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Preparation of Nano-Composite $Ca_{2-\alpha}Zn_{\alpha}(OH)_4$ with High Thermal Storage Capacity and Improved Recovery of Stored Heat Energy

Abstract: Thermal energy storage has very important prospects in many applications related to the use of renewable energies (solar energy, etc.) or other energy sources, such as waste heat from industrial processes. Thermochemical storage is very attractive for long-term storage, since it could be conducted at room temperature without energy losses. In the present paper, a novel nano-composite material, $Ca_{2-\alpha}Zn_{\alpha}(OH)_4$, is prepared using co-precipitation methodology and is characterized by XRD and DSC tests. The XRD result shows that the grain size of the nano-composite ranges from 40 nm to 95 nm. The DSC test result shows that the nano-composite exhibits high thermal storage capacity: 764.5 J/g at α = 0.8555. Its thermal decomposition temperature was found to be approximately $180°$. It was found possible to recover 63.25% of the stored heat energy.

1 Introduction

Given that the increase of traditional energy consumption results in significant atmospheric pollution, it is necessary to find new ways to use a variety of renewable and sustainable energy sources, including natural sources, such as solar and geothermal energies, and industrial waste heat. It is thus highly desirable to develop high efficiency heat storage materials for the effective utilization of thermal energy.

Heat storage is a necessary measure to harmonize heat production and heat consumption processes in, respectively, industry and civil life. In this way, the supply of solar energy and industrial waste heat energy can meet the demands of the actual application. In addition, the use of thermal energy storage and conversion (TESC) can increase the thermal energy efficiency of a process by reusing the waste heat from industrial processes, solar energy or other sources. Furthermore, TESC could contribute to the reduction in CO_2 emissions and to substantial energy savings.

Heat is the most widely used type of energy in industry and in civil life. In industry, after delivering work, most of heat energy is degraded into a lower level and is released into the environment through cooling water, cooling towers, etc. This kind of 'waste heat' is released out due to its relatively low grade. The use of TESC allows this waste heat to be reused, or even upgraded to a relatively higher grade by the use of chemical heat pump technology. Furthermore, by using TESC, heat could be transported long distances between the thermal demand unit and the supplier. Lastly, the adoption of TESC could make it possible to eliminate the time gap between energy supply and energy demand, such as Summer and Winter seasons, day-time and night-time, or even between sunny and cloudy days [1].

Presently, phase changing materials (PCMs) are frequently used to store heat; however, these offer a storage density of 100 ~ 400 kJ/kg, typically. In addition, there exist important disadvantages of PCMs, such as:

a) it cannot be used as long-term storage material due to the need for effective heat insulation;
b) there is small or null gap between solidification temperature and the melting one;
c) the capacity of heat energy storage could deteriorate gradually due to phase separation.

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Combustion of fossil fuels is a chemical reaction that releases the chemical energy stored in these fuels for geological time-scales, thus supplying a large amount of thermal energy. The chemical energy stored in fossil fuels has a notably high storage density. Inversely, thermal energy could be converted into chemical energy and thus stored for a long period. Therefore, reversible chemical reaction is an appropriate choice for heat energy storage purpose. During the endothermic process, it adsorbs thermal energy, and during the reverse exothermic process it releases the stored heat.

Generally speaking, there are three kind of thermal energy storage systems: sensible heat storage; latent heat storage; and thermochemical energy storage (TCES). TCES has many advantages such as lower heat loss and higher energy storage density as compared to the first two heat storage techniques [2]. The thermal decomposition reaction of hydroxides is an ideal route for thermal energy storage among the chemical heat storage materials, which is owing to its low cost and abundant resources.

The reversible chemical reaction for TCES is,

$$AB \leftrightarrow A + B \qquad (1)$$

It allows heat absorption in the course of the decomposition process, which is endothermic. The reverse synthesis reaction is exothermic, resulting in the return of the stored heat.

