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Efficiency improvement of heat storage materials for $MgO/H_2O/Mg(OH)_2$ chemical heat pumps

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HIGHLIGHTS

- A new approach was used to develop a hybrid material (DP-MG) for chemical heat pump.
- $Mg(OH)_2$ was finely dispersed on exfoliated graphite by deposition–precipitation route.
- DP-MG sample showed enhanced stability and efficiency to chemical heat pump cycles.

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ABSTRACT

$MgO/H_2O/Mg(OH)_2$ chemical heat storage of waste energy from industrial processes is a promising technology in view of a more efficient use and saving of primary energy sources. A new approach was used to develop a hybrid heat storage material made of magnesium hydroxide ($Mg(OH)_2$) and exfoliated graphite (which is used to improve the heat transfer with its high thermal conductivity). $Mg(OH)_2$ nanoplatelets were directly grown on graphite surface via a deposition–precipitation method to increase the compatibility between the two materials. The material thus obtained, named DP-MG, was experimentally tested to determine its heat storage and output capacities. An improvement of the material efficiency was obtained with a higher storage capacity at lower reaction temperature and a higher heat output rate.

1. Introduction

A significant amount of energy is inevitably wasted in the form of heat as by-product of industrial processes and oil and gas processing thus reducing their overall efficiency. Hence, in light of the 2020 EU climate and energy package and of the carbon tax, thermal energy storage of waste heat is a key issue for industries to make their processes more efficient and to reduce fuel consumption [1–4]. A promising technology for the recovery of waste heat are chemical heat pumps (CHPs) that are based on a reversible chemical reaction for heat storage and reuse on demand [5–7]. Different kind of substances can be used in a CHP system involving reversible gas–gas reactions ($NH_3/N_2/H_2$, $SO_3/O_2/SO_2$, $CH_3OH/H_2/CO$, cyclohexane/benzene/hydrogen) [8–11], liquid–gas reactions (isopropanol/acetone/hydrogen) [12,13] and solid–gas reactions ($BaO_2/O_2/BaO$ [14], $ZnO/O_2/Zn$ [15], $PbO/CO_2/PbCO_3$ [16], $CaO/CO_2/CaCO_3$ [17], $CaO/H_2O/Ca(OH)_2$ [18,19]). The choice of storage material depends on the temperature range in which the storage system will to operate. Specifically, this study focuses on the solid–gas $MgO/H_2O/Mg(OH)_2$ CHP which operates in the temperature range 200–400 °C and whose feasibility has already been demonstrated by Kato and co-workers [20]:

$$Mg(OH)_2(s) \leftrightarrow MgO(s) + H_2O(g) \quad \Delta H^0 = \pm 81\ \text{kJ/mol} \tag{1}$$

Dehydration, being endothermic, represents the energy storage step while the exothermic hydration of MgO releases the thermal energy when required (Fig. 1). The water vapour produced during the dehydration reaction is condensed in a reservoir and then reused in vapour phase for the hydration reaction closing the pump cycle.

The main requirements that a storage system has to satisfy are (i) high energy density (per-unit mass or per-unit volume) of the storage material, (ii) good heat transfer through the storage medium, (iii) mechanical and chemical stability of the storage material, (iv) high durability to a large number of charging/discharging cycles, (v) low thermal losses. The $MgO/H_2O/Mg(OH)_2$ CHP complies with these requirements. However, the low thermal conductivity of the reagents ($Mg(OH)_2$ and MgO) may lower the performance of the CHP. Moreover, the thermal decomposition of

