Phase change in modified hierarchically porous monolith: An extra energy increase

Yuchao Wang, Liyan Zhang, Shengyang Tao [*], Yonglin An, Changgong Meng, Tao Hu

School of Chemical Engineering, Dalian University of Technology, Dalian, Liaoning, PR China

ABSTRACT

Composite phase change material (PCM) was prepared by loading pure PCM in the hierarchically porous silica (HPS) matrix. Via the modification by organic silanes, the surface property of the hybrid silica material was effectively controlled. The functional surface groups were not only helpful to reach high loading capacity for PCM (up to 3.5 times of HPS's weight), but beneficial to enhance the energy storage capacity in confinement. An extra energy increase (about 10% of the total enthalpy value) could be revealed during the phase change process due to the strong van der Waals interaction between modified surface and PCM. The latent heat values of composite PCM (including HPS) could be 163.0 J g^{-1}. The PCM in modified HPS showed high thermal storage capability (about 99.34% to pure PCM). It was important to study the influence of modified surface on energy storage in confined space. The discussion would be useful to advance high-performance PCM composites.

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1. Introduction

As a new sort of porous material, hierarchically porous silica (HPS) has attracted great attention all over the world [1–5]. Pores in different sizes are combined together; so various functions from these pores are integrated in one system. For example, HPS with both macro- and meso-pores usually has a large surface area (from mesopores), and fast molecule diffusion pathway (from macropores). The hierarchically porous materials have been used in several fields, such as separation [6,7], catalysis [8,9], absorption [10,11], chemical sensing [12,13], and hydrogen storage [14,15]. In the past years, most efforts have been devoted to adjusting the porous structure, but the surface property of HPS is lack of attention. As is well-known, surface properties, including wettability, polarity, or defects, has significant effects to the chemical process, which happens in the porous materials. Lu reported that MCM-41 modified with trimethylchlorosilane could remove organic compounds from streams or wastewater [16]. Inumaru and coworkers created hydrophobic microenvironment in the pores of mesoporous silica/H$_3$PW$_{12}$O$_{40}$ hybrid to increase its ester-hydrolysis catalytic ability in water [17]. Recently, it has been found that hybrid HPS can remove oil from water, quickly and efficiently [18]. Like a container, the hierarchical structure supplies enough space for storing oil. The long-chain alkanes on the porous surface create

a highly hydrophobic and oleophilic microenvironment, so the adsorbed oil will be firmly captured. Such kinds of confined space with controlled chemical environment seem to be appropriate for the design of novel micro-reactors.

Micro-reactors have raised a lot of interests of researchers [19,20]. Traditional micro-reactors have series of micro-channels for the transmission and reaction of molecules. Usually, such material possesses an unmodified inner surface. Herein, we believe that the monoliths with hierarchical structure and controllable superwetting surface will be extremely suitable as micro-reactor for phase change materials (PCM).

Phase change materials (PCM) are compounds that can be reversibly switched between two phases, such as solid–liquid or crystalline-amorphous phase, typically through melting and annealing [21–23]. As a micro-reactor, the porous silica monolith not only can increase mass transport, but also carry a large amount of PCM. In this paper, several kinds of hybrid PCMs were prepared by compositing alkanes and carboxylic acid with HPS monolith. Such porous material is able to carry enough PCM up to 3.5 times of its weight. As an ideal matrix, HPS materials cannot reduce the natural thermal storage performances of inside PCM. Although, the silica matrix has low thermal conductivity, the continuous PCM part in the throughout interconnected porous channels is able to keep the heat-transfer efficiency without obvious decline. After modification with special organic groups, there will be strong interaction between PCM and porous surface. It insures that PCM has been held tightly and can not spill out of the channels during

the phase change process. Moreover, in the confined porous space of HPS, there are some interesting phenomena different from the ones observed in macroscopic systems. Yin and coworkers [24,25] have proved that confined space significantly controlled the crystallisation of TiO_2. Similarly, the crystallisation of PCM in HPS is also restricted. During the phase change of PCM, an additional enthalpy of phase change (more than 10%) can be obtained. It is confirmed that the process of phase change is affected by intermolecular interactions between PCM and surface of HPS. Thus, it is possible to enhance the energy storage capacity of hybrid PCM by controlling the surface properties. This discovery is meaningful to explore the reaction mechanism in confined space. The hybrid HPS can be used to develop high-performance energy storage materials and micro-reactors for chemical engineering.

2. Experimental

2.1. Materials

Tetramethoxysilane (TMOS) was bought from the Chemical Factory of Wuhan University (Wuhan, China). P123, n-octyltriethoxysilane, and n-octadecyltrimethoxysilane were obtained from Aldrich Chemical Co. Inc. Nitric acid (AR) was purchased from Beijing Chemical Reagents Factory (Beijing, China). 25 wt% ammonia (AR), ethanol (AR), toluene (AR) and petroleum ether (AR) were purchased from Fuyu Fine Chemical of Tianjin Co., Ltd. (Tianjin, China). Octadecane and stearic acid were obtained from Aladdin Chemistry (Shanghai) Co., Ltd.