Usually, a TCES system can be used to either cool, generate or amplify heat. The latter two modes constitute the so called 'chemical heat pumping'. The temperature can be managed by selecting appropriate exothermic reaction conditions.

Dehydration of metallic hydroxides, such as those shown in Eq. 2, have been studied for storage of heat at temperatures of 500° and 350°, respectively. For moderate-temperature chemical heat storage, blending of hydroxides has been proposed to be an appropriate route.

$$\begin{aligned} Ca(OH)_2 &\leftrightarrow CaO + H_2O(gas), \\ Mg(OH)_2 &\leftrightarrow MgO + H_2O(gas) \end{aligned} \qquad (2)$$
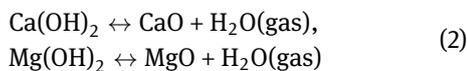
Nano-composites are a new class of chemical heat storage materials for moderate-temperature storage owing to its comparatively lower decomposition temperatures [1]. Such nano-composites are generally co-precipitated metallic hydroxides. However, these co-precipitated metallic hydroxides exhibit comparatively lower thermal storage capacity [3]- [6]. Table 1 presents properties of co-precipitated metallic hydroxide nano-composites reported in recent literature.

From Table 1, it can be seen that vermiculite impregnated with $Mg(OH)_2$ possesses the highest thermal storage capacity among co-precipitated metallic hydroxide nano-composites, at 540 J/g, while its dehydration temperature is about 300°. The dehydration temperature of $Mg(OH)_2 + Co(OH)_2$ is slightly lower, i.e. 280°, but its thermal storage capacity is only 358 J/g.

In this paper, a new nano-composite material, $Ca_{2-\alpha}Zn_\alpha(OH)_4$, that was expected to have lower decomposition temperature, is prepared by co-precipitation method. Differential scanning calorimetry (DSC) test is conducted to test the variation of thermal storage capacity of the co-precipitated metallic hydroxide nano-composite with respect to its chemical composition.

2 Experimental methodology

The chemical reagents and the experimental equipment employed in this study are listed in Table 2.

Since the solubility of ZnO in $Ca(OH)_2$ solution is high at elevated temperature, co-precipitation method could be employed to prepare the nano-composites of these hydroxides, which leads to the co-presence of calcium and zinc ions in solution in a short time, followed by co-precipitation. The advantage of this method is that a homogeneous nano-composite could be obtained through the chemical reaction in the solution directly. The chemical composition of $Ca_{2-\alpha}Zn_\alpha(OH)_4$ was controlled by the initial chemical content parameter α, which ranged from 0.334 to 1.701. The preparation process is illustrated in Fig. 1.

The DSC test of composite was performed using a ZF-DSC-D2 equipment under the nitrogen atmosphere protection. It is preheated to 50°, held at this temperature for 2 min, and then scanned with a heating rate of 10°/min.

3 Experimental results

By DSC test, the thermal storage capacity of $Ca_{2-\alpha}Zn_\alpha(OH)_4$ was obtained. Fig. 2 shows the DSC curve of $CaZn(OH)_4$, which shows a thermal decomposition peak at 174.4°. As a comparison, Figs. 3 and 4 give the DSC curves of pure $Ca(OH)_2$, and ZnO, respectively. The mark "treated" in Figs. 3 and 4 indicates the curves for those samples prepared through the "preparation process" of Fig. 1 using pure $Ca(OH)_2$ or ZnO only, while the mark "as received" in Figs. 3 and 4 represents those of fresh $Ca(OH)_2$ or ZnO as obtained from the suppliers. The DSC curve of $CaZn(OH)_4$ differs from those of pure Ca(OH)2 and ZnO significantly, which implies the formation of new composition.

Table 1: Properties of the co-precipitated metallic hydroxide nano-composites.

