Synthesis and characterization of CaO@SiO₂ nanoparticle for chemical thermal storage

Chika TAKAI YAMASHITA, Jongmin SO and Masayoshi FUJI[†]

Advanced Ceramics Research Center, Nagoya Institute of Technology, 3-101-1 Honmachi, Tajimi, Gifu 507-0033, Japan

Preparation of CaO core-SiO₂ shell nanoparticles as a chemical thermal storage through hydration/de-hydration of CaO/Ca(OH)₂ was proposed. Firstly, SiO₂ was coated on CaCO₃ template surface using sol-gel route and then the core-shell particles were heated at 700°C to form CaO@SiO₂ nanoparticle by de-carbonization. A thermal storage performance of the CaO@SiO₂ was confirmed by a thermogravimetry (TG) analysis and the result was compared with that of as-received CaCO₃. The heating program was performed as following steps as (i) at 700°C for 30 min for de-carbonization under nitrogen (N₂) atmosphere, (ii) at room temperature for 60 min for hydration under water vapor, and (iii) at 500°C for de-hydration under N₂. By repeating of (ii) hydration/(iii) de-hydration cycle, effect of the number of cycles on thermal storage ability was investigated. An efficiency of thermal storage was defined as difference in weight change between hydration/de-hydration reactions. For the as-received CaCO₃ nanoparticles, with increase in the number of cycles, the thermal storage performance gradually decreased. The microscopic results showed that the heating cycles induces coalescence of CaCO₃ nanoparticles and that decreases specific surface area. On the other hands, efficiency of thermal storage of CaO@SiO₂ didn't reach theoretical value because CaCO₃ didn't completely transform into CaO owing to SiO₂'s thermal insulation ability. By decreasing SiO₂ coating thickness, the thermal storage performance of CaO@SiO₂ was improved. The microscopic results showed that the SiO₂ coating prevented from coalescence of CaCO₃ nanoparticles.

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1. Introduction

A core-shell particle, in which a shell material is coated on a core particle, was developed to protect core materials, to improve its functionality, etc. Silicon dioxide, SiO₂, is often utilized as shell materials, owing to have rather good affinity with lots of core materials such as titanium dioxide, gold, polystyrene, etc.¹⁻³⁾ In addition, microstructure of a SiO₂ shell such as thickness, porosity, density can be easily controlled by adjustment of sol-gel reacting conditions.^{1,4)} In order to improve thermal storage performance of CaO, synthesize and characterization of CaO core@SiO₂ shell nanoparticles were focused.

The thermal storage technology is categorized into following three; using sensible heat with temperature change, latent heat with phase change, and chemical thermal storage with chemical thermal energy. The chemical thermal storage technique has lots of merits such as having large thermal storage density, high reaction rate, long-term thermal storage, and so on. As one of the techniques, CaO/Ca(OH)₂ using their reversible hydration/de-hydration reactions has been reported.⁵⁾ The reversible reaction is shown in Eq. (1). When heat around 400–500°C is applied to Ca(OH)₂, de-hydration reaction occurs. By separately storage of the formed CaO and water vapor, heat can be stored. When CaO is contacted with water vapor, heat can be released by the hydration reaction.

The chemical thermal storage using CaO/Ca(OH)₂ has excellent because of high reaction rate, high thermal storage density,

and good reversible performance, however, the problem that degradation of thermal storage performance with repeatedly hydration/de-hydration cycles still remains.

A slightly volume change occurs during the reversible transformation between CaO and Ca(OH)₂, which promotes deformation and coalescence of these materials. This decrease in specific surface area induces the performance degradation. In order to improve performance, immobilization of particles as thermal storage materials on a carrier material was reported. Watanabe developed CaO supported porous carbonaceous materials through reduction of polymeric carrier and Ca(NO₃)₂.⁶⁾

In this study, synthesis of CaO@SiO₂ nanoparticles for thermal storage materials was proposed. SiO₂ has thermal resistance during de-hydration process of Ca(OH)₂. In addition, high surface area of CaO nanoparticles can be kept by SiO₂ coating on CaO. As well known, CaO easily transforms into CaCO₃ by reaction with CO₂ in the air. It is difficult to make SiO₂ coating on CaO directly. Here, CaCO₃ is used as a template. According to our earlier results, CaCO₃ have good affinity with SiO₂. Additionally, there are small pores exist in the SiO₂ shell which is formed by sol-gel reaction. Water vapor can penetrate through the pores to react with CaO.⁷⁾ After SiO₂ coating on CaCO₃, heating treatment is conducted to obtain CaO@SiO₂ by de-carbonization. The SiO₂ coating could suppress volume change before/after de-carbonization and the resultant CaO has large surface area to react with water vapor.

