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Pore structure modification of silica matrix infiltrated with paraffin as phase change material

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ABSTRACT

Temperature-controlling solid–liquid phase change material (PCM) infiltrated in a porous matrix is becoming attractive for aerospace applications. The properties of the pore structure are crucial factors in the selection of porous materials for PCM infiltration. The main purpose of this study is to adjust the pore structure of porous silica matrices with different molar ratios of ethanol (EtOH) and tetraethoxysilane (TEOS) for PCM infiltration. Five compositional ratios of EtOH/TEOS were introduced to prepare the silica with different pore size through sol–gel processing, and the pore structures were analyzed by N_2 adsorption–desorption measurements and scanning electron microscopy. Results indicate that the pore size increases with a larger value of the EtOH/TEOS molar ratio. Open cell pore structure and pore size of silica were observed and calculated. For EtOH/TEOS ratios of 10 and 20, the synthesized silica matrices had average pore sizes of 53.1 nm and 56.0 nm, respectively, exhibiting better infiltration. Moreover, the maximum mass fraction of paraffin as PCM in the silica matrices reached up to 75 wt%.

Keywords: Porous ceramics; Paraffin; Phase change materials; Microstructure

1. Introduction

Currently, temperature-controlling solid–liquid phase change material (PCM) is one of the most interesting passive thermal management techniques due to its inherent advantages of simplicity and reliability (Sharma and Sagara, 2005). The latent heat absorption phenomenon associated with the melting of a suitable PCM can be effectively used to delay or modify the temperature rise of the surface that is subjected to high flux (Kaul, 2005). However, leakage of organic PCM impregnated in the porous matrix under the service temperature, which is influenced by the pore structural properties of the porous matrix, is a serious problem in aerospace application. Sarı et al. (2006) reported that Eudragit S/fatty acid blends is a form-stable PCM that displays no leakage of fatty acid at the temperature range of 50–70 °C for several heating cycles. Recently, Sarı et al. (2008) used styrene maleic anhydride copolymer (SMA) as the supporting material to prevent the leakage of the fatty acid and showed that no leakage of fatty acid occurs even when the temperature of the form-stable PCM is over the melting point of the fatty acid in the composite. However, the poly wall of this composite PCM has low structural strength and service temperature. To solve this problem, porous ceramics such as porous silica or expanded graphite (EG) are exploited as the matrix to improve the weakness.

Chapotard and Tondeur (1983) showed that the mean pore size of activated carbon foam has a great effect on its performance. If the pores are too small, the PCM cannot be completely infiltrated, which will affect the latent heat capacity of the storage. On the other hand, if the pores are too big, there will not be enough capillary force to retain the wax liquid phase inside the matrix. Sarı and Karaipekli (2008) investigated the properties of capric acid (CA)/expanded perlite (EP) composite. Later, because the mass fraction of CA as PCM in EP was not very large, Sarı and Karaipekli (2009) also prepared the palmitic acid (PA)/expanded graphite (EG) composite. The PA/EG composite showed maximum mass fraction of PA in the

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Nomenclature

W	the weight of gas sorbed at P/P_0
W_m	the weight of sorbate for monolayer sorption
C	a constant that relates to the energy of monolayer sorption
r_k	critical Kelvin radius
x	relative pressure, P/P_0
γ	surface tension of liquid nitrogen, 8.85×10^{-3} N/m
υ_m	volume per diagram, 34.65 cm^3/g
ϕ	contact angle, 0°
t	thickness of the adsorbed layer
t_m	thickness of the nitrogen monolayer molecules, 0.354 nm
d	the critical pore size

EG reaching up to 80 wt%, which means considerable latent heat energy storage potential. However, it is still not suitable for aerospace application due to its high thermal conductivity.

Because of its low density and high mesoporosity, sol–gel derived silica aerogel is an attractive candidate for many unique thermal, catalytic, and chemical applications (Morris et al., 1999). Harel et al. (2006) investigated the pore structure and connectivity of silica aerogel used as porous media. Synthesis of mesoporous silica with regular pore arrays such as MCM and FSM type materials (pore size 2–50 nm) by supramolecular templating and synthesis of crystalline zeolites with regular pore architecture (pore size < 2 nm) by molecular templating have been reported (Raman et al., 1996). In supramolecular and molecular templating, silica network structures with organic template-filled cavities are formed by the interaction of silica and organic templates. The removal of organic templates creates silica with porous cavities. Porous silica materials are also obtained by the conventional sol–gel route (Brinker and Scherer, 1990). Generally the silica products from the conventional sol–gel approach have different pore size distribution or pore structure depending on the compositional ratios of the reactants.

