

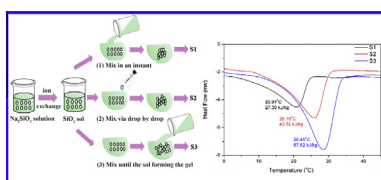
# The dependence of phase change enthalpy on the pore structure and interfacial groups in hydrated salts/silica composites via sol–gel



Yuping Wu, Tao Wang\*

State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

## GRAPHICAL ABSTRACT



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## ABSTRACT

It was found that the procedures for incorporating hydrated salts into silica, including mixing with sol in an instant (S1 procedure), mixing with sol via drop by drop (S2 procedure) and mixing until the sol forming the gel (S3 procedure), had pronounced effects on the phase change enthalpy of hydrated salts/silica composite via sol–gel process. The discrepancy of phase change enthalpies of the composites with the same content of hydrated salts can be as high as 40 kJ/kg. To unveil the mechanism behind, the pore structure of silica matrix and interfacial functional groups were investigated extensively. It was revealed that different incorporation procedures resulted in distinct pore structure of silica matrix and different intensities of interfacial Si–OH groups. The S3 procedure was beneficial to induce the silica matrix with bigger pore size and fewer Si–OH groups. Consequently, the phase change enthalpy of the hydrated salts/silica composite prepared by this procedure was the highest because of its lower size confinement effects and weaker adsorption by Si–OH groups. This study will provide insight into the preparation of shape-stabilized phase change materials for thermal energy storage applications.

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## 1. Introduction

Latent heat storage using phase change materials (PCMs) has attracted increasing interests in thermal energy storage, as it can provide higher energy storage density within smaller temperature swing [1–3]. Recently, researchers focus on the preparation of shape-stabilized PCMs with high energy storage density, good thermal reliability and good thermal conductivity by means of microencapsulation [4–6], impregnation [7–9] and sol–gel [10,11].

Sol–gel is a process that involves a sequence of hydrolysis and condensation reactions of precursors, during which various inor-

ganic or organic species can be trapped inside the pores of the formed three dimensional networks [12]. The sol–gel route allows the preparation of sophisticated materials without the use of extreme thermal or chemical conditions. Therefore, sol–gel method has been widely used in the preparation of shape-stabilized PCMs [13,14]. However, it should be noted that although the mesopores formed through sol–gel approach can effectively inhibit the leakage of the PCMs due to the capillary force, the phase change behavior of PCMs in mesopores is much more complicated and quite different from that of the bulk PCM. Numerous literatures [15–18] have reported the observed phase change temperature shift and enthalpy decrease in porous media. The changes are generally considered to result from the pore size distribution, geometrical shape of pore, network inter-connection of

\* Corresponding author. Fax: +86 10 62784877.

E-mail address: taowang@tsinghua.edu.cn (T. Wang).

pore, and interactions between PCM and pore surface [19,20]. Current researches are limited to the elucidation of the confinement effects on the phase change behaviors of the PCMs. Up to now, there have not been any reports about the effects of the incorporation procedures, by which the PCM was introduced into the matrix, on phase change enthalpies of PCMs. Nevertheless, it is of significant importance for guiding the preparation of shape-stabilized PCMs with good performance.

In this work, we aimed to reveal the relationship between the incorporation procedures of hydrated salts into silica and the phase change enthalpies in terms of the pore structure of the silica matrix and the interfacial functional groups. The pore structure of silica matrix was investigated by nitrogen adsorption analyzer and scanning electron microscopy (SEM). The interfacial functional groups were characterized by Fourier transform infrared spectroscopy (FT-IR) and solid-state nuclear magnetic resonance (NMR). The thermal weight loss of interfacial functional groups was evaluated by thermogravimetric analysis (TGA). Phase change properties were determined by a differential scanning calorimetry (DSC).

## 2. Experimental section

### 2.1. Materials

Sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , AR), sodium metasilicate nonahydrate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , AR), sodium phosphate dodecahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , AR) were purchased from Beijing Modern Eastern Fine Chemicals, China.

Na-type cation exchange resin (732) was obtained from Beijing Modern Eastern Fine Chemicals, China. It was pretreated by immersing in sodium hydroxide (3 wt%) and hydrochloric acid (5 wt%), so that it can be transformed into the H-type cation exchange resin for ion exchange with  $\text{Na}^+$ .

