Applied Thermal Engineering 72 (2014) 153–159

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Innovative zeolite coatings on graphite plates for advanced adsorbers

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ARTICLE INFO

Article history:
Received 29 November 2013
Received in revised form
17 April 2014
Accepted 22 April 2014
Available online 28 June 2014

Keywords:
Zeolite
SAPO 34
Adsorption chiller
Graphite exchanger
Advanced heat exchanger

ABSTRACT

In this work, a new family of zeolite coatings and an innovative heat exchanger concept are presented. Zeolite SAPO-34 coatings have been prepared and deposited on high-density graphite plates to investigate the feasibility of a new concept of adsorber for adsorption chillers. Different coating formulations have been prepared and characterized.

Results demonstrated that SAPO-34 coatings maintain the characteristic adsorption properties of the native zeolite, develop an optimum bonding to the graphite plates and make it possible to improve the coating process for a better control of the layer thickness, in order to obtain different values of the final zeolite/support mass ratio.

Finally, the schematic of an innovative graphite exchanger for heat pumps and chillers is provided. A bonded plate configuration have been adopted to remove bulky and heavy components such as the clamping plates. To this end experimental work have been conducted to address the suitable adhesive foe bonding the heat exchanger plates.

The external shapes have been designed on the basis of the characterizations performed on small-scale samples, whereas inner fluid paths (heat transfer fluid side) have been developed by using Computational Fluid Dynamics in order to enhance heat transfer rate and temperature uniformity on the plate surface.

Further, the main components of a full scale advanced exchanger has been showed and described.

1. Introduction

Adsorption chillers are a promising green-technology in solar or waste heat driven air conditioning for their reduced primary energy consumption and low environmental impact. However, improvements in efficiency and performance are needed to make those systems economic and competitive to traditional technologies [1]. The search for efficient adsorbent materials having a moderate hydrophilicity, i.e. regenerable at low temperature (80–150 °C), and high water adsorption capacity is the main goal for the development of a low temperature adsorption heat pump [2]. Zeolites belonging to the alumino-silicon-phospur family, like SAPO-34, show adsorption properties at low equilibrium temperatures and pressures that are particularly appropriate to the range of operating conditions of such heat pumps [3]. However, the low thermal conductivity of zeolites has a negative impact on the heat transfer efficiency of the entire heat exchanger. Therefore, there is a need of new engineered materials joining sorbent and heat transfer properties. With this respect, the use of zeolite-graphite composites represents a valid strategy for the ideal combination of low density, low heat capacity and high thermal conductivity shown by the graphitic substrates. In the past, some authors proposed a composite made by compressing graphite grains with hygroscopic salts or zeolites [4] to improve the thermal conductivity of the adsorbent bed. Such a combination, however, despite leading to a better thermal conductivity, resulted in an excessive rise in resistance to the water vapour mass transfer [5]. An alternative solution was proposed by the direct synthesis of SAPO-34 on porous carbon supports, like carbon papers [6] or graphite foams [7], to combine the needed vapour diffusivity with the thermal properties of carbon materials.

In this paper, we propose a new composite material based on the deposition of SAPO-34 on high density graphite plates which can be easily machined to provide opportune configurations for the design of an advanced heat exchanger for solar cooling or automotive applications.

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http://dx.doi.org/10.1016/j.applthermaleng.2014.04.079
1359-4311/

2. Experimental

Fuel cell grade graphite plates have been used as supports for zeolite deposition. The plates have dimensions 40 × 40 × 3.5 mm, bulk density = 1.9 g/cm^3, flexural strength = 40–50 MPa, hardness = 60 SSH, thermal conductivity = 55–60 (W/mK), specific heat = 0.72 kJ/kgK.

One surface of the plates was machined to obtain three different geometries of channels (depth = 2 mm) like the drawings in Fig. 1.

The coating of the graphite plates was obtained by two different methods, direct synthesis and dip coating. Some graphite supports were preliminary oxidized by a nitric acid solution (68 wt.%) at room temperature for 1 h.

Hydrothermal synthesis of SAPO-34 was obtained according to the following procedure: a reacting mixture was prepared by mixing aluminium isopropoxide (98% $Al(OC_3H_7)_3$ Aldrich), orthophosphoric acid, the organic compound tetraethilammonium-hydroxide (40% TEAOH Fluka) and an aqueous solution of colloidal silica (40% SiO_2 Aldrich) for the final gel formulation: $0.6SiO_2{:}1Al_2O_3{:}1P_2O_5{:}70H_2O{:}0.5TEAOH$.

The deposition was carried out by immersing a graphite plate sample directly in the reacting solution which was heated at 200 °C for 72 h in a PTFE-lined autoclave (under autogenous pressure). At the end of the synthesis time, the sample was removed from the autoclave, accurately rinsed and dried at 80 °C overnight. The coated samples were, then, calcinated at 200 °C for 24 h in air to remove the template from the zeolite porosity.

