Doping Magnesium Hydroxide with Ce(NO$_3$)$_3$: A Promising Candidate Thermochemical Energy Storage Materials

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Abstract. Development of advanced materials with high energy density for thermochemical energy storage may contribute to the efficient utilization of solar energy and waste heat. In this work, Ce(NO$_3$)$_3$/Mg(OH)$_2$ as a new heat storage material for TCEs was investigated. The effect of Ce(NO$_3$)$_3$ on dehydration of Mg(OH)$_2$ was investigated by differential scanning calorimetry and thermogravimetry techniques. The addition of Ce(NO$_3$)$_3$ can significantly reduce the dehydration temperature and accelerate the dehydration of Mg(OH)$_2$. The temperature reduction depends on the Ce(NO$_3$)$_3$ content W and reaches 29 °C at W= 10 wt%, while the dehydration heat was reduced only slightly (1086 J/g). The new material exhibits an adjustable decomposition temperature, fast dehydration rate and large heat storage density, and may be considered as a promising candidate for thermochemical storage of concentrated solar energy.

1. Introduction
The efficient utilization of thermal energy is conducive to decrease the depletion of fossil fuels and to reduce the greenhouse gas pollutant emissions[1]. Thermal energy storage technologies provide a viable means of recovering industrial waste heat energy, improving solar energy utilization, and solving thermal energy mismatch between supply and demand in time and location. These technologies that provide green energy include sensible heat storage, latent heat storage and chemical thermal storage. Among these techniques, thermochemical heat storage (THS), which depends on a reversible chemical reactions to store and release thermal energy, typically high heat storage density and long-term heat storage with little or nothing loss[2]. In recent years, a large number of thermochemical materials have been studied. For example, salt hydrates and salt ammoniate are promising candidates for low temperature (< 200 °C) heat storage. Metal hydroxides are suitable thermochemical materials for middle-temperature (200 - 400 °C) heat storage[3]. In order to use waste heat efficiently, many scholars began to look for materials for middle-temperature heat storage. The potential substances for middle-temperature thermal energy storage include Mg(OH)$_2$ and Ca(OH)$_2$. However, both of them suffer from the low hydration and dehydration rate and low thermal conductivity. These disadvantages limit them direct used in heat storage. A number of reports indicate that some Mg(OH)$_2$-composites are promising TCMs. Kato’s team reported that the addition of LiCl and LiBr could significantly increase the dehydration rate of Mg(OH)$_2$[4][5]. Expanded graphite (EG)-Mg(OH)$_2$ and carbon nanotubes (CNTs)-Mg(OH)$_2$ composite material had higher thermal conductivity and reactivity than pure Mg(OH)$_2$[6][7]. Recently, the dehydration temperature of Mg(OH)$_2$ can be reduced by 50-80 K with the additives of NaNO$_3$ and LiNO$_3$[8][9]. Similar results was observed with the additives of LiOH[10]. In this study, a new material Ce(NO$_3$)$_3$/Mg(OH)$_2$ was examined by differential scanning calorimetry and thermogravimetry techniques.
calorimetry and thermogravimetry techniques in order to shed light of the Ce(NO₃)₃ effect on dehydration temperature and dehydration dynamics.

2. Experimental

2.1. Materials Preparation
Mg(OH)₂ was prepared via neutralization of commercial magnesium hydroxide (95.0%) with nitric acid, filtration and precipitation with aqueous ammonia. The precipitate was calcined at 900 °C for 6 h to remove carbonate impurities and then mixed with distilled degassed water. The mixture was sealed in an autoclave and kept at 110 °C for 24 h. The resultant Mg(OH)₂ was filtered and dried at 120 °C for 12 h. Commercially available Ce(NO₃)₃ ⋅ 6H₂O was dissolved in distilled degassed water and filtered under vacuum. The filtrate was concentrated under reduced pressure. The solid material was dried at 120 °C for 12 h. Composites Ce(NO₃)₃/Mg(OH)₂ with a varied Ce(NO₃)₃ content of 1-10 wt% were prepared by mixing Mg(OH)₂ with Ce(NO₃)₃. We refered to a sample with Ce(NO₃)₃ weight content W% as CM-W.