Material	Composition ratio	Particle size	Storage capacity [J/g]	Cyclic property	Decomposition	Reference
$Mg(OH)_2$	1	10 μm	2120	—	300°, 120 min.	Schaube et al., 2012 [7]
$Ca(OH)_2$	1	5.26 μm	1410	After 25 cycles, stable.	500°, 90 min	Schaube et al., 2012 [7]
Graphite + $Mg(OH)_2$	0.5:0.5	C : 0.07 μm $Mg(OH)_2$: —	—	—	300°, 65 min	Kim et al., 2013 [8]
Vermiculite + $Mg(OH)_2$	0.326:0.674	Pore : 15 – 200 nm $Mg(OH)_2$: 37nm, MgO : 19nm	540	After 5 cycles, stable.	300°, 30 min	Shkatulov et al., 2012 [9]
Graphite + $Mg(OH)_2$ + $CaCl_2$	0.5:0.5:0.1	C : 0.07 μm $Mg(OH)_2$: – $CaCl_2$: –	95.7	—	300°, 40 min	Schaube et al., 2012 [7]
LiCl + $Mg(OH)_2$	0.231:0.769	50 μm	—	—	280 °, 20 min	Ishitobi et al., 2013 [10]
$Mg(OH)_2$ + $Ni(OH)_2$	0.5:0.5	Atomic size	165	After 3 cycles, down to 75%, After 70 cycles, stable.	280 °, 15 min	Kato et al., 2009 [11]
$Mg(OH)_2$ + $Co(OH)_2$	0.5:0.5	Atomic size	358	—	280 °, 15 min	Ryu et al., 2009 [12]

Table 2: Chemical reagents and equipment used in this experiment

Reagent/Equipment	Specification	Manufacturer
$Ca(OH)_2$	AR	Tianjin Haiguang Chemical Reagent Factory
$Zn(OH)_2$	AR	Tianjin Guangfu Fine Chemical Industry Research Institute
ZnO	AR	Xi'an Chemical agent factory production
Distilled water		Self-produced
Magnetic stirrer	DF-101S	Gongyi Yuhua Instrument Co Ltd
Electric thermostatic drier	DHG-9055A	Shanghai Qixin Scientific Instrument Co.
Electronic analytical balance	PL2001-L testing	Mettler of Switzerland
Differential scanning calorimeter	ZF-DSC-D2	Chengde Desheng Scientific Instrument Co.

Fig. 5 shows the XRD diffractogram of $CaZn(OH)_4$. Analysis of the peak pattern suggests the occurrence of $Ca(Zn_2(OH)_6)(H2O)_2$, $Ca(OH)_2$ and $CaCO_3$ in the composite, and a grain size ranging from 40 nm to 95 nm. The presence of calcium carbonate is due to the fact that $Ca(OH)_2$ may easily change into $CaCO_3$ upon air exposure, therefore it is necessary to protect the material from CO_2 during application. The expected application of this nanocomposite is in solar energy storage.

The thermal storage capacity of $Ca_{2-\alpha}Zn_\alpha(OH)_4$ can be obtained from the integral of the DSC curve, which varies with the chemical content parameter α, as is shown in Fig. 6. It can be seen that the new nano-composite material $Ca_{2-\alpha}Zn_\alpha(OH)_4$ prepared by co-precipitation method exhibits the highest thermal storage capacity at $\alpha = 0.8555$. The DSC analysis indicates that the corresponding thermal storage capacity is 524.7 J/g in range of 100 to 250° and 764.5 J/g in total temperature range (100 to 500°), respectively.