The dip coating method consisted in the preparation of an aqueous solution of SAPO-34 powder (particle size <10 μm) which was added with 15 wt.% of a N-propyl-trimethoxy-silane solution (5 vol%) and stirred at room temperature for 24 h. The plate samples were then immersed in the zeolite solution for 30 s. Afterwards, the coated samples were cured in an oven at 100 °C for 4 h. The SAPO-34 powder used for the solution was prepared by the same procedure used for the direct growth.

The coatings and the SAPO-34 powders grown by direct synthesis were evaluated by X-ray diffractometry for phase identification. All coated samples were morphologically characterized by scanning electron microscopy (SEM), while mechanical properties of deposited layers were evaluated by pull-off adhesion test.

To directly evaluate the water adsorption behaviour of coated samples a thermogravimetric McBain adsorption system was used and the results were compared with the adsorption isobars of SAPO-34 zeolite measured by a Cahn microbalance. The system consists in a sample holder hung to a micro-load cell (range: $0 \div 1$ g $\pm$ 0.0002) inside a quartz tube that is connected to a vacuum pump and a thermostated evaporator by a 2-way valve. The sample temperature is controlled by a thermocouple placed in the sample holder and it can be varied by an external ring heater separately controlled [7]. A typical measurement of water uptake was carried out putting a sample of coated graphite (for a total weight of ≈700 mg) in the sample holder for a preliminary activation at $T = 150$ °C in vacuum ($P = 0.01$ mbar) for 12 h. The sample was, then, cooled down (in vacuum) to a fixed temperature, Tf, and the quartz tube connected to the evaporator at $P = 10$ mbar of vapour pressure (absolute). The sample holder weight was let stabilize (not less than four hours) then the weight value recorded to measure the adsorbed water (water uptake). The measurement was repeated for different Tf values, from 30 °C to 150 °C. The water uptake is expressed as percentage weight increase of the total mass of deposited zeolite, which was calculated from the mass increment of each sample after coating.

3. Results and discussion

Both deposition processes, by direct synthesis and by dip coating, showed better characteristics in terms of surface coverage and adhesion properties when the graphite plates were pre-oxidized. The as-provided supports, in fact, similarly to other carbonaceous materials are mostly hydrophobic, then scarcely wetted by the synthesis solution or the coating solution. In the first case, it is very important to create nucleation sites on the support surface, i.e. locations on the surface were the nuclei formation is preferentially induced. By the preliminary treatment the number of oxygenated groups on the surface of the graphite supports increased significantly improving the plate wettability [8].

The coatings obtained on the pre-treated plates by direct synthesis are made of several layers of SAPO-34 crystals forming aggregates of tightly packed particles where the typical cubic shape of SAPO-34 is missed (Fig. 2a), whereas the dip coating method created a uniform distribution of zeolite crystals so that the coating morphology appeared more regular (Fig. 2b). However, the main difference between the two methodologies was in the coating thickness, which resulted limited to tens of microns for the direct synthesis while by dip coating it was possible to obtain layers 100 to 200 microns thick.

The pull-off tests were carried out on flat graphite plates coated by direct synthesis and by dip coating. The different thicknesses of the coatings due to the different deposition methods influenced the fracture mechanism of the coating layers more than their mechanical resistance. The direct-grown coatings, in fact, showed a (mean) mechanical resistance of 0.78 MPa and the dip coated plates of 0.82 MPa. However, in the first case the fracture occurred at the support - coating interface, while the binded coatings fractured preferentially among the zeolite layers (Fig. 3).

Nevertheless, the values of mechanical resistance obtained in both cases were comparable with those of polymeric coatings.

In Fig. 4 are shown two samples of machined graphite plates after the SAPO-34 deposition, by direct synthesis (Fig. 4a) and by dip coating (Fig. 4b). The surface coverage was good in both cases

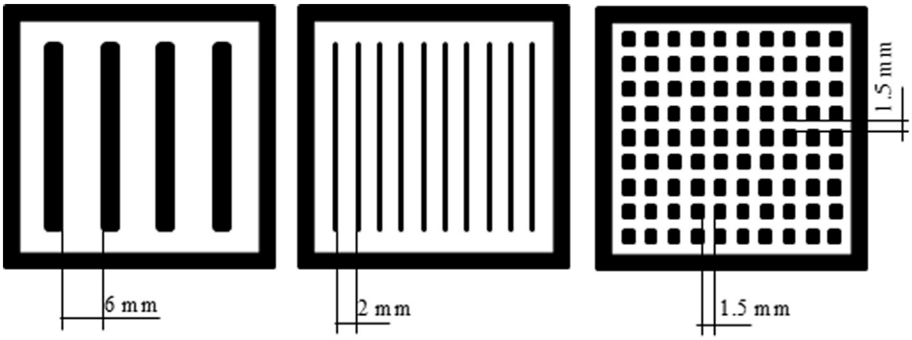

Fig. 1. Drawing of channel geometries for SAPO-34 deposition tests.