The transformation of CaCO₃@SiO₂ to CaO@SiO₂ was analyzed by an X-ray diffraction (XRD) and the thermal storage performance of CaO@SiO₂ was confirmed by thermo-gravimetric (TG) analysis. The results were compared with that of as-received CaCO₃.

[†] Corresponding author: M. Fuji; E-mail: fuji@nitech.ac.jp

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2. Experimental procedure

Calcium carbonate (CaCO₃, Brilliant-1500) with average size of 150 nm was used as a template and kindly provided by SHIRAIISHI CALCIUM KAISHA, LTD. A 1.65 g of CaCO₃ was dispersed in ethanol (12.0 ml, purity: 99.5%) with distilled water using an ultrasonication for 10 min. For SiO₂ coating, 1.0 ml of 25% ammonia (Wako Pure Chemical Industries, Ltd.) and tetraethoxysilane (TEOS, 0.5, 1.0 ml, Wako Pure Chemical Industries, Ltd.) were added in the suspension and stirred for 2 h using a magnetic stirrer. The 2-hour-reaction is enough for TEOS consumption according to our earlier result.⁸⁾ The suspension was washed with ethanol three times to remove ammonia. Then the precipitates were dried at 80°C for 2 h under vacuum. The CaCO₃@SiO₂ particles were heated at 700°C in a furnace for 60 min as mentioned below.

To confirm crystal structure change before/after heating, an X-ray diffractometry (XRD, Ultima IV, Rigaku Cooperation) was used with range of 3–70°. For observation of core-shell particles, the obtained particles were dispersed in ethanol and dropped on a copper microgrid. The samples were observed by a scanning electron microscope (SEM, JSM-7600F, JEOL Ltd.). For reference, as-received CaCO₃ was heated in the same way. For observation, CaCO₃ nanoparticles were immobilized on copper plate with carbon tape and coated with osmium.

An efficiency of thermal storage was characterized using difference in weight change between hydration and de-hydration of the samples. The sample weights during reactions were recorded using thermo-gravimetry (TG, TG-8120, Rigaku Cooperation). The samples were put in an Al₂O₃ pan. **Figure 1** shows the heating program using TG. Firstly, temperature is increased up to 700°C (15°C/min) and kept for 30 min for de-carbonization [Fig. 1(i)]. Then it was cooled down to room temperature (20°C/min) and kept for 60 min for the first hydration [Fig. 1(ii)]. For the hydration, water vapor/nitrogen mixture was flowed at rate of 0.3 ml/min. For de-hydration, it was heated up to 500°C [15°C/min, Fig. 1(iii)]. The steps of (ii) and (iii) are one cycle for hydration/de-hydration. The second hydration starts as shown in Fig. 1(iv). Except for the hydration, nitrogen gas was flowed at rate of 0.3 ml/min.

3. Results and discussion

Figure 2(a) shows weight loss of as-received CaCO₃ with increase in temperature up to 900°C (10°C/min) to investigate behavior of de-carbonization. The weight loss started at around 600°C and completely finished at around 750°C. The weight loss was around 44%, which correspond to difference between CaCO₃

(100.09 g/mol) and CaO (56.07 g/mol). The sample was expose to water vapor for enough time and heated in the same way. The weight loss of the sample was shown in Fig. 2(b). The weight loss started at less than 400°C and completely finished at 450°C. The weight loss of the sample was 24%, which corresponds to difference between Ca(OH)₂ (74.09 g/mol) and CaO (56.07 g/mol). From these results, for de-carbonization in this experiment, the heating temperature was fixed as 700°C, which seems the lowest energy not to promote coalescence of CaCO₃ nanoparticles each other. For de-hydration, the temperature was fixed as 500°C.

As a reference, thermal storage performance of as-received CaCO₃ was characterized. **Figure 3** shows weight change of CaCO₃ with four hydration/de-hydration cycles by TG. The first large weight loss [Fig. 3(i)] caused by de-carbonization (at 700°C

Fig. 2. TG analysis of (a) de-carbonization of CaCO₃ and (b) de-hydration of Ca(OH)₂.

Fig. 1. Heat cycle pattern of (i) de-carbonization, (ii) hydration, (iii) de-hydration, and (iv) 2nd hydration.

Fig. 3. Thermal storage performance of as-received CaCO₃ during (i) de-carbonization, (ii) hydration, and (iii) de-hydration.

Fig. 4. Weight change during (a) hydration and (b) de-hydration reactions at each cycle as shown in Fig. 3.