In the present work, porous silica is prepared through sol–gel hydrolysis followed by condensation, solvent exchange, and supercritical drying. The structural pore properties of the silica matrix with different molar ratios of ethanol (EtOH)/tetraethoxysilane (TEOS) are investigated to determine suitable porous matrices for PCM.

2. Experimental procedures

2.1. Materials and preparation

The molar ratios of EtOH and TEOS were designed as the reactants to prepare the porous silica. Silica gels were first prepared by a two-step sol–gel process using TEOS as the precursor and the co-precursor diluted in EtOH solvent. Initially, the hydrolysis and condensation were carried out under the acidic (nitric acid (HNO_3)) and basic (ammonium hydroxide (NH_4OH)) catalyzation conditions, and the molar ratio of HNO_3:NH_4OH was set at 1:2. Acid- or base-catalyzed hydrolysis and condensation reactions of the sol–gel process as a prerequisite to the formation of silica gels are shown below.

Hydrolysis:

$$Si(OR)_4 + H_2O \xrightarrow{[H^+/OH^-]} Si(OR)_3OH + ROH,$$

$$Si(OR)_3OH + H_2O \xrightarrow{[H^+/OH^-]} Si(OR)_2(OH)_2 + ROH, \text{ etc.}$$

Condensation:

$$Si(OR)_4 + Si(OR)_3OH \rightarrow (OR)_3Si - O - Si(OR)_3 + ROH,$$

$$Si(OR)_3OH + Si(OR)_3OH \rightarrow (OR)_3Si - O - Si(OR)_3 + H_2O, \text{ etc.}$$

The gels were then supercritically dried in an autoclave above the critical temperature (T = 270 °C) and critical pressure (7.5 MPa) after gelation and aging in ethanol. The final silica showed a different pore structure with the change of EtOH/TEOS.

Next, paraffin (technical grade paraffin (n-alkenes, 58 #) with a melting temperature of 56–58 °C from Nanyang, the fine chemical manufacturer in PR China) was heated to over its melting temperature, and the porous silica was added into the melted paraffin. A paraffin/porous silica composite was obtained by melting infiltration. The mass fraction of the melted paraffin infiltrated into the porous silica was closely related to the pore structure of silica. The mass fractions of the paraffin in silica matrices prepared by different molar ratios of EtOH/TEOS were recorded to determine the relation between the mass fraction of paraffin and the silica matrices.

2.2. Characterization

The adsorption–desorption measurements were performed by ASAP 2000 micromeritic apparatus. The samples were previously degassed at 150 °C and 10^{-3} Torr for several hours until constant weights were achieved. The adsorption–desorption measurements were then performed on the degassed samples at liquid nitrogen temperature (77 K) and 10^{-6} Torr vacuum pressure. Successive known volumes of N_2 gas were admitted to the adsorbent at programmed intervals and equilibrium pressure was measured. Similarly, desorption isotherms were obtained by measuring the quantities of gas removed from the sample as the relative pressure was lowered. Analysis of the surface areas of the porous silica samples was conducted by Brunauer–Emmett–Teller (BET) method (Gregg and Sing, 1982). The BET equation of the multilayer gas sorption at relative P/P_0 is given as Eq. (1).

$$\frac{1}{W((P/P_0)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \cdot \frac{P}{P_0} \tag{1}$$

For nitrogen, the C values were in the range of 50–250, an acceptable range to calculate the nitrogen molecular cross-sectional area considering the hexagonal close-packed liquid nitrogen monolayer at 77 K. The multiplication product between the nitrogen molecular cross-sectional area and number of nitrogen molecules covering the solid surface as determined from W_m was the measurement of solid surface area. In this case, the successive multilayer sorption was disallowed, and the pore size of such a molecule approached the size of nitrogen molecules. Thus, the Kelvin and Halsey equations, Eqs. (2) and (3), were performed to calculate the relative pressure, P/P_0. Hence, the critical pore size d (nm) is calculated by Eq. (4) (Barrett et al., 1951).

$$r_k = \frac{-2\gamma \upsilon_m \cos\phi}{RT \ln x} \tag{2}$$