All the reagents mentioned above were used without further purification.

2.2. Preparation of sample gels (HPS) and surface modification

The hierarchically porous silica monolith was prepared and modified by a phase separation paralleling to the sol–gel transition and the reaction with silylation reagent reported before [26]. The as-prepared samples were labeled as HPS8 and HPS18 were modified by n-octyltriethoxysilane and n-octadecyltrimethoxysilane, respectively. The experimental detail was shown in Supplementary Material.

2.3. Preparation of the composite phase change materials (PCM)

Small pieces of as-prepared samples mixed with octadecane and stearic acid, respectively. After heated at 80 °C in a vacuum, the composite PCMs were separated out and cooled down to RT. HPS-O, HPS8-O and HPS18-O were the hybrid materials composited with octadecane. HPS18-S stood for the as-prepared materials composited with stearic acid.

2.4. The spillage of PCM

The as-prepared composite PCM was hanged up and heated at 80 °C after weigh. 10 min later, the composite PCM was removed on another glass slide, naturally cooled down to RT, and weighed again.

2.5. Characterization

The scanning electron microscopy (SEM) images were taken with a JEOL JSM-6700F field emission scanning electron microscope (FESEM, 20 kV). The surfaces of samples were coated with Au before test. Mercury porosimeter (PORESIZER-9320, Micromeritics Co. Ltd.) was used to measure the size distribution of macropores. The nitrogen adsorption and desorption isotherms were measured at 77 K using an ASAP 2010 analyzer (Micromeritics Co. Ltd.). Before measurement, samples were degassed under vacuum at 373 K for 8 h. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore volume and pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) model. Thermal gravimetric analysis (TGA) was carried out using TGA/Q50 coming from TA Instruments, USA. The samples were heated progressively from 0 to 800 °C with a heating rate of 5 °C min^{-1} in air. Differential Scanning calorimetry (DSC) was measured by DSC/Q20 coming from TA Instruments, USA. The heat capacity was measured over a temperature range of 15–90 °C with a heating rate of 5 °C min^{-1}. A SL200B (Solon Tech. Inc., Ltd. Shanghai) contact-angle goniometer (CA) was used for static contact angle measurements. The software offered by the instrument manufacturer calculates the contact angles based on the method of the tangent. The oil contact angle is obtained using octadecane at 35 °C. FTIR spectra (4000–500 cm^{-1}) in KBr were collected on a Nicolet Avatar 360 FTIR spectrometer. The powder of HPSs was mixed with KBr and pressed to a thin disc for FTIR detection. X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX-2400 X-ray powder diffraction (Japan) using Cu Kα radiation, operating at 40 kV and 10 mA. Raman spectra were collected using a Nicolet Almega XR Raman system with 532 nm excitation laser from Thermo Fisher Scientific Inc. All the measurements were performed at room temperature with droplets of deionized water.

3. Results and discussion

3.1. Fabrication and structural properties

During the gelation, plastic tubes were used as container to form HPS with uniform shape and same diameter. The length of HPS cylinder (0.8 cm in diameter) can reach up to 3 cm (Fig. 1a). The HPS was easy to be cut into a certain length or get other shapes by corresponding molds. After composited with PCM, the material could hold its shape and size without change (Fig. 1b). HPS should have a highly interconnected pore structure to contain PCMs as much as possible. As shown in Fig. 1c, the macropores were around 2.6 μm according to the result in Fig. S1 in Supplementary Material. Such a markedly porous material with hierarchical microstructure was beneficial for adsorption and storage. Co-continuous structure and well-defined macropores were observed distinctly from both the bare and modified HPS (Fig. S2 in Supplementary Material). The modification process did not show obvious effect to the macroporous structure of HPS. A large amount of PCMs occupied the inter space of HPS after adsorption, and the macroporous channels were totally blocked as Fig. 1d shown.

Besides macropores, there were also plenty of mesopores in HPS. More details of them were investigated from the nitrogen sorption isotherms. As Fig. S3a in Supplementary Material shown, all the isotherms of as-prepared HPS belonged to type-IV isotherm according to IUPAC classification [27]. It illuminated that the hierarchically porous structure was held during the modification process. The H1-type hysteresis loops in the adsorption–desorption isotherms revealed that there were uniform mesopores with narrow pore size distribution [28]. The diameter of mesopores (D_p) in unmodified material was 15.72 nm (in Table 1 and Fig. S3b). After modification, the mesopore size decreased. In particular, the mesopore diameter of HPS18 (17.65 nm) was obviously larger than the others. The abnormal result could be explained through the effect of long-chain alkyl groups [29]. In addition, the mesopore volumes (V_p) of modified materials were smaller than HPS (1.88 cm^3 g^{-1}), but still larger than many other reported hybrid mesoporous silica materials [30–34]. The lager pore volume was beneficial for adsorbing and storing PCM molecules. The slightly