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Nano-porous Carbon Supported Magnesium Hydroxide for Thermochemical Heat Storage Performance Enhancement

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ABSTRACT

The reversible thermochemical reaction between magnesium hydroxide and magnesium oxide is recommended for storing heat energy in the middle temperature range of 300-500 °C. However, the low hydration rate of magnesium oxide limits the heat storage performance for practical applications. In this study, the nano-porous carbon supported composite was prepared by calcination method for improving the heat storage performance. The hydration and dehydration experiments were carried out. The results show that the overall heat storage density of composite can be improved to 1053 kJ/kg, which is 1.4 times that of pure material. Compared with other experimental results, the heat storage density of the composite has been improved by more than 30%.

Keywords: thermochemical heat storage, hydration, magnesium hydroxide, nano-porous carbon

NONMENCLATURE

Abbreviations	
NC	Nano-porous carbon
Symbols	
ε	Mass content [%]
S_{BET}	Specific surface area [m^2/g]
X	Hydration ratio
M	Molecular mass [g/mol]
m	Mass [g]

1. INTRODUCTION

Middle-low heat energy (below 500 °C) such as industrial waste heat and solar energy has the characteristics of great potential utilization and wide distribution [1]. Compared to sensible heat storage, latent heat storage, thermochemical heat storage is more suitable for efficient utilization of thermal energy due to their high heat storage densities, large range of temperatures and probably no energy loss. Due to its high energy density (1396 kJ/kg) and low price, magnesium hydroxide was selected as the promising candidate for efficiently storing the middle temperature thermal energy. However, the low hydration rate of thermochemical heat storage materials as an important influence factor still limits the performance of $MgO/H_2O/Mg(OH)_2$ thermochemical heat storage system [2,3].

A series of scientific research mainly carried out the composite modification by supporters. Mastronardo et al. [2,3] modified the $Mg(OH)_2$ with expanded graphite and carbon nanotubes by deposition-precipitation method, which can improve the thermal conductivity and reaction activity of composites. Li et al. [4] used 3D graphene as supporter to modify $Mg(OH)_2$ by deposition-precipitation method, which also improved the reaction rate and thermal conductivity of $Mg(OH)_2$ composites. However, the above researches have improved the hydration rate of the material, the mass content of $Mg(OH)_2$ is limited to about 50% by the preparation method. Therefore, the heat storage density improvement of overall material was limited by the insufficient reactive substance content. Haruki et al. [5] prepared the composites by mixing $Mg(OH)_2$ mechanical grinding powder directly with expanded graphite, and the mass content of $Mg(OH)_2$ was increased to 83%. Their experimental results show that this method can improve the reaction rate and overall heat storage density, but reduce the hydration conversion rate.

In this paper, we focus on nano-porous carbon (NC) as supporter to improve the thermochemical heat storage performance of the composite materials. NC is a mesoporous carbon material with concentrated pore size distribution. For improve the heat storage density, a calcination method is proposed to prepare composite. The hydration rate and heat storage density of composite were conducted to the hydration and dehydration experiments.

2. EXPERIMENTAL

2.1 Synthesis and structural characterization

The nano-porous carbon (NC) supported composite was synthesized by calcination method. Firstly, nano-porous carbon was added to magnesium acetate solution and stirred 180 min for impregnation at ambient temperature. Then, the mixture solution was heated to 90 °C for solvent evaporation to obtain the composite precursor. Finally, the composite precursor was placed in a tubular furnace and calcined at 450 °C with nitrogen flow of 100 mL/min for 180 min. Thus, the MgO is formed on the nano-porous carbon under high temperature decomposition of magnesium acetate. The calcined product was ground into powder and hydrated with water vapor to obtain nano-porous carbon supported magnesium hydroxide. The mass content of MgO in the composite is determined by burning the carbon material by thermogravimetric analyzer. Two kinds of nano porous carbon (NC1 and NC2) with different pore volume and specific surface area were used, and the pore structures of them are shown in Table 1. The mass content of Mg(OH)2 was measured by burning the nano-porous carbon.

Surface topography was observed by scanning electron microscopy (SEM, S-4800, Hitachi co., Ltd.) and trans-mission electron micrographs (TEM, JEM-2100F, JOEL Co. Ltd). X-ray diffraction (XRD) analysis was performed on composites using an X-ray diffractometer (D8-advance X, Bruker Co. Ltd) with Cu target (40 kV, 40 mA). The pore structure of the composite was calculated by nitrogen adsorption isotherms at 77 K and relative pressure of 0.1-1.0 using a gas adsorption apparatus (Nova 4200e, Quantachrome Instruments Co. Ltd).

