Synthesis and characterization of CaO@SiO\textsubscript{2} nanoparticle for chemical thermal storage

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Preparation of CaO core-SiO\textsubscript{2} shell nanoparticles as a chemical thermal storage through hydration/de-hydration of CaO/Ca(OH)\textsubscript{2} was proposed. Firstly, SiO\textsubscript{2} was coated on CaCO\textsubscript{3} template surface using sol-gel route and then the core–shell particles were heated at 700°C to form CaO@SiO\textsubscript{2} nanoparticle by de-carbonization. A thermal storage performance of the CaO@SiO\textsubscript{2} was confirmed by a thermogravimetry (TG) analysis and the result was compared with that of as-received CaCO\textsubscript{3}. The heating program was performed as following steps as (i) at 700°C for 30 min for de-carbonization under nitrogen (N\textsubscript{2}) atmosphere, (ii) at room temperature for 60 min for hydration under water vapor, and (iii) at 500°C for de-hydration under N\textsubscript{2}. 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 CaCO\textsubscript{3} 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\textsubscript{3} nanoparticles and that decreases specific surface area. On the other hands, efficiency of thermal storage of CaO@SiO\textsubscript{2} didn’t reach theoretical value because CaCO\textsubscript{3} didn’t completely transform into CaO owing to SiO\textsubscript{2}’s thermal insulation ability. By decreasing SiO\textsubscript{2} coating thickness, the thermal storage performance of CaO@SiO\textsubscript{2} was improved. The microscopic results showed that the SiO\textsubscript{2} coating prevented from coalescence of CaCO\textsubscript{3} 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, SiO\textsubscript{2}, is often utilized as shell materials, owing to have rather good affinity with lots of core materials such as titanium dioxide, gold, polystyrene, etc.\textsuperscript{1–3} In addition, microstructure of a SiO\textsubscript{2} shell such as thickness, porosity, density can be easily controlled by adjustment of sol–gel reacting conditions.\textsuperscript{4,5} In order to improve thermal storage performance of CaO, synthesize and characterization of CaO core@SiO\textsubscript{2} 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)\textsubscript{2} using their reversible hydration/de-hydration reactions has been reported.\textsuperscript{5,6} The reversible reaction is shown in Eq. (1). When heat around 400–500°C is applied to Ca(OH)\textsubscript{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.

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CaO + H_2O \leftrightarrow Ca(OH)_2 + 104.2 \text{kJ/mol} \quad (1)
\]

The chemical thermal storage using CaO/Ca(OH)\textsubscript{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)\textsubscript{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(NO\textsubscript{3})\textsubscript{2}.\textsuperscript{6}

In this study, synthesis of CaO@SiO\textsubscript{2} nanoparticles for thermal storage materials was proposed. SiO\textsubscript{2} has thermal resistance during de-hydration process of Ca(OH)\textsubscript{2}. In addition, high surface area of CaO nanoparticles can be kept by SiO\textsubscript{2} coating on CaO. As well known, CaO easily transforms into CaCO\textsubscript{3} by reaction with CO\textsubscript{2} in the air. It is difficult to make SiO\textsubscript{2} coating on CaO directly. Here, CaCO\textsubscript{3} is used as a template. According to our earlier results, CaCO\textsubscript{3} have good affinity with SiO\textsubscript{2}. Additionally, there are small pores exist in the SiO\textsubscript{2} shell which is formed by sol–gel reaction. Water vapor can penetrate through the pores to react with CaO.\textsuperscript{7} After SiO\textsubscript{2} coating on CaCO\textsubscript{3}, heating treatment is conducted to obtain CaO@SiO\textsubscript{2} by de-carbonization. The SiO\textsubscript{2} 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 CaCO\textsubscript{3}@SiO\textsubscript{2} to CaO@SiO\textsubscript{2} was analyzed by an X-ray diffraction (XRD) and the thermal storage performance of CaO@SiO\textsubscript{2} was confirmed by thermo-gravimetric (TG) analysis. The results were compared with that of as-received CaCO\textsubscript{3}.

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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 SHIRAISHI 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. 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 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 exposed 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
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 CaCO₃ nanoparticles \( (E_{CaCO₃}) \).

To investigate effect of number of hydration/de-hydration cycles on \( E_{CaCO₃} \), 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 CaCO₃, (b) de-carbonized sample 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 CaCO₃ 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)].

Considered from difference in density between CaO (3.35 g/cm³) and Ca(OH)₂ (2.21 g/cm³), 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 CaCO₃ decreases its efficiency of thermal storage ability as shown in Fig. 4. To overcome these problems, core–shell nanoparticles (CaCO₃@SiO₂) were prepared with addition of 1.0 ml of TEOS. The SiO₂ coating thickness on CaCO₃ was estimated as 4.76 nm which was calculated from weight of CaCO₃ and the added amount of TEOS. The CaCO₃@SiO₂ nanoparticle with 1.0 ml TEOS consists of 85.84% of CaCO₃ and 14.16% of SiO₂ by weight. Assuming that CaCO₃ 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 CaCO₃@SiO₂ with 1.0 ml of 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 \( (E_{c₁}) \) and the value was around 6%. The area filled with diagonal line is thought to be water adsorption on the sample. The experimental \( E_{c₁} \) (6%) was less than half of theoretical (15.45%). It can be thought that CaCO₃ core didn’t transform to
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 dehydration 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 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/dehydration 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 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 SiO₂ coating prevented from coalescence of CaCO₃ nanoparticles.

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