The anti-supercooling effect of surface-modified nano-scaled SiO$_2$ in hydrated salts phase transition system

Xiaolin Wu$^1$, Yihai Wang$^1$, Rong Sun$^{1*}$, Maobai Lai$^1$, Ruxu Du$^{1,2}$ and Zhijun Zhang$^3$

$^1$ Shenzhen Institute of Advanced Integration Technology, Chinese Academy of Sciences and The Chinese University of Hong Kong, Shenzhen 518067, China;

$^2$ The Chinese University of Hong Kong, Hong Kong SAR;

$^3$ Henan University, Henan 475004, China

Email: rong.sun@siat.ac.cn (Corresponding author)

Abstract. Phase change characteristics of hydrate salt were analyzed for a system consisting of three types of SiO$_2$ nano-particles doped phase change materials (PCMs). By using the three nano-particles of Aerosol SiO$_2$, RNS-A SiO$_2$ and Liquid phase SiO$_2$, the surface effect of the interaction between nano-particles and hydrate salts was investigated. The time-temperature curves and Differential Scanning Calorimeter (DSC) testing results showed that Aerosol SiO$_2$ had the most effective and stable performance as the nucleators for hydrate salts. The analysis of FT-IR showed that there were strong characteristic hydr oxyl bonds on the surface of Aerosol SiO$_2$. And the designed hydroxyl controllable silica gel system could prove the effect of hydroxyl bonds on suppressing supercooling of hydrate salts. It was concluded that supercooling of hydrate salts could be easily suppressed by the nano-additives with high specific surface area and strong polar hydroxyls in the surface. The ion-exchange attraction between hydroxyls and hydrate salts might mainly result in the supersaturation of hydrate salts in the interface of nano-particles. And then the supercooling of hydrate salts could be suppressed. The theoretical analysing model based on interionic attraction is a novel approach for investigating the nucleation of hydrate salts. And this result might provide a potential low-cost approach for the applications of nano-additivs in building energy storage and coolant.

1. Introduction

Hydrate salts, a type of low cost phase change materials (PCMs), have attracted more attention owing to its high volumetric energy storage density. However, their applications are limited by supercooling.

There are two kinds of nucleation for hydrate salts: homogeneous nucleation which involves the formation of nucleation particles in the liquid phase from the PCMs itself and heterogeneous nucleation which involves the formation of nucleation particles on foreign particles or sites [1]. Homogeneous nucleation always has more serious supercooling than heterogeneous nucleation. So, heterogeneous nucleation is the main method to suppress supercooling. In order to solve the problem of supercooling, many studies about heterogeneous nucleation have been done. Telkes [2] introduced
classic isomorphous and isotypic nucleators, which have crystal structures and lattice parameters nearly identical with, the substrate salts to control supercooling of hydrate salts. Lane [1] introduced epitaxial nucleation, which had different crystal morphology with substrate. It had preferred surface characteristics, which were suitable for deposition of the substrate crystal. However, there is little work about the effect of nano-additives on the phase change characteristics of hydrate salts.

In previous researches, nano-additives, such as nano-tube [3], nano-fibre [4], etc., which had very high surface to volume ratio, very low thermal resistance, great compatibility and light weight [5,6] were used in PCMs for improving the thermal conductivity [7-10] of organic PCMs. The measured values of latent heat for wax with SWCNT showed a good enhancement over the latent heat of pure wax. A maximum enhancement of approximately 13% was observed for the wax/SWCNT composite corresponding to 1% loading of SWCNT.

Some work had been done about the effect of nano-additives on organic PCMs. However, the effect of nano-additives with different surface characteristics on hydrate salts is not clear. In our present work, nano-SiO$_2$ powders with three kinds of surface characteristics were investigated to enhance thermal performance of hydrate salts. Different mass ratios of the three types of nano-scaled SiO$_2$ were added into saturated hydrate salts solution. The thermal characteristics of the new nanocomposites were tested to study the effect of the nano-scaled additives on hydrate salts. And a comparative study was performed to study the effect of nano-SiO$_2$ surface characteristics on the enhancement of the hydrate salt thermal performances. At the end, a novel theoretical analyzing model based on interionic attraction was introduced to illuminate the nucleation of nano-particle doped hydrate salts. This result can provide a latent low cost solving method to suppress supercooling and improve thermal performances for the applications in building energy storage and coolant.