2.2 Hydration and dehydration experiments

The hydration rates of materials are tested by thermogravimetriy (TG) method. As shown in Fig. 2, the TG mainly including high-precision balance (HR-150AZ, A&D Co., Ltd.), vertical tubular furnace, steam generator (FD-HD, Suzhou Friend Experimental Equipment Co., LTD.). In the hydration experiments, the sample was slowly heated to the target temperature of 110 °C with heating rate of 10 °C/min, and maintained this condition for 120 min. The partial water vapor pressure was kept at 57.8 kPa by controlling the nitrogen gas flow rate of 35 mL/min and the injected water flow rate of 37 µL/min. Thus, the conversion ratio, X [%], was calculated using the following equation:

$$\mathrm{X} = \frac{\Delta m_{\mathrm{H_2O}} \times M_{\mathrm{MgO}}}{m \times \varepsilon \times M_{\mathrm{H_2O}}} \times 100 \qquad (1)$$

where Δm_{H_2O} is the mass change in the sample caused by the hydration reaction, m is the initial mass of the sample, ε is the mass content of MgO in the sample, and $\mathrm{M_{MgO}}$ and $M_{\mathrm{H_2O}}$ are the molecular masses of MgO and H_2O, respectively.

After hydration experiments finished, the dehydration experiments were carried out on a thermogravimetric and differential scanning calorimetric analyzer (TGA3+, Mettler Co. Ltd.). Thus, the heat storage densities of samples are obtained from the experimental results.

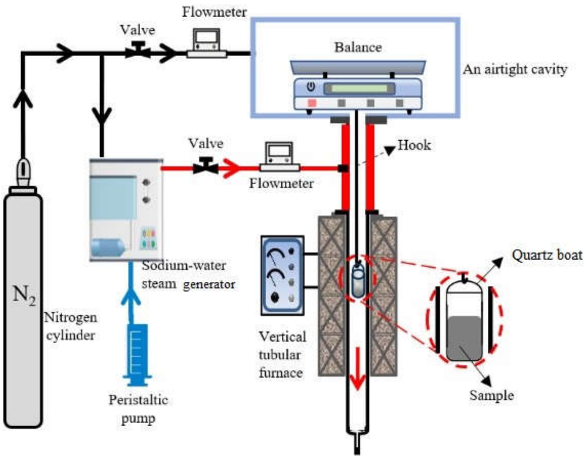

Fig. 1 Schematic of thermogravimetry.

3. RESULTS AND DISCUSSION

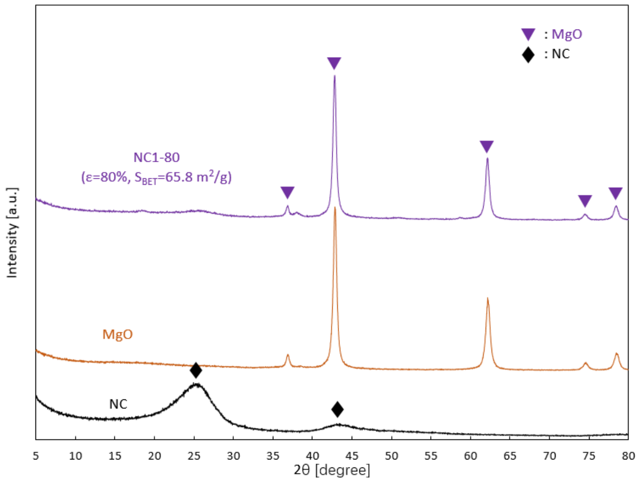

Fig. 2 XRD patterns of NC, MgO and composite.

The XRD patterns of NC, MgO and composites are shown in Fig. 2. The XRD patterns of NC show two circular inclusion peaks at 26 ° and 44 °, which corresponded to the (002) and (100) crystal planes of graphite structure, indicating that NC has been graphitized. The three composite have five sharp diffraction peaks at 36.8 °, 42.8 ° , 62.1 °, 74.5 ° and 78.4 °. The values match MgO very well. The five diffraction peaks correspond to (111), (002), (022), (113) and (222) crystal planes of MgO respectively (PDF 01-074-1225).