2.2. Materials characterization

Differential Scanning Calorimetry (DSC). The DSC measurements were carried out with a SHIMADZU DSC-60 apparatus at a constant heating rate (10 °C/min) in dry nitrogen flow (50 mL/min). The sample and the empty reference crucible were heated from room temperature to 450 °C. The endothermic heat was calculated from the area under the peak, and its temperature was estimated by a tangent at a point of greatest slope on the face portion of the peak. The dehydration temperature was characterized by either onset temperature T_{onset} or peak temperature T_{peak}. The differences between the onset temperatures and peak temperatures of the modified and non-modified materials were determined as

\[
\Delta T_{onset} = T_{onset}(Mg(OH)₂) - T_{onset}(Ce(NO₃)₃/Mg(OH)₂) \\
\Delta T_{peak} = T_{peak}(Mg(OH)₂) - T_{peak}(Ce(NO₃)₃/Mg(OH)₂)
\]

Thermogravimetric Analysis (TGA). The dehydration kinetics was measured by a TGA technique under isothermal conditions. The weight loss curves were recorded using SDT-Q600 TGA. The dehydration kinetics were studied at T=250 - 300 °C and P(H₂O)=23 mbar. The conditions of kinetic measurements were chosen so as to imitate those in a closed cycle THS unit.

The dehydration conversion degree \(\alpha(t)\) was determined as

\[
\alpha(t) = \frac{m_0 - m(t)}{m_{H₂O}}
\]

where \(m_0\) is the initial sample mass, \(m(t)\) is the sample mass at time \(t\), and \(m_{H₂O}\) is the maximal theoretical mass loss.

3. Results and discussion

3.1. DSC analysis
The dehydration process of different materials CM-W and pure Mg(OH)₂ are studied by DSC technique. The DSC curves of the composites CM-W show a strong endothermic peak that caused by dehydration of Mg(OH)₂ at high temperatures (Fig 1a). The position of the peak depends on the Ce(NO₃)₃ content: the T_{peak} decreases from 370 °C to 341 °C when the Ce(NO₃)₃ content increases from 0 to 10 wt% (Figure 1b). The onset temperature of 2 wt% Ce(NO₃)₃ is reduced by a maximum of 22 °C compares to pure Mg(OH)₂. However, as the content of Ce(NO₃)₃ is increased, T_{onset} is not decreased further. Therefore, the effect of Ce(NO₃)₃ on T_{onset} reduction is not quantitatively dependent. The maximum \(\Delta T_{peak}\) and \(\Delta T_{onset}\) is respectively 29 °C and 31 °C given by 10% Ce(NO₃)₃. They are all greater than 22 °C (maximum \(\Delta T_{onset}\)). Thus, the addition of Ce(NO₃)₃ can significantly reduce the initial dehydration temperature of Mg(OH)₂.
Figure 1. DSC-curves of CM-W materials (a) and the dehydration temperature at various Ce(NO\textsubscript{3})\textsubscript{3} contents(b).

Figure 2 shows the heat absorbed by the dehydration process of different materials CN-W and pure Mg(OH)\textsubscript{2}. The integration of the dehydration peaks yields the dehydration heat (Q), which shows an estimate of the heat storage capacity. As the content of Ce(NO\textsubscript{3})\textsubscript{3} increased, the Q value is decreased from 1278 J/g of pure Mg(OH)\textsubscript{2} to 1086 J/g of composite CM-10 with 10% Ce(NO\textsubscript{3})\textsubscript{3} content. However, the reduction of the composite material CM-10 with a 10% Ce(NO\textsubscript{3})\textsubscript{3} content is only 15%. Considering the dehydration temperature and the heat storage density, we prefer chose the composite CM-10 to study its thermal storage kinetics.

Figure 2. Integral dehydration heats Q of Mg(OH)\textsubscript{2} and CM-W materials.