Fig. 5. SEM images of (a) CaCO_3 , (b) de-carbonized sample at 700°C for 30 min, (c) hydrated/de-hydrated sample, and (d) 2-time-hydrated/de-hydrated sample.

for 30 min) was 43.0% which roughly agreed with theoretical value (44.02%). When the formed CaO was exposed to water vapor at room temperature for 60 min, the weight rapidly increased [Fig. 3(ii)] by hydration. Then the weight sharply decreased by heating at 500°C [Fig. 3(iii)] by de-hydration. The area which was filled with diagonal line was thought to be water adsorption on the formed Ca(OH)_2 . The quantity between two breaking lines was weight change during hydration/de-hydration, which can be defined as an efficiency of thermal storage of the as-received CaCO_3 nanoparticles (E_{CaCO_3}).

To investigate effect of number of hydration/de-hydration cycles on E_{CaCO_3} , Fig. 4 shows weight change at each (a) hydration and (b) de-hydration reactions as shown in Fig. 3. With increase in the number of cycle, weight changes at both hydration and de-hydration gradually decreased. Figure 5 shows SEM observations of (a) as-received CaCO_3 , (b) de-carbonized at 700°C for 30 min, (c) hydrated/de-hydrated sample, and (d) 2-time-hydrated/de-hydrated sample. As shown in Fig. 5(a), the as-received CaCO_3 nanoparticles have cubic structure with angular and the boundaries among particles were clearly shown. After de-carbonization at 700°C [Fig. 5(b)], the angles of particle were rounded off and the particle boundaries slightly disappeared. When de-hydration after hydration was finished [Fig. 5(c)], boundaries among particles almost disappeared and consolidation of particles was progressed. The 2-time-hydration induced further particle consolidation [Fig. 5(d)].

Fig. 6. Thermal storage performance of $\text{CaCO}_3@\text{SiO}_2$ with 1.0 ml of TEOS; (a) overall view and (b) enlarged view of boxed with breaking line in (a).

Considered from difference in density between CaO (3.35 g/cm^3) and Ca(OH)_2 (2.21 g/cm^3), obvious volume change occurs between hydration and de-hydration. The repeated heating process induces deformation and consolidation of particles, and decreasing specific surface area of CaCO_3 decreases its efficiency of thermal storage ability as shown in Fig. 4.

To overcome these problems, core-shell nanoparticles ($\text{CaCO}_3@\text{SiO}_2$) were prepared with addition of 1.0 ml of TEOS. The SiO_2 coating thickness on CaCO_3 was estimated as 4.76 nm which was calculated from weight of CaCO_3 and the added amount of TEOS. The $\text{CaCO}_3@\text{SiO}_2$ nanoparticle with 1.0 ml TEOS consists of 85.84% of CaCO_3 and 14.16% of SiO_2 by weight. Assuming that CaCO_3 completely transforms into CaO during heating, the sample weight ratio must decrease down to 62.25% by de-carbonization. Similarly, when CaO transforms into Ca(OH)_2 , the sample weight ratio increases up to 77.70% by hydration. The difference between them can be a theoretical efficiency of thermal storage, that is, 15.45%.

The experimental thermal storage performance of $\text{CaCO}_3@\text{SiO}_2$ with 1.0 ml TEOS was confirmed in the same way and shown in Fig. 6 [(a) overall view and (b) enlarged view]. As shown in overall view [Fig. 6(a)], the first large weight loss was observed by de-carbonization [Fig. 6(a)-(i)]. The weight loss was 38.04% at maximum, which roughly agreed with theoretical (37.75%). When the sample was exposed to water vapor, the weight gradually increased by hydration [Fig. 6(a)-(ii)]. Then the weight sharply decreased by heating at 500°C [Fig. 6(a)-(iii)]. As shown in the enlarged figure [Fig. 6(b)], the weight change between two breaking lines is efficiency of thermal storage (E_{CS1}) and the value was around 6%. The area filled with diagonal line is thought to be water adsorption on the sample.

The experimental E_{CS1} (6%) was less than half of theoretical (15.45%). It can be thought that CaCO_3 core didn't transform to

Fig. 7. Thermal storage performance of CaCO₃@SiO₂ with 0.5 ml of TEOS.

CaO completely. One of the reason is that thermal energy at 700°C didn't reach CaCO₃ core owing to SiO₂'s thermal insulation ability.⁹⁾

To decrease the thermal insulation effect of SiO₂ coating, the added amount of TEOS was decreased to 0.5 ml. The estimated SiO₂ coating thickness is 2.46 nm. The core-shell particle consists of 92.38% of CaCO₃ and 7.62% of SiO₂ by weight. Assuming that CaCO₃ completely transforms into CaO by heating at 700°C, the sample weight ratio decreases to 59.37% by de-carbonization and increases up to 76.0% by hydration. The theoretical thermal storage of this particles can be calculated as 16.63%.