Table 1 shows the pore structure of samples. As can be seen from the table, the average pore size of the composite decreases slightly. With the increase of mass content of reactive substance, the specific surface area and pore volume of composites decreased. The results show that the larger pore volume and specific surface area of supporter (NC2>NC1) could increase the those of the composite.

Table 1 Pore structures of samples in this study.

Sample	$Mg(OH)_2$ mass content and supporter	Average pore size [nm]	Pore volume [cm^3/g]	Specific surface area [m^2/g]
NC1	-	14.1	0.79	227.6
NC2	-	14.1	2.06	454.6
MgO	-	13.5	0.15	44.1
NC1-30	30%, NC1	14.1	0.62	175.1
NC1-80	80%, NC1	12.9	0.21	65.8
NC2-80	76%, NC2	12.4	0.34	108.6

The SEM, TEM and EDS images of the samples are shown in Fig. 3 and Fig. 4. The surface morphology of carbon materials does not seem to change from the SEM results. The white particles on the surface of NC were MgO according to the XRD results. The TEM and EDS images show that the MgO particles are evenly dispersed.

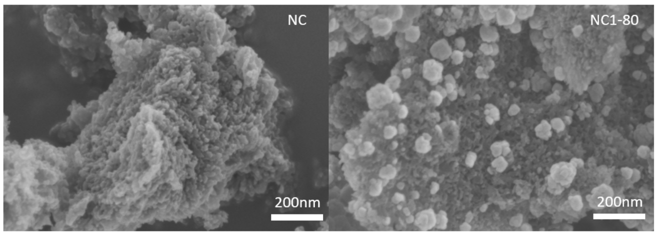

Fig. 3 SEM images of NC and NC1-80 before hydration.

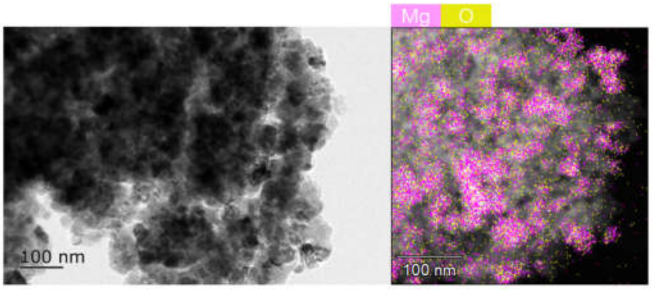

Fig. 4 TEM and EDS images of NC1-80 before hydration.

Fig. 5 shows the hydration ratio of MgO of samples when each sample was hydrated at temperature of 110 °C and water vapor pressure of 57.8 kPa. Compared with pure MgO, the nano-porous structure of composite is conducive to the diffusion of water vapor to the reaction interface, which promotes the hydration reaction. The results also represent the mass content and specific surface area affect the hydration rate, which need to be considered comprehensively.

Fig. 6 shows the overall heat storage density of pure MgO and the composites for hydration time of 120 min. As shown in the figure, the heat storage density of MgO was 730 kJ/kg, and that of composite was increased with the increase of mass content of $Mg(OH)_2$. The NC1-80 shows the highest heat storage density of 1053 kJ/kg, which is 1.4 times that of pure MgO.

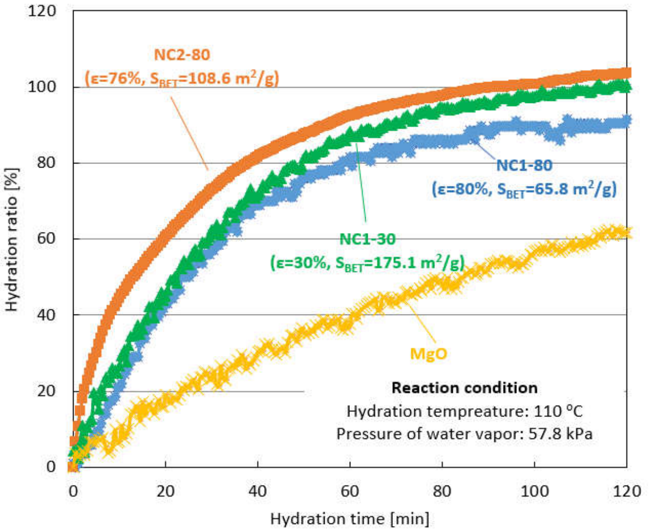

Fig. 5 Hydration ratio of MgO and composite according to mass content, ε, and specific surface area, S_{BET}.