2. Experimental method

Three types of SiO$_2$ were used as the additives. They were Aerosol SiO$_2$ prepared by gas phase method with lots of active hydroxyl bonds in the surface, RNS-A SiO$_2$ which is a kind of surface modified SiO$_2$ with reactable bonds like double bonds, hydroxyl bonds, amidogen bonds, etc. in the surface and Liquid SiO$_2$ prepared by liquid phase method. The sizes of them were about 12nm, 40nm and 50nm, respectively. The phase change materials used contained Na$_2$SO$_4$·10H$_2$O, Na$_2$HPO$_4$·12H$_2$O and Na$_2$S$_2$O$_3$·5H$_2$O. The nano-additives doped hydrate salt samples were subjected to mixing by using mechanical stirring for about 5 min to obtain a well dispersed suspension.

We made a simple device to record the temperature in time. The samples were placed on test tubes with a thermal couple in the centre. The tubes were initially heated to 40 °C to reach the liquid phase. Then the tubes were immersed into a water cooler. The temperature histories were recorded using a multipoint recorder (IDAQ-8018+) and the data were stored in a computer via an RS-232 port.

In order to analyze the phase transition in microscopic level, Differential Scanning Calorimeter (DSC) was used with nitrogen atmosphere. Samples were placed in a sealed aluminium pan with a mass of about 30.00 mg. The pan was placed in DSC and analyzed from -20 to 45 °C with a linear heating rate of 7 °C/min. The nitrogen flow rate was 50 ml/min. The accuracy of the DSC temperature measurements was ± 0.02 °C. The latent heat was calculated as the total area under the peaks of solid-liquid transitions.

To study the microstructure of the samples, we used Transmission Electron Microscopy (TEM), x-ray Diffraction (XRD) and Fourier Transformation Infrared (FT-IR) Spectroscopy. For TEM analysis, the surface of sample was first coated by gold. TEM images were acquired on a JEM-2010 microscope at 22 °C. For XRD curves, powder samples were put into the sample room directly. Then the microstructure characteristics could be gotten. For FT-IF spectroscopy, the samples were prepared by pressing potassium bromide troche KBr at 10 °C.

3. Results and discussion
3.1. Structure of the three types of SiO₂ nano-particles

TEM and XRD were used to test the microstructure characteristics of the three nano-particles. Figures A-C in figure 1 are the TEM images of Aerosol SiO₂, Liquid SiO₂ and RNS-A SiO₂ nano-particles. No regular morphology of the three nano-particles could be seen from these figures. The size of Aerosol SiO₂ is smaller than the other two types of SiO₂. Figure D is the typical XRD result of these three types of nano-particles. It shows that these nano-particles have amorphous structures.

![Figure 1](image)

Figure 1. (A) TEM image of Aerosol SiO₂ nano-particles, (B) TEM image of Liquid SiO₂ nano-particles, (C) TEM image of RNS-A SiO₂ nano-particles, (D) XRD of SiO₂ nano-particles

3.2. Time-temperature curves of hydrate salts with three types of SiO₂ nano-particles

The three nano-SiO₂ particles mentioned above were used as additives of sodium sulfate decahydrate. With the adding of Liquid SiO₂ and RNS-A SiO₂, the solutions of hydrate salts were both chaotic suspensions. However, the hydrate salts with Aerosol SiO₂ was a colloid system, which was caused by lots of hydroxyl bonds in the surface of the SiO₂. Table 1 summarizes the experimental results of hydrate salts with different weight percentage of the three nano-particles.

