



Silicone composite foams for adsorption heat pump applications



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ABSTRACT

The development of multi-functional adsorbent materials and systems is an important design step to improve engineering and technology of adsorption heat pumps (AHP).

In this work a new engineering solution was proposed in order to better manage classical needs in AHP. The proposed idea is based on the development of an innovative multi-functional composite silicone-zeolite foams. In particular foamed zeolite-silicone structure is obtained by combined crosslinking and foaming reactions due to dehydrogenative coupling of siloxane constituents.

The physico-chemical characterisation of the composite material aimed to evaluate its industrial applicability is discussed. The results obtained evidenced that the morphology of the composite foams is related to the interaction between zeolite filler and silicone matrix. Furthermore adsorption tests evidenced that zeolite embedded in the foam is effectively able to participate to sorption and desorption processes, giving to these adsorbents materials greater advantages than other zeolite containing systems (e.g. coating, picking, direct growth etc....) for heat pump applications.

1. Introduction

Thermally-driven adsorption heat pumps and chillers have the clear advantage over traditional heating/cooling systems in their low environmental impact and their ability to efficiently use low grade heat sources, such as solar energy, industrial or automotive waste heat, underground resources [1]. Details on the operating principles of adsorption heat pumps are reported elsewhere [2]. Most commonly employed porous adsorbent/adsorbate working pairs are reported in [3].

High adsorption capacity, high thermal conductivity, thermal stability and low costs are important issues that need to be satisfied by adsorbent materials. In this concern, zeolite–water, silica gel–water, active carbon–methanol or active carbon–ammonia are some of the common adsorbent–adsorbate pairs used in adsorption heat pump systems [4,5].

Among zeolite, the aluminophosphate SAPO 34 is considered as the most promising water adsorbent especially for application with low temperature heat sources ($T < 100\text{ }^{\circ}\text{C}$) [6].

Current R & D in the field is focused on the energy efficiency (COP) and Specific Cooling Power (SCP) improvement, allowing to design compact adsorption machine that are more competitive with respect to absorption and compression systems [7].

Adsorption heat pump power density enhancement can be achieved by the appropriate integration of the adsorbent material into the heat exchanger (HEX) allowing intensification of the heat transfer quality in the “adsorbent – Heat Exchanger” adsorber unit (AdHEX). Utilization of large surface area HEXs coated by a thin layer of adsorbent material is considered as an attractive way to design dynamically efficient adsorbers. The most promising coating methods are in-situ zeolite growth [8–11] and binder-based coating processes [12–14]. Direct accretion of zeolite crystals on the metal surface allows a nearly perfect thermal contact. However, multiple depositions are necessary in order to reach an acceptable zeolitic layer thickness ($< 0.1\text{ mm}$). Hydrothermal synthesis of SAPOs is a quite complex and expensive process, as a long treatment in autoclave under high pressure and temperature is required. Moreover, problems of different thermal expansion between the zeolite layer and the metal substrate are possible, due to the high temperature reached during the treatment (up to $550\text{ }^{\circ}\text{C}$ for SAPOs). The binder-based coating method represents an alternate way to deposit a thin layer of adsorbent on the heat exchanger surface. An advantage of this method is the possibility to easily vary coating thickness in the range $0.1\text{--}1\text{ mm}$ by, for example, controlling the viscosity of the liquid suspension and the dipping velocity. Full scale adsorbers prepared via dip coating were experimentally tested in [15], returning encouraging results in terms of reduced adsorption cycle time

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and elevated specific power.

J. Sauer, B. Dawoud et al. from Viessmann GmbH and Nanoscape Ag invented [16] a coating method which allows the production of adsorbent layers bonded to metal substrate made of adsorbent material and a colloidal binding material reinforced by inorganic fibres. Possible adsorbent materials are common zeolites as well as the advanced FAM molecular sieve (from Mitsubishi). The resulting adsorbent layer has a thickness of 300 to 500 μm .

In general, the advantages related to the use of coating technologies are:

- possibility of easily coat complex heat exchanger geometries with an adsorbent layer, maintaining a uniform thickness
- tunable coating thickness by changing the formulation parameters, typically between 0.1 and 0.5 mm,
- reduce heat and mass transfer resistances, thanks to the good contact between adsorbent layer and heat exchanger surface and to the low adsorbent thickness

Nevertheless, still some issues are present. The coating is usually characterised by poor mechanical strength that favours easy loss of zeolite particles from the supports upon repeated temperature swings, due to the difference in their thermal expansion coefficients. A drawback of this route is the low zeolite amount in the adsorber, due to the limited coating thickness, that induces low adsorbent density (typically 150–300 g/dm^3). Furthermore the coated adsorber systems are characterised by low ratio between the heat capacity of the adsorbent material and that on of the metallic heat exchanger, typically between 0.2 and 0.3, strongly affecting the adsorption heat pump performance (mainly related to single-sided mass transport to and from the films).

To overcome these practical problems related to zeolite coating use, a possible approach is to increase coating surface area to generate a porous structure that fill the heat exchanger volume without reducing mass flow rate. In this sense the best solution is the development a zeolite based foam with interconnected macropores for easier internal molecular diffusion [17–20].