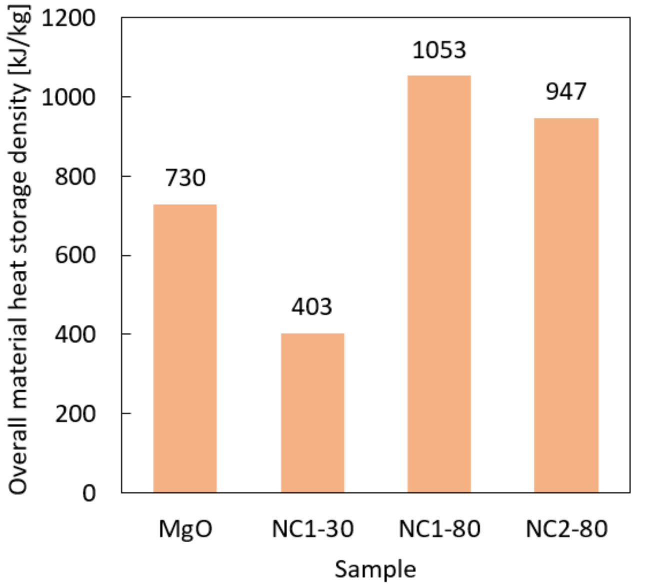

Fig. 6 Heat storage densities of MgO and composites for hydration time of 120 min.

Table 2 shows the comparison of heat storage performance between the prepared composite and others in the literature. It can be seen from the table that the prepared composite has a high mass content of $Mg(OH)_2$ and a high hydration ratio. The heat storage density of this composite is at least 30% higher than that of other composites.

Table 2 Comparison of heat storage performance of composite for hydration time of 120 min.

Composite material	$Mg(OH)_2$ mass content	Supporter	Theoretical heat storage density [kJ/kg]	Experimental Heat storage density [kJ/kg]	Reference
EG/$Mg(OH)_2$	50%	Expanded graphite	698	600#	[2]
CNTs/Mg(OH)2	52%	Carbon nanotubes	726	598#	[3]
3D-Graphene/$Mg(OH)_2$	47%	Porous graphene	656	610	[4]
EG/$Mg(OH)_2$	83%	Expanded graphite	1159	811#	[5]
NC1-80	80%	Nano porous carbon	1117	1053	This work

The approximate calculated value is obtained from the experimental results of the literature.

4. CONCLUSIONS

In view of the low hydration rate of MgO for middle temperature thermochemical heat storage material, nano-porous supported composite was prepared by calcination method. The prepared composite has higher specific surface area and mass content of reactive substance, and the hydration rate and heat storage density are greatly improved. When the mass content of $Mg(OH)_2$ increase to 80%, the overall heat storage density of composite can be improved to 1053 kJ/kg, which is 1.4 times that of pure material. Compared with the experimental results in other literature, the overall heat storage density of the proposed composite increased by at least 30% after hydration for 120 min.

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REFERENCE

[1] Papapetrou M, Kosmadakisb G, Cipollina A, Commare U, Giorgio M. Industrial waste heat: Estimation of the technically available resource in the EU per industrial sector, temperature level and country. Applied Thermal Engineering 2018;138:207-216.

[2] Mastronardo E, Bonaccorsi L, Kato Y, Piperopoulos E, Milone C. Efficiency improvement of heat storage materials for MgO/H2O/Mg(OH)2 chemical heat pumps. Applied Energy 2016;162:31-39.

[3] Mastronardo E, Bonaccorsi L, Kato Y, Piperopoulos E, Lanza M., Milone C. Thermochemical performance of carbon nanotubes based hybrid materials for MgO/H2O/$Mg(OH)_2$ chemical heat pumps. Applied Energy 2016; 181:232-243.

[4] Li S, Yang X, Li X, Qu W, Zhou T, Dong T, Deng L, Zhang J, Zhao J. A high energy density 3D nano-carbon based magnesium hydroxide reversible chemical reaction heat storage material synthesis and heat transfer performance investigation. J. Energy Storage 2022;50:104260.

[5] Haruki M, Saito K, Takai K, Fujita M, Onishi H, Tada Y. Thermal conductivity and reactivity of Mg(OH)2 and MgO/expanded graphite composites with high packing density for chemical heat storage. Thermochimica Acta 2019;680:178338.