As shown in table 1, with the increasing of weight percentage, the additives of Liquid SiO₂ and RNS-A SiO₂ can suppress supercooling of hydrate salts until their weight percentages are about 7% or more. But for Aerosol SiO₂, even 0.7% is enough to suppress supercooling of hydrate salts. This result indicates that the improvement of concentration caused by increasing the percentage of additive is not the key reason for suppressing supercooling of hydrate salts.
Table 1. Summaries of the experimental results: supercooling situation of hydrate salts with different weight percentage of the three types of nano-particles

| Additives/weight percentage | 0.7%   | 1.2%   | 3.3%   | 5%    | 7%    |
|-----------------------------|--------|--------|--------|-------|-------|
| Liquid SiO₂                 | supercooling | supercooling | supercooling | supercooling | Phase change Temperature: 25°C |
| RNS-A SiO₂                  | supercooling | supercooling | supercooling | supercooling | Phase change Temperature: 29°C |
| Aerosol SiO₂                | Phase change Temperature: 26~29°C | Phase change Temperature: 26~29°C | Phase change Temperature: 26~29°C | Phase change Temperature: 26~29°C |

Figure 2 shows time-temperature (t-T) curves of hydrate salts without additives and with three nano-SiO₂ during cooling process. Figure 2 (a) corresponds to the t-T curve of hydrate salts without additives. There is serious supercooling with the phase change temperature about 28°C. Curves 1 to 3 in figure 2 (b) indicate the phase change of hydrate salts with RNS-A SiO₂, Aerosol SiO₂ and Liquid SiO₂ nano-additives. The weight percentages of them are all about 7%. From the three curves, there is only one successful phase change process without supercooling. The phase change temperatures are about 29°C, 28°C and 25°C, respectively. Additives of RNS-A SiO₂ and Aerosol SiO₂ show better effect on hydrate salts.

![Figure 2. t-T curves of sodium sulfate solution (a) without additives (b) with three nano-additives](image-url)

3.3. DSC comparative results of hydrate salts with three types of the SiO₂ nano-particles

From figure 2 (b), it still can be found that at the beginning process before phase change happening, the slope values of the curves are different. The slope values of the curves of hydrate salts with Liquid SiO₂ and RNS-A SiO₂ are nearly the same. They are larger than the slope value of hydrate salts with Aerosol SiO₂. That means the heat transfer rate of hydrate salts with Liquid SiO₂ and RNS-A SiO₂ nano-particles is higher than with Aerosol SiO₂ nano-particles.
The precise DSC testing method was used to provide more detail phase behaviour in the thermal storage media. Figure 3 are the DSC curves of saturated sodium sulphate hydrate with and without nano-particles during heating process. Curve 1, 2 and 4 are the hydrate salts with the same weight percentage of additives of Liquid SiO₂, RNS-A SiO₂ and Aerosol SiO₂, respectively. Curve 3 is the hydrate salts without additives.

![DSC curves of saturated sodium sulfate hydrate during heating process](image)

**Figure 3.** DSC curves of saturated sodium sulfate hydrate during heating process

In figure 3, the phase change temperature of hydrate salts with Aerosol SiO₂, Liquid SiO₂ and RNS-A SiO₂ are 28.40°C, 25.99°C and 23.05°C with the latent heat of 103.60J/g, 81.11J/g and 82.51J/g, respectively. The heat charging peak is caused by the melting of eutectic of sodium sulphate decahydrate-water [11]. Compared with curve 3 and connected with the analysis results in figure 2, it can be concluded that with the adding of Aerosol SiO₂, the latent heat of hydrate salts can be improved and the phase change process is stable. But for Liquid SiO₂ and RNS-A SiO₂, even they can increase the heat transfer of hydrate salts, their effects on latent heat of hydrate salts are small, even worse. And the phase change process is unstable.

