transformer
COP	coefficient of performance
SCHP	specific cooling/heating power
p_{H20}	water vapour pressure
Δm	water uptake
m_{ads}	wet adsorbent material weight
m_0	dry adsorbent material weight
EI	efficiency index
$M_{evaluated}$	mechanical feature experimentally evaluated
$M_{threshold}$	threshold value of the mechanical feature

Restuccia et al. [15] proposed an exhaustive experimental and theoretical study on stainless steel tubes coated by zeolite NAa. Alumina gel precipitated in situ was used as binder. The authors have demonstrated that this configuration permitted to increase on the one hand the effective thermal conductivity of the adsorbent, slightly, and on the other hand the metal/adsorbent wall heat transfer coefficient, highly.

Coatings based on zeolite/zeotype adsorbents are an attractive option in this research field. Indeed, these materials are made by alternating silica and alumina tetrahedra linked together and composed in 3D structures, they are nanoporous crystalline aluminosilicates with architectures consisting of channels and cavities with well-defined size. Their porous architecture and their high surface area make them extremely useful in a wide variety of industrial application, as "molecular sieves", catalysts and ion exchangers in solution [16]. Due to their silico-aluminate structure, their surface is covered by silanol groups which guarantees a relatively high chemical reactivity. Based upon this fact, the reaction with various agents, including silanes, can take place by means of a superficial interaction [17].

The silane matrix acts as a coupling agent and generates an interlayer with a good adhesion and homogeneity, able to provide a further barrier action, as protective layer [18]. It is expected that, the realization of a zeolite-based composite coating maintains the same adsorbent properties of the zeolite itself (thereby ensure the industrialization potential for the adsorption heat pumps), but at the same time create a coating with the typical mechanical resistance and durability characteristic of silane coatings.

Recently, Okamoto et al. [19] presented a deep study on a coating composition based on a commercial SAPO 34 produced by Mitsubishi Plastics Inc., called AQSOA Z02 and an organic binder. The procedure allowed coating lamellas of a heat exchanger with an average coating thickness of 0.3 mm. They found an increase of effective thermal conductivity of the coating (0.36 W/m K) respect to powders (0.113 W/m K). In addition, the authors demonstrated the durability of the coating performing up to 200,000 ad/desorption cycles.

In previous studies, the addition to the silane matrix of particle component, such as zeolite crystals, demonstrated to be a favourable approach to obtain effective and adsorptive coatings with good mechanical properties [20] and long durability in aggressive environmental conditions [21,22]. In [8] Freni et al. introduced a new coating composition, employing SAPO 34 powder as adsorbent and silane as binder. The complete thermo-physical characterization was presented, confirming the goodness of the developed technique. Moreover, kinetic characterization of small scale coated samples with a thickness of 0.3 mm, by means of the Isothermal Differential Steps Method, was performed. The results showed that the binder does not modify the water vapour transport through the layer, nevertheless a slight lowering in kinetic performance, with respect to pure adsorbent material, was detected. Another coating methodology proposed by Freni et al. [23] involves an inorganic clay as binder for AQSOA Z02 adsorbent material. Also in this case, the coated samples were prepared by dip coating technique, reaching thicknesses variable between 0.2 and 0.8 mm. Their hydrothermal as well as mechanical stability were tested, proving sufficient performance. Also, Kummer [24] performed a research on coatings prepared out of an aqueous emulsion based on silicone resin and two different adsorption materials (SAPO 34 and zeolite Y). The authors observed that, comparing the coating results with pure adsorbent, the presence of the binder does not influence the adsorption performances of the zeolites, although less relevant modifications in the profile of the isobars are observed. In addition, the authors have studied the hydrothermal stability of the coating and they found that, after 3000 ad/desorption cycles, no visible degradation occurs, employing a binder content of 25 wt%.

It would be extremely useful understanding the relationship between the structure of the constituents of the coating and its performances, in order to design effective coatings.

It has been claimed that the silane coupling agents lead to a significant improvement of filler dispersion, reducing the clumping of particles and improving the wettability by polymers [25].

The properties of the alkyl chain in the silane compounds play a relevant role in the performances of the protective coating. Frignani et al. [26] have found that the presence of long aliphatic chains in the silane molecule vastly increased the protective action of the silane layers. In particular, a more evident effect was observed for longer alkyl chains. Calabrese et al. [27] confirmed that good hydrophobic behaviour of composite silanes with long alkyl chains could be associated with a regular and orderly arrangement of the long carbon chains linked to the generation of induced dipoles along the same plane.

All the cited studies do not analyse the influence of different binders on the achievable mechanical and adsorption properties of the adsorbent coatings in order to be effectively employed in adsorption heat pump applications. Therefore, an empty room still exists for the search of adsorbent coatings based on zeolite/zeotype and silane binders. Aim of this paper is the comprehensive study of coatings obtained with a commercial SAPO 34 and three types of silanes by means of the evaluation of their structural, morphological and mechanical properties and, especially, their adsorption capacity. The water sorption isobars of the samples were valued by a thermogravimetric system, under real operating conditions. The morphological and structural features of the coatings were examined by means of nitrogen physisorption measurements, X-ray diffraction, wettability test and SEM analysis. Finally, pull-off test, peel test and impact test were carried out in order to evaluate the mechanical stability of the realized coatings.

2. Materials and methods

Three types of silane:

1. S2: dimethyl-dimethoxy-silane (Sigma Aldrich, ⩾95%, MW 120.22)
2. S3: N-propyl-trimethoxy silane (Sigma Aldrich, ⩾97%, MW 164.27)
3. S8: Octyltriethoxysilane (Sigma Aldrich, ⩾97.5%, MW 276.49)