Applied Thermal Engineering 85 (2015) 1–8

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research paper

Versatile siloxane based adsorbent coatings for fast water adsorption processes in thermally driven chillers and heat pumps

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HIGHLIGHTS

- We report a versatile silicone based coating procedure.
- Various samples with coating thickness between 130 and 290 μm were achieved.
- We measured very fast rise up times between 24 s and 29 s.
- The hydrothermal stability has been proven over 3000 cycles.
- The coating procedure is inexpensive and environmental benign.

ARTICLE INFO

Article history:
Received 4 July 2014
Accepted 7 March 2015
Available online 3 April 2015

Keywords:
Zeolite
SAPO-34
Adsorbent coating
Adsorption heat pump
Adsorption chiller
Dehumidification

ABSTRACT

In this work a versatile and hydrothermally stable binder based coating with fast adsorption kinetics for the use in thermally driven adsorption chillers, heat pumps and within dehumidification processes is reported. Two different adsorbents, a SAPO-34 with a typical adsorption isotherm favorable for low desorption temperatures and a zeolite Y for higher desorption temperatures were used. The coatings were prepared out of an aqueous dispersion for different binder contents with a minimum of 2.5 wt%. The performance of the coating and the influence of the binder on the equilibrium and dynamic adsorption characteristics were evaluated by means of thermogravimetry and a volumetric pressure jump method. Finally the hydrothermal stability under typical application boundary conditions was evaluated with surprisingly fair stability even for a very low binder content of a 2.5 wt%.

1. Introduction

Zeolite coatings on different support structures have attracted a growing interest for the use in heat transformation processes like adsorption chillers, thermally driven heat pumps or dehumidification within the last years [1–5]. Compared to granules used e.g. in a fixed bed, coatings show an improved heat and mass transfer. This holds true even in comparison to very small granules, as the firm and sturdy fixation of these on a heat exchanger surface without gluing is a difficult task. This is especially important in the application in focus of this work, as the underlying principle is a cyclic ad- and desorption of the working fluid into the inner cavities of the porous material. By improving the heat and mass transfer, faster adsorption and desorption times may be realized [6–8]. Thus, shorter cycle times with a high working fluid capacity, i.e. the refrigerant uptake during adsorption and the release during desorption, can be achieved, leading to an improved cooling or heating power density of such systems.

The improvement of the power density by the use of zeolite coatings on heat exchanger surfaces was impressively demonstrated in several publications [3,6,9–11]. However, the preparation of mechanical and hydrothermal stable coatings with different adsorbents and adjustable properties by simple and efficient methods is still a challenging task [12–15].

Depending on the application and the corresponding boundary conditions, especially the different temperature levels, a proper choice of the adsorbent is a key issue [16,17]. Thus, different adsorbents may be favorable for the same application depending e.g. on the driving temperature level. For low desorption temperatures (less than 90 °C) Silica Gels and Silica-aluminophosphates (SAPO) like the SAPO-34 may be advantageous, whereas for high desorption and adsorption temperatures zeolites may be attractive [18]. The optimum coating thickness can vary in a broad range, depending not only on the adsorbent but also on the heat

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http://dx.doi.org/10.1016/j.applthermaleng.2015.03.042
1359-4311/

Nomenclature

Symbol

D_{50}	classification for particle sizes: 50% of the particles have a diameter that is equal or smaller than the D_{50} value.
m	mass, kg
m_{dry}	dry mass, kg
$m_{ads,amb}$	mass of the adsorption material (including adsorbed water at ambient conditions), kg
$m_{liq,bin}$	mass of the liquid binder emulsion, kg
p	pressure, Pa
p_{sat}	saturation pressure, Pa
p_0	saturation pressure for the given sample temperature, Pa
p_{rel}	relative saturation pressure, also expressed at p/p_0
T	temperature, absolute in °C, differences in K
t	time, s
$t_{0.15}$ ($t_{0.5}$, $t_{0.8}$)	time to reach 15% (50%, 80%) of equilibrium uptake
w	mass fraction, mass of a constituent divided by the total mass of all constituents in the mixture
x	loading, kg kg^{-1}
x_{ads}	calculated loading of the pure adsorption material in the coating, kg kg^{-1}
x_{coat}	loading of the coating including binder and adsorption material, kg kg^{-1}
x_{eq}	equilibrium loading under given boundary conditions, kg kg^{-1}
v_s	sorption speed, kg kg^{-1} s^{-1}