3.2. Dehydration kinetics
At T = 270 °C and P(H\textsubscript{2}O) = 23 mbar, the pure Mg(OH)\textsubscript{2} dehydration exhibits a pronounced induction period and sigmoid behavior, which is typical for nucleation and growth kinetic models. However, under the same conditions, the dehydration of the composite material CM-W occurs rapidly without any induction period and can be described by an exponential equation (Fig 3a). This sigmoid-to exponential-dynamics transformation of the dehydration indicates that the addition of Ce(NO\textsubscript{3})\textsubscript{3} causes a positive change in the dehydration pathway as described later.
The half-conversion time $\tau_{0.5}$ for CM-W dehydration measured at $T = 270$ °C and $P(H_2O) = 23$ mbar are significantly shortened to 276, 90, 68 and 58 min that the Ce(NO$_3$)$_3$ addition are 1%, 2%, 5% and 10%, respectively. The half-conversion time $\tau_{0.5}$ of pure Mg(OH)$_2$ dehydration is 717 min. Therefore, the Ce(NO$_3$)$_3$ additive significantly promotes the dehydration of Mg(OH)$_2$. The largest reduction of the $\tau_{0.5}$ is by a factor of 12.3 led by composite CM-10. The kinetic curves also shows that the dehydration conversion degree $\alpha$ of the heat storage materials is sharply increased with the addition of Ce(NO$_3$)$_3$. The final conversion degree $\alpha$ for CM-10 is up to 0.90 in 150 min. The rate of the dehydration reaction increases with the addition of Ce(NO$_3$)$_3$ increases. However, the dehydration reaction rates of CM-5 and CM-10 are almost the same. Therefore, the fastest dehydration reaction may be related to a constant Ce(NO$_3$)$_3$ amount and the dehydration reaction rate does not always increases with the addition of Ce(NO$_3$)$_3$ increases.

The heat stored in the materials CM-W by the time t curves $Q_w(t)$ are shown in Figure 3b. The composite material CM-10 stores the maximum heat (956 kJ/kg) in a short period of time (150 min), which is 25.8 times higher than pure Mg(OH)$_2$ (37 kJ/kg) at the same time. The heat stores by composite CM-10 is rapidly increased. It’s clearly that the addition of 10% Ce(NO$_3$)$_3$ would reduce the time of efficient heat storage and improve the heat storage efficiency.

The heat stored in the materials CM-W by the time t curves $Q_w(W, t) - t$ are shown in Figure 3b.

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Figure 3. Dehydration kinetic curves (a) and the stored heat $Q_w$ for various composites CM-W.

Figure 4. Dehydration kinetic curves for Mg(OH)$_2$ (a) and CM-10 (b) at $P(H_2O)=23$ mbar and various temperature.
Isothermal dehydration kinetics for pure Mg(OH)\(_2\) and composite CM-10 are investigated at \(P(\text{H}_2\text{O}) = 23\) mbar and different temperature (Figure 5a and 5b). The half-conversion time \(\tau_{0.5}\) for Mg(OH)\(_2\) and CM-10 decreases with the temperature rising. At 260 °C, no dehydration of Mg(OH)\(_2\) is detected after 800 min. However, the values of \(\tau_{0.5}\) is 181 min for CM-10 under the same conditions. Hence, the addition of 10% Ce(NO\(_3\))\(_3\) exhibit a adjustable decomposition temperature and can storage waste heat and solar energy at 250 °C < T < 300 °C.

4. Conclusions
In this study, we have investigated a new candidate for thermochemical energy storage material that is doped Mg(OH)\(_2\) by Ce(NO\(_3\))\(_3\). The effect of Ce(NO\(_3\))\(_3\) on dehydration of Mg(OH)\(_2\) is investigated by differential scanning calorimetry and thermogravimetry techniques. It is found that the doping of Mg(OH)\(_2\) by 10% Ce(NO\(_3\))\(_3\) results in a significant acceleration of the dehydration as well as in the reduction of the dehydration temperature by 29 °C as compared with the pure Mg(OH)\(_2\). While the dehydration heat is reduced only slightly (1086 J/g). The new material exhibit a adjustable decomposition temperature, fast dehydration rate and large heat storage density, and may be considered as a promising candidate for thermochemical storage of concentrated solar energy.

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