3.4. **Surface properties of the three types of nano-particles**

Figure 4 gives the FT-IR spectrum of the three types of nano- SiO₂ particles. Curves 1 to 3 are the FT-IR spectrum of Aerosol SiO₂, Liquid SiO₂ and RNS-A SiO₂, respectively.
According to the results above, the characteristic peaks of the three types of nano-particles are in the same sites. The FT-IR spectrum of the nano-additives indicates the existence of three main absorption bands at 468.01, 802.13 and 1107.03 cm\(^{-1}\) which can be assigned to bending vibration, symmetric and asymmetric stretching of SiO\(_2\) [12,13]. The band at 1654.03 cm\(^{-1}\) is associated to the bending of the absorbed H\(_2\)O molecules [12]. The characteristic band for stretching (OH) groups is found at 3447.67 cm\(^{-1}\) [14]. It can conclude that the surface chemical bonds characteristics of the three nano-particles are nearly the same. For Aerosol SiO\(_2\), there are strong characteristic hydroxyl bonds on its surface.

3.5. Effects of nano-additive Aerosol SiO\(_2\) on other saturated hydrate salts

Figure 5 are the t-T curves of (a) Na\(_2\)HPO\(_4\) \cdot 12H\(_2\)O and (b) Na\(_2\)S\(_2\)O\(_3\) \cdot 5H\(_2\)O with about 2% weight percentage of Aerosol SiO\(_2\). There is no supercooling during their solidifying process. That means the nano-additives of Aerosol SiO\(_2\) is still suitable for some other hydrates to suppress supercooling.

3.6. A possible mechanism of anti-supercooling in our systems
To conclude, the nucleation processes of hydrate salts with nano-additives belong to heterogeneous nucleation. The improvement of heat transfer and concentration of hydrate salts should not be the most effective parameter for suppressing supercooling. According to the studies of nano-additive effects on organic PCMs [3,4], the interaction between the surfaces of nano-additives and PCMs should be surface dependent. The three nano-additives are all amorphous structures with nearly the same surface chemical bonds. However, Aerosol SiO₂ has higher specific surface area with more and stronger active hydroxyl bonds on the surface. We first presumed that the effect of hydroxyl bonds was the key effective parameter.

To prove the effect of hydroxyl bonds, the amorphous silica gel system was designed. Saturated hydrate salts were confined in it by in-situ polymerization. The changing of its microstructure controlled the situation of hydroxyls in the surface of the gel.

Figure 6 (a) shows the molecular structural characteristics of silica gel with hydrate salts by FT-IR spectrum. The absorption band at 1099.43 cm⁻¹ is stretching groups of Si-O. The band at 1618.22 cm⁻¹ is associated to the bending of the absorbed H₂O molecules. At 2103.77 cm⁻¹, the absorption bond may be the vibrating groups of Si=O. The characteristic band for stretching (OH) groups is found at 3477.66 cm⁻¹. The characteristic bond is wide. It indicates that free hydroxyls and associated hydroxyls exist at the same time. Employing NMR techniques, Sindorf and Maciel [15,16] have shown that the single hydroxyl group is likely to be the most prolific.

In this solid-gel system, the supercooling of hydrate salts could not be suppressed. That could be proved by curve 2 of the t-T curves in figure 6 (b). But after the solid gel stirred homogeneously, it changed into white liquid homogenous suspending solution of gel particles. Then the supercooling of hydrate salts could be suppressed like curve 1 in figure 6 (b). After staying the suspending solution for some time, it changed into solid gel again and it still could suppress supercooling of hydrate salts like curve 1 in figure 6 (b). During the stirring process, a lot of Si-O-Si bonds of silica gel were broken up and changed into lots of single or more silanol groups on the surface of silica gel [15,16]. The regelling of silica gel was caused by the physical hydrogen bond absorption instead of lots of Si-O-Si bonds prepared by condensation reaction. So, there were still a lot of free hydroxyl bonds on the surface. All the analysis above indicates that the effect of hydroxyl bonds is the key effective parameter.