Foamed materials, due to their intrinsic high surface area, allows to obtain a large amount of zeolite coating per unit volume acting also the foam porosity as preferential pathways for the vapour diffusion. This approach allows to improve the amount of adsorbent material in the adsorber, even if at the same time add a further passive mass in the adsorber module that could limit the AHP performances. In this concern Bonaccorsi et al. [21] recently proposed a low weight graphite foam structure as macro-porous substrate for direct synthesis of SAPO-34 zeolite for adsorption chillers obtaining promising results.

In this article a procedure to produce an adsorbent zeolite based composite silicone foam for adsorbent heat pumps applications is proposed. Our aim was to obtain a product with significant advantages in terms of cheapness of the synthesis process (employing water as low-cost solvent and reduced curing temperature), low weight and large adsorbent thickness, high vapour diffusion permeability and good hydrothermal and mechanical stability. A polydimethylsiloxane (PDMS) base matrix was used as foaming binder. PDMS is known to allow the permeation of gas and water vapour [22]. In particular the water vapour permeability is about fifty time higher than oxygen or hydrogen permeability [22,23]. Zeolite filled PDMS were investigated in the literature mainly as membrane composite materials [24–27]. The zeolites have a significant interaction with the silicone polymer. Apart from physical cross-linking attributed to van der Waals interactions by Vankelecom [28], a chemical cross-linking was proposed involving reactions of the surface hydroxyls on the zeolite with the polymer chains. The high chemical affinity between the two components improve their application as composite gas separation membranes. Kittur et al. [29] evidenced an enhancement of hydrophobicity, selective adsorption and the establishment of molecular sieving action with increasing zeolite content in the membrane matrix. Vane et al.

[30] confirmed that the performance of PDMS silicone membranes can be significantly enhanced through the incorporation of alcohol-selective high-silica zeolite (ZSM-5) particles.

In this concern the PDMS high permeability to water vapour plays a relevant role in its use as a polymer matrix in zeolite based adsorbent composites for adsorption heat pumps applications. In order to maximize the exchange area of adsorbed material with water vapour, the realization of a composite open foam represents a potentially effective engineering solution to maximize performance and functionality of these systems [31].

In the first part of the paper, the preparation procedure is detailed and the foaming mechanism of the composite zeolite sponges is discussed. Afterwards, structural properties and morphology of the realised samples are investigated by FTIR and SEM analysis. Water vapour adsorption properties have been also determined by thermogravimetric technique under real adsorption heat pumps operating conditions.

2. Experimental part

2.1. Foam synthesis

Macrocellular zeolite filled silicone foams were produced following a direct foaming approach. The foaming mixture was composed by two reactants (supplied by Gelest Inc., Morrisville, USA): a poly(methylhydrosiloxane) (PMHS, M.W. 1400-1800 CAS: 63148-57-2) and a silanol terminated polydimethylsiloxane (PDMS, M.W. 110000 CAS: 70131-37-8) compounds containing Tin(II)2-ethylhexanoate, (M.W. 405.11, 50%, CAS. 301-10-0) as catalyst. In particular, the foam preparation was carried out according the following procedure: SAPO-34 filler (FAM-Z02 supplied by Mitsubishi Chemicals, grain size 2–4 μm), at different wt%, was dispersed under high shear mixing in polydimethylsiloxane (PDMS) for about 60 s. In order to reduce the solution viscosity, water and ethanol were added to the mixture as solvents. Then, the polymethylhydrosiloxane (PMHS) was thoroughly mixed with the SAPO-34/PDMS mixture with a siloxane PDMS/PMHS weight ratio 1:2 for 15 s. Finally, the tin catalyst was added under vigorous mixing, for about 15 s. The so obtained mixture was poured into a cylinder mould to obtain blowing. Foaming was started putting the sample into an oven kept at a controlled temperature (60 $^{\circ}\text{C}$) for 24 h to obtain a complete compounds reaction. Foams containing different amount of SAPO-34 filler, in the range 29 wt%–50 wt% of siloxane matrix (PDMS + PMHS), were realised. A list of all produced formulations with details of compound amounts and zeolite filler content are reported in Table 1. As reference an unfilled silicone foam was considered (Z0-Foam). Zeolite/matrix [%] is the percentage of zeolite compared with the amount of foam matrix constituents (PDMS and PMHS).

2.2. Constituents and foam characterisation

Zeolite filler and siloxane compounds were evaluated by FTIR analysis using a Cary 670 Agilent spectrometer. The spectra were recorded from 500 to 4000 cm^{-1} on KBr based pellets.

Foam adsorption performances were investigated by thermogravi-

Table 1
Siloxane matrix mixture compositions at varying zeolite content.

		Z0-Foam	Z29-Foam	Z37-Foam	Z44-Foam	Z50-Foam
PDMS	Siloxane	24.4%	18.9%	16.9%	15.4%	14.1%
PMHS	Siloxane	48.8%	37.7%	33.9%	30.8%	28.2%
Water	Solvent	12.2%	9.4%	8.5%	7.7%	7.0%
Ethanol	Solvent	6.1%	4.7%	4.2%	3.8%	3.5%
Sn(II)	Catalyst	8.5%	6.6%	5.9%	5.4%	4.9%
Zeolite	Filler	0.0%	22.6%	30.5%	36.9%	42.3%
Zeolite/Foam [%]		0.0%	28.6%	37.5%	44.4%	50.0%

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