Abbreviations

RH	relative humidity, %
COP	coefficient of performance
SAPO	a silica-aluminophosphate
LPJ	large pressure jump method
TG	thermo gravimetry
wt%	weight percentage

Subscripts

ads	adsorbent
amb	ambient
bin	binder
coat	coating
dry	dry
liq	liquid
r	rise up time
s	sorption
sat	saturation
sol	solid

exchanger design and the optimization criteria, i.e. the thermal coefficient of performance (COP) or the maximum power output [6,8].

An optimum layer of 75–150 μm for a zeolite coating directly synthesized on stainless steel was reported in order to maximize the energy gain during a specific period of time [19]. With regard to high sorption capacity and fast sorption kinetics for a direct coating consisting of a SAPO-34 a sufficient layer thickness of 80–100 μm on aluminum was reported [3].

A layer thickness of 200–300 μm of SAPO-34 on a full scale heat exchanger was reported, showing a good compromise between high COP and short cycle time [7].

In addition these coatings must be hydrothermally and mechanically stable over thousands of cycles during the apparatus lifetime. First investigations on pure sorption materials and different coatings over 50,000 cycles revealed partially strong degradations [20]. Recently, a broad investigation on the mechanical stability for heat pumping applications with several tests including peel and bend test on samples prepared by dip coating has been reported by Freni et al. [21] showing very promising results.

Within the last years, several coating techniques with regard to the application in adsorption heat pumps or chillers have been reported. In principle, the different techniques can be divided into in situ and ex situ methods.

For in situ methods, the synthesis of the adsorbent and the coating is realized in one step. Several procedures on different supports can be found for zeolite A [9,13,22], zeolite X [15] and zeolite Y [1]. A special case is the consumptive SAPO-34 coating [10] on aluminum and the direct synthesis of a metal-organic framework material on a metallic support [23].

In ex situ methods, synthesis of the adsorbent and preparation of the coating is achieved in different steps. Various methods for preparation of the coatings are reported, ranging from simple gluing of pellets to sophisticated binder based coatings realized in dip, slurry or wash coating processes [9,18–21]. Several binders out of different classes are described like polymer binder (e.g. polyvinyl alcohol) or mineral binders (e.g. aluminum oxide or silicon dioxide containing binders). The properties of the binder are crucial for the hydrothermal stability and the dynamic adsorption characteristics. In general, organic binders show a good flexibility with moderate temperature stability, whereas inorganic binders show high temperature stability with a fair flexibility.

Polyorgano siloxanes combine these attributes as they have a high temperature resistance up to 400 °C and an excellent flexibility compared to inorganic binders to withstand the mechanical stress due to the hydrothermal treatment.

In this work, the silicone resin SilRes® MP 50E from Wacker Chemie AG has been used as binder to prepare water based dispersions for coatings on a $AlMg_3$ support with a base area of 50 × 50 mm^2 [24]. The water based emulsion containing the silicone resin used in this work is environmental friendly and less-toxic compared to solvent based slurries.

Colloidal coatings were prepared with two micron sized adsorption materials. In order to address low and high temperature applications, a SAPO-34 AQSOA® FAM Z-02 from Mitsubishi Chemical Corporation and a sodium form Y-zeolite CBV100 from Zeolyst were used. Both materials show a promising water uptake and a good hydrothermal stability for the application in focus of this work [18].

2. Sample preparation and characterization

2.1. Preparation of the samples

For each adsorption material 4 different samples were prepared with varying binder contents from $w = 25$ wt%, i.e. 25 weight percent binder content compared to the total mass, down to 2.5 wt% (approx. 25 wt%, 10 wt%, 5 wt%, 2.5 wt%). In addition, one reference coating consisting of pure binder SilRes® MP 50E was prepared.