From the information of solid surface absorption and surface characteristics of silica gel [17], the absorption relationship between hydroxyl bonds on kinds of SiO₂ surface and salt solution belongs to polar absorption. The surface silanol groups are ionized in aqueous solutions of electrolytes:

\[ \equiv Si - OH \leftrightarrow Si - O^- + H^+ \] (1)
The metal cations can be absorbed on the surface:

\[ Si - OH + M^{n+} \Leftrightarrow Si - OM^{(n-1)+} + H^+ \]  \hspace{1cm} (2)

Another possible mechanism of hydroxyl bonds effect can be complex surface-induced hydrolysis:

\[ Si - OH + M^{n+} + H_2O \Leftrightarrow Si - OM^{(n-1)+}OH^- + 2H^+ \]  \hspace{1cm} (3)

So, the main reason that nano-SiO$_2$ can suppress supercooling of hydrate salts should be caused by the ion-exchange absorption relationship between strong polar functional -OH bonds and ions of hydrate salts. The magnitude of the free hydroxyl bonds should be enough to provide sufficient congregation of hydrate salts on the interface. For the three nano-additives, Aerosol SiO$_2$ has higher specific surface area and lots of free hydroxyls on the interface, which are more suitable for the congregation of ions of sodium sulphate. So, only small weight percentage of it can suppress supercooling of hydrate salts successfully.

4. Conclusion

By using three different types of SiO$_2$ nano-partiles as the anti-supercritical agents, we investigated the surface effect of the interaction between nano-particle and hydrate salts during the phase changing process. Aerosol SiO$_2$ showed the most effective and stable performance as the nucleators for hydrate salts. Supercooling of hydrate salts can be easily suppressed by the nano-additives, which have high specific surface area and strong polar hydroxyl bonds in the surfaces. Through the ion-exchange absorption between the ions of nano-additivs and hydrate salts, the supersaturation of hydrate salts in the interface of nano-additives can be obviously changed. Then the phase changing properties were improved by increasing phase transition efficiency of hydrate salts. These results might provide a potential low-cost approach for the applications of nano-additives in building energy storage and coolant.

**ACKNOWLEDGEMENT:** The presented research is partially supported by a research grant from Shenzhen/ Hong Kong Innovation Circle Fund.

**References**

[1] Lane G A 1992 *Solar energy materials and solar cells* 135-160 27
[2] Telkes M 1952 *Ind. Eng. Chem.* 1308-1310 44
[3] Shaikh S, Lafdi K and Hallinan K 2008 *Journal of Applied Physics* 094302-1-6 103
[4] Elgafy A and Lafdi K 2005 *Carbon* 3067 – 3074 43
[5] Xavier P Y, Regis O and Sylvain M 2001 *Int. J. Heat Mass Transfer* 2727 – 2737 44
[6] Mesalhy O, Lafdi K and Elgafy A 2006 *Carbon* 2080-2088 44
[7] Bugaje I M 1997 *Int. J. Energy Res.* 759-766 21
[8] Erk H F and Dudukovic M P 1996 *AIChE J.* 791-808 42
[9] Hasnain M S 1998 *Energy Conversion and Management* 1127 – 1138 39
[10] Jianfeg W, Ouyang Y and Chen G 2001 *Int. J. Energy Res.* 439 – 447 25
[11] Ashbee E and Ashbee G H K 1985 *Journal of Materials Science Letters* 249-250 4
[12] Bruni S, Cariati F, Casu M, Lai A, Musinu A, Piccaluga G and Solinas S 1999 *Nanostruct. Mater.* 573–586 11
[13] Innocenzi P 2003 *J. Non-Cryst. Solids* 309–319 316
[14] Moreno M E, Zayat M, Morales P M, Serna J C, Roig A and Levy D 2002 *Langmuir* 4972–4978 18
[15] Sindorf W D and Maciel E G 1983 *J. AM. Chem. Soc.* 1487-1493 105
[16] Sindorf W D and Maciel E G 1983 *J. Phys. Chem.* 5516-5521 87
[17] Gordeeva G L, Gubarev V A, Plyasova M L, Malakhov V V and Aristov Y A 2005 *Kinetics and Catalysis* 736-742 46