The experimental thermal storage ability was analyzed by TG and shown in Fig. 7. Similarly, (i) the first large weight loss by de-carbonization, (ii) gradual weight increase by hydration, and (iii) sharply weight decrease by de-hydration were observed. The area filled with diagonal line can be excess weight increase by water adsorption on Ca(OH)₂. The weight change between the breaking lines was about 11%.

By decrease in TEOS amount, the thermal storage ability of CaO@SiO₂ was improved. However, the value (11%) didn't reach to the theoretical value (16.63%) yet. To investigate the reason, change in crystal structure of the core-shell particles during hydration/de-hydration reactions was characterized by XRD. Figure 8(a) shows XRD patterns of (i) as-received CaCO₃, (ii) CaCO₃@SiO₂, (iii) CaO@SiO₂ with 0.5 ml TEOS, and (iv) CaO@SiO₂ with 1.0 ml TEOS.

The as-received CaCO₃ [Fig. 8(a)-(i)] and CaCO₃@SiO₂ [Fig. 8(a)-(ii)] showed strong calcite structure. The broad peak around 20° derived from amorphous SiO₂ coating appeared in CaCO₃@SiO₂, CaO@SiO₂ with 0.5 and 1.0 ml of TEOS [Figs. 8(a)-(ii)–8(a)-(iv)]. After heating of CaCO₃@SiO₂ particles, CaCO₃ almost disappeared and CaO appeared [Figs. 8(a)-(iii) and 8(a)-(iv)].

As shown in enlarged view [Fig. 8(b)], with 0.5 ml of TEOS, CaCO₃ was almost consumed to transfer into CaO [Fig. 8(b)-(i)]. While with 1.0 ml of TEOS, small peak of CaCO₃ remained and Ca₂SiO₄ appeared with CaO [Fig. 8(b)-(ii)]. During heating at 700°C for 30 min, CaCO₃ core is decomposed into CaO with CO₂ generation. At the boundary between CaCO₃ core and SiO₂ coating, the formed CaO reacts with SiO₂. This reaction is not reversible, therefore, consumed CaO didn't contribute as thermal storage.

The estimated SiO₂ coating thicknesses are 2.46 (0.5 ml of TEOS) and 4.76 nm (1.0 ml of TEOS), respectively. In the thinner SiO₂ coating, CaO preferentially formed. In the thicker SiO₂

Fig. 8. (a) XRD patterns of (i) CaCO₃ core, (ii) CaCO₃@SiO₂, (iii) CaO@SiO₂ with 0.5 ml TEOS, and (iv) CaO@SiO₂ with 1.0 ml TEOS. (b) shows enlarged spectra of CaO@SiO₂ with addition of (i) 0.5 ml and (ii) 1.0 ml of TEOS.

Fig. 9. SEM images of (a) CaCO₃@SiO₂, (b) CaO@SiO₂ nanoparticle.

coating, thermal energy retains in the SiO₂ because of SiO₂'s insulation ability that promotes Ca₂SiO₄ formation. According to our earlier results, in the thick SiO₂ coating, an interfacial reaction is promoted due to increase in inner pressure of core-shell.¹⁰⁾

Figure 9 shows SEM observations of (a) CaCO₃@SiO₂ and (b) CaO@SiO₂. Compared with as-received CaCO₃ [Fig. 5(a)] and CaCO₃@SiO₂ [Fig. 9(a)], CaO@SiO₂ particles have similar cubic structure with angular even after heating [Fig. 9(b)].

From these results, SiO₂ coating protects from CaCO₃ nanoparticle coalescence and depression of specific surface area during heating cycle. In addition, by adjustment of SiO₂ coating condition, CaO formation is promoted and Ca₂SiO₄ formation is suppressed. The proposed technique have possibility to improve thermal storage ability of CaO nanoparticles.

4. Conclusion

Preparation of CaO core-SiO₂ shell nanoparticles as a chemical thermal storage through hydration/de-hydration of CaO/Ca(OH)₂ was proposed. A thermal storage performance of the CaO@SiO₂ as confirmed by a thermogravimetry (TG) analysis and the result was compared with that of as-received CaCO₃. For the as-received CaCO₃ nanoparticles, with increase in the number of cycles, the thermal storage performance gradually decreased. The microscopic results showed that the heating cycles induces

coalescence of CaCO_3 nanoparticles and that decreases specific surface area. On the other hands, efficiency of thermal storage of CaO@SiO_2 didn't reach theoretical value because CaCO_3 didn't completely transform into CaO owing to SiO_2 's thermal insulation ability. By decreasing SiO_2 coating thickness, the thermal storage performance of CaO@SiO_2 was improved. The microscopic results showed SiO_2 coating prevented from coalescence of CaCO_3 nanoparticles.

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