4 Recovery of stored heat energy

The recovery of stored heat energy is an important parameter for an energy storage material [13]. Fig. 7 shows the cy-
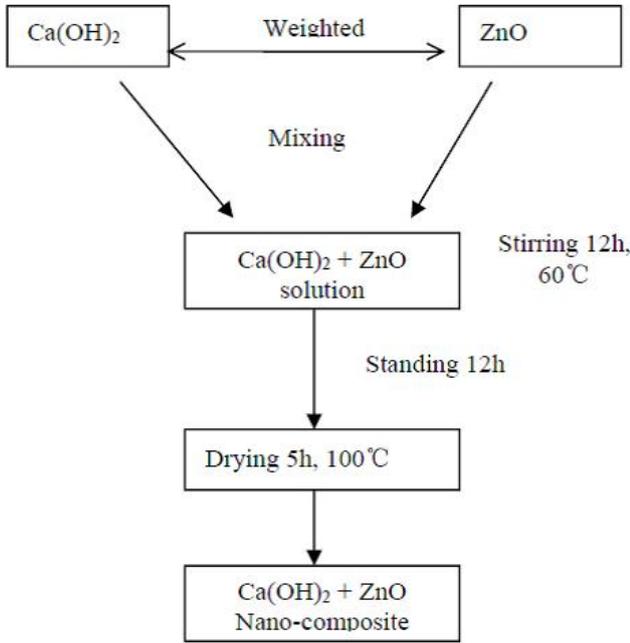
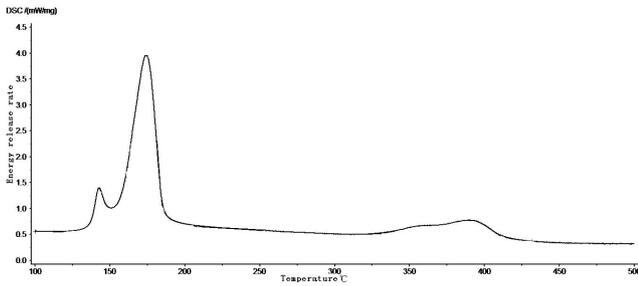**Figure 1:** The preparation process of $Ca_{2-\alpha}Zn_\alpha(OH)_4$.

Figure 2: DSC curve of $CaZn(OH)_4$.
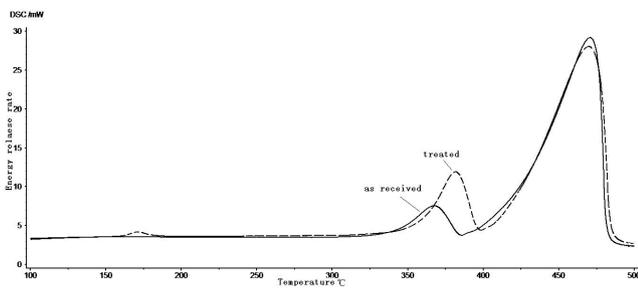
Figure 3: DSC curves of as received and treated $Ca(OH)_2$.

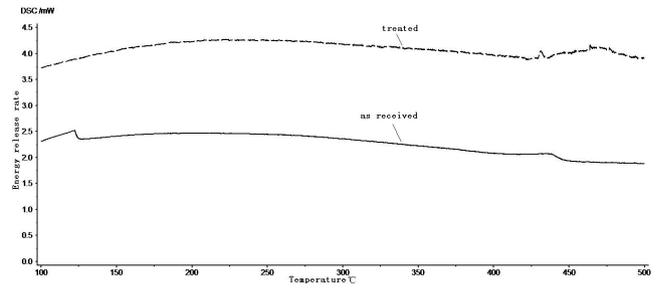**Figure 4:** DSC curves of as received and treated ZnO.
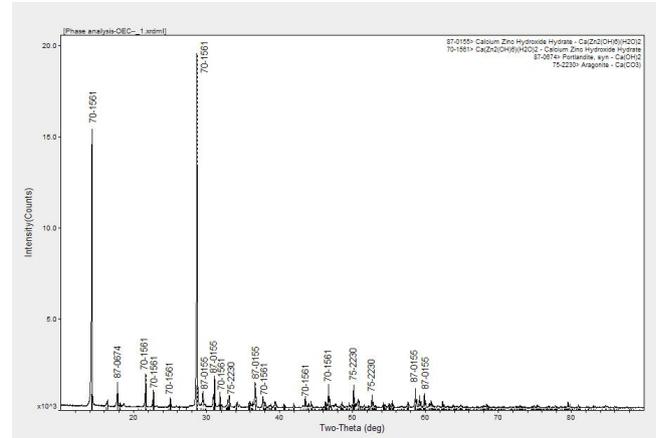
Figure 5: XRD diffractogram of prepared $CaZn(OH)_4$; peak indication: 87-0155 $Ca(Zn_2(OH)_6(H_2O))_2$, 70-1561 $Ca(Zn_2(OH)_6(H_2O))_2$, 87-0674 $Ca(OH)_2$, 75-2230 $Ca(CO)_3$.