### 2.2. Preparation of hydrated salts/silica composites by three incorporation procedures

$\text{Na}_2\text{SiO}_3$  was chosen as the silica precursor, and a mixture of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in mass ratio of 4:1 (denoted as hydrated salts in the following) was used as the phase change material. Three incorporation procedures were adopted for the preparation of hydrated salts/silica composites. Typical procedures

were depicted in Scheme 1. First, the pH of 20 mL of  $\text{Na}_2\text{SiO}_3$  solution (0.5 mol/L) was adjusted to 6.5 by introducing the H-type cation exchange resin to exchange  $\text{Na}^+$  for  $\text{H}^+$ . Then, the mixture of molten hydrated salts, which was firstly heated by a thermostat water bath at 40 °C, was incorporated into the  $\text{SiO}_2$  sol by three means in the following:

- (1) The mixture of molten hydrated salts was added into the  $\text{SiO}_2$  sol in an instant to make a rapid mix at a stirring rate of 500 rpm. After that, the solution was stirred for another 1 min and then aged at 30 °C for 2 h.
- (2) The mixture of molten hydrated salts was added into the  $\text{SiO}_2$  sol with the speed of 2.8 mL/min drop by drop at a stirring rate of 500 rpm. After that, the solution was stirred for another 1 min and then aged at 30 °C for 2 h.
- (3) Subsequently, 10 mL of  $\text{NH}_4\text{HCO}_3$  (0.01 g/mL) solution was added into  $\text{Na}_2\text{SiO}_3$  solution at 30 °C to promote the  $\text{SiO}_2$  sol to form the gel. After aging for 5 h, the generated gel was washed three times with deionized water to remove the remaining  $\text{NH}_4\text{HCO}_3$ . Then, the mixture of molten hydrated salts was poured into the gel and kept at 30 °C for 48 h to guarantee that the penetration of hydrated salts into the gel was complete.

Finally, all the three composites were dried at 10 °C for 48 h. The hydrated salts/silica composites prepared by three incorporation procedures above were denoted as S1, S2 and S3, respectively.

### 2.3. Characterization

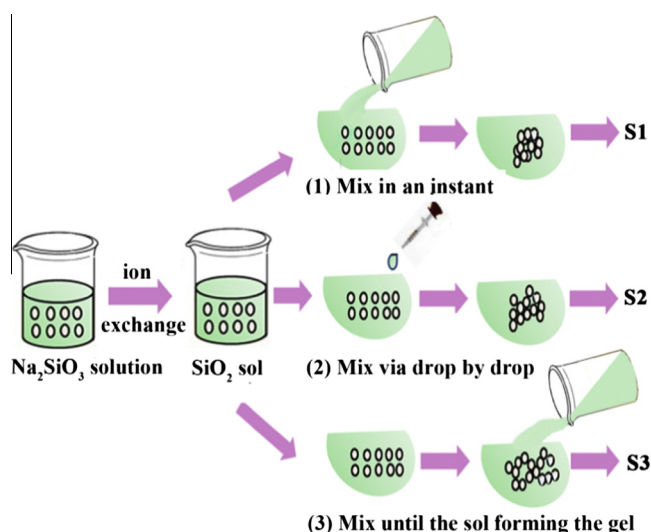
To obtain the silica matrix, the hydrated salts/silica composites were immersed in deionized water repeatedly until the whole hydrated salts were completely removed. After that, the silica matrix was dried at room temperature until it kept the weight constant. The pore structure of the silica matrix was characterized by a nitrogen adsorption analyzer (Autosorb-1-C, Quantachrome, USA) at liquid nitrogen temperature. The pore size distribution, the average pore diameter and the pore volume were calculated by the Barrett Joyner and Halenda (BJH) method on the basis of the adsorption–desorption isotherms. The morphology of the silica matrix was observed by a scanning electron microscopy (SEM, JSM7401, Shimadzu, Japan). The samples were coated with gold and observed with an accelerating voltage of 3.0 kV. The thermal weight loss of silica matrix was measured by a thermo analyzer instrument (TGA, STA409PC, Netzsch, Germany) from 25 to 1000 °C at a rate of 10 °C/min under the nitrogen atmosphere at a flow rate of 20 mL/min.

The interfacial functional groups of the hydrated salts/silica composites was studied by Fourier transform infrared spectroscopy (FT-IR, Tensor 27, Bruker, Germany) in the wavenumber range of 400–4000  $\text{cm}^{-1}$  at room temperature. The samples were mixed with KBr and pressed into a pellet before analysis. Cross-polarization solid-state  $^{29}\text{Si}$  NMR spectra of the hydrated salts/silica composites were obtained by nuclear magnetic resonance (NMR, AV 300, Bruker, Germany) at a frequency of 5 kHz.

Phase change properties of the hydrated salts/silica composites were determined by a differential scanning calorimetry (DSC, Q2000, TA, USA). The samples of approximately 10 mg were sealed in an alumina pan and heated from –5 to 50 °C at a rate of 5 °C/min in purified nitrogen atmosphere.

## 3. Results and discussion

Fig. 1 displayed the DSC spectra of hydrated salts/silica composites prepared by three different incorporation procedures. It was



**Scheme 1.** Schematic illustration of three procedures for incorporating hydrated salts into silica.

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