Figure 6: Variation of the thermal storage capacity of $Ca_{2-\alpha}Zn_\alpha(OH)_4$ with respect to chemical content parameter α

cle for a thermal storage using the reaction $Ca(OH)_2 \rightarrow CaO + H_2O$ per mole [13]. The decomposition of $Ca(OH)_2$ into $CaO + H_2O$ requires an energy input of 148.6 kJ (=54.0 heating + 94.6 decomposition) to decompose 1 mol of $Ca(OH)_2$ at 25° into $CaO + H_2O$ at 510° [13]. The produced CaO can be stored easily as a solid at 25°, after losing 23.5 kJ.
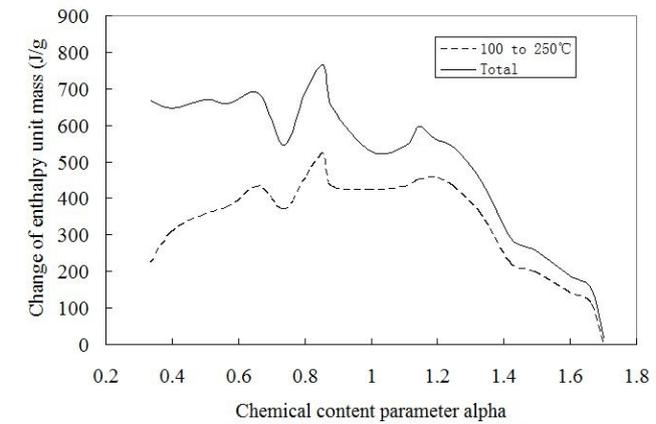
From Fig. 7, if the high temperature steam at 510° is allowed to escape to the atmosphere, instead of storing in the vapor phase, an additional heat energy of 61.5 kJ is lost. In this case, a total of 57.2% (23.5+61.5=85.0 kJ) of the input energy is released, which results in a loss of the sensible heat of the products. The actual remaining energy is only 42.8% (63.6 kJ), which is stored in the form of chemical en-
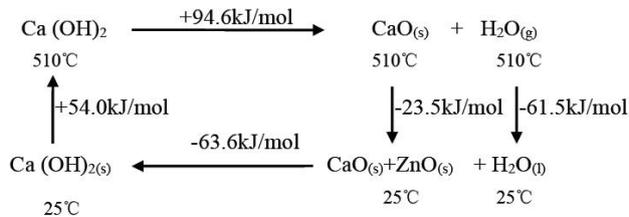
$$\text{Ca (OH)}_2 \xrightarrow{+94.6\text{kJ/mol}} \text{CaO}_{(s)} + \text{H}_2\text{O}_{(g)}$$
$$510°C \qquad\qquad\qquad 510°C \qquad 510°C$$

Figure 7 diagram with energy values: +54.0kJ/mol, −63.6kJ/mol, −23.5kJ/mol, −61.5kJ/mol

$$\text{Ca (OH)}_{2(s)} \xleftarrow{-63.6\text{kJ/mol}} \text{CaO}_{(s)} + \text{ZnO}_{(s)} + \text{H}_2\text{O}_{(l)}$$
$$25°C \qquad\qquad\qquad 25°C \qquad\qquad 25°C$$

Figure 7: Dehydration/hydration cycle for $Ca(OH)_2/CaO$

ergy [13]. When the stored high temperature steam at $510°$ is used in the hydration step, 125.1 kJ could be recovered, i.e., 84.2% of the initial input of energy.

In comparison, the decomposition of $Ca_{2-a}Zn_a(OH)_4$ into $CaO+H_2O$ and $ZnO+H_2O$ exhibits a higher recovery of the stored heat energy. Fig. 8 displays the cycle for the thermal storage using the reaction $Ca_{0.8555}Zn_{1.1445}(OH)_4 \rightarrow CaO+ZnO+H_2O$ per gram of composite. The decomposition energy of 764.5 J/g is obtained from the DSC test for $Ca_{0.8555}Zn_{1.1445}(OH)_4$ (Fig. 6), while the other thermal parameters are estimated from Fig. 7 accordingly.

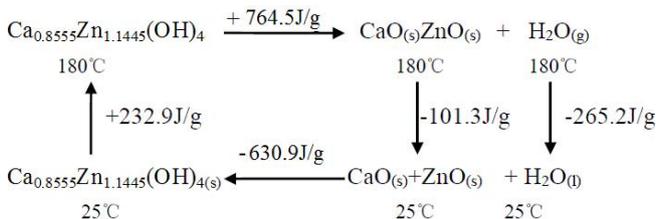$$\text{Ca}_{0.8555}\text{Zn}_{1.1445}(\text{OH})_4 \xrightarrow{+764.5\text{J/g}} \text{CaO}_{(s)}\text{ZnO}_{(s)} + \text{H}_2\text{O}_{(g)}$$
$$180°C \qquad\qquad\qquad 180°C \qquad\qquad 180°C$$

Figure 8 diagram with energy values: +232.9J/g, −630.9J/g, −101.3J/g, −265.2J/g

$$\text{Ca}_{0.8555}\text{Zn}_{1.1445}(\text{OH})_{4(s)} \xleftarrow{-630.9\text{J/g}} \text{CaO}_{(s)}+\text{ZnO}_{(s)} + \text{H}_2\text{O}_{(l)}$$
$$25°C \qquad\qquad\qquad\qquad 25°C \qquad\qquad 25°C$$

Figure 8: Dehydration/hydration cycle for $Ca_{0.8555}Zn_{1.1445}(OH)_4/CaO+ZnO$.

Similarly as the case from Fig. 7, if high temperature steam at $180°$ is allowed to escape to the atmosphere, rather than storing in vapor phase, heat energy in the amount of 265.2 J/g is lost additionally. That is, in total 36.75% (366.5 J/g) of input energy is lost from the sensible heat of the products. The actual remaining energy is 63.25% (630.9 J/g) of the input energy, which is stored in the form of chemical energy. Evidently, the recoverable energy in the $Ca_{0.8555}Zn_{1.1445}(OH)_4/CaO+ZnO$ system is higher than that for the decomposition system of $Ca(OH)_2/CaO+H_2O$.

5 Conclusions

A novel nano-composite material for storage of heat with the temperature level of $180°$ has been prepared by co-

precipitation of calcium and zinc hydroxides. The decomposition temperature of the combined hydroxide was found to be some $300°$ lower than that of the bulk hydroxides. The optimal thermal storage capacity was achieved for a chemical content parameter α (for $Ca_{2-a}Zn_a(OH)_4$) of 0.8555. The DSC analysis indicated that the corresponding thermal storage capacity is 764.5 J/g. The actual recovery of the stored heat energy for the decomposition of $Ca_{2-a}Zn_a(OH)_4$ was 63.25%, which is higher than that for the decomposition of $Ca(OH)_2$ into $CaO+H_2O$. Further study on the new nano-composite material is warranted to better understand the mechanism of the decomposition temperature reduction, which may lead to further enhancement of the heat storage capacity.

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