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Nomenclature

EG	exfoliated graphite
I_{001}, I_{101}, I_{110}	intensity reflections respectively of [001], [101] and [110] planes
m_{in}	initial sample mass (g)
m_{ist}	instantaneous mass (g)
$M_{Mg(OH)2}$	molecular weight of $Mg(OH)_2$ (g mol^{-1})
M_{MgO}	molecular weight of MgO (g mol^{-1})
pH_{PZC}	point of zero charge
Q_r	released heat per initial mass unit of $Mg(OH)_2$ (kJ $kg^{-1}_{Mg(OH)2}$)
q_r	heat output rate (kW $kg^{-1}_{Mg(OH)2}$)
Q_s	stored heat per initial mass unit of $Mg(OH)_2$ (kJ $kg^{-1}_{Mg(OH)2}$)
Q_r^V	released heat per unit volume (kJ cm^{-3})
Q_s^V	stored heat per unit volume (kJ cm^{-3})
S_{BET}	specific surface area (m^2 g^{-1})
T_d	dehydration temperature (°C)
T_h	hydration temperature (°C)
t_h	hydration time (min)
T_{onset}	onset temperature of dehydration reaction (°C)
t_r	total reaction time (min)
w	mass ratio between EG and $Mg(OH)_2$

Greek symbols

β	reacted fraction (%)
β_d^f	reacted fraction at the end of the dehydration treatment (%)
β_d^i	reacted fraction at the beginning of the dehydration treatment (%)
β_d	reacted fraction of $Mg(OH)_2$ after dehydration (%)
β_h	final reacted fraction of MgO at the point of water supply termination (%)
Δm_{real}	instantaneous real mass change (%)
Δm_{th}	theoretical mass change due to the dehydration of Mg $(OH)_2$ normalized to the total amount present in the sample (%)
$\Delta\beta_d$	dehydration conversion (%)
$\Delta\beta_h$	hydration conversion (%)
ρ_c	density of the composite (g cm^{-3})

$Mg(OH)_2$ is always accompanied by the sintering of the newly formed MgO product, which leads to its grain growth and to the loss of pore volume thus hindering MgO rehydration. It has been already observed by Zamengo et al. [21] that a physical mixture of magnesium hydroxide and expanded graphite can improve the poor thermal conductivity of pure $Mg(OH)_2$. Nevertheless, because of the weak interaction between the inorganic ($Mg(OH)_2$) and organic (expanded graphite) phase, the hybrid material exhibits a poor durability to repetitive reactions. Kim et al. [22] and Myagmarjav et al. [23] introduced a hygroscopic salt in the mixture of $Mg(OH)_2$ and graphite, respectively calcium chloride ($CaCl_2$) and lithium bromide (LiBr), which should promote the adhesion of $Mg(OH)_2$ on the graphite surface and enhance the reactivity of the heat storage material. However, these salts are well known to be highly corrosive, especially the combination of $CaCl_2$ with expanded graphite [24,25].

The state of the art demonstrates that a more efficient heat storage material for $MgO/H_2O/Mg(OH)_2$ CHP needs to be developed for the industrial application of such a technology. This study examines a novel synthesis route for the deposition of $Mg(OH)_2$ on graphite surface to enhance the compatibility between the two phases, thus improving the stability of the composite under operating conditions and avoiding MgO sintering. A deposition–precipitation method is used for the direct growth in aqueous medium of $Mg(OH)_2$ crystals on exfoliated graphite surface (consisting in thin layers split along the *c* axis). The compatibility between the active phase ($Mg(OH)_2$) and exfoliated graphite is improved by the electrostatic interaction promoted by the different point of zero charge (pH_{PZC}) of the materials. The performance of the resulting hybrid heat storage material was evaluated by thermogravimetric analysis which simulates the CHP cycle and compared with that of a physical mixture of $Mg(OH)_2$ and exfoliated graphite.

2. Experimental section

2.1. Deposition–precipitation

For the deposition–precipitation (DP) method the following raw materials were used: magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$, 99% Sigma Aldrich) as magnesium source, ammonia solution (NH_4OH, 30 wt.% Carlo Erba) as precipitating agent and exfoliated graphite (TIMREX C-THERM 002 TIMCAL Ltd. for briefness named EG). The DP procedure was carried out as follows: under magnetic stirring 50 ml of $Mg(NO_3)_2{\cdot}6H_2O$ solution were gradually added (2.5 ml/min) through a peristaltic pump to 150 ml of NH_4OH solution containing a specified amount of EG (weight ratio $Mg(OH)_2$/EG = 1). The final solution (pH ~ 11.5) was aged at ambient conditions for 24 h, then it was vacuum filtered (0.22 μm) and the collected solid was washed with deionized water and dried in a vacuum oven at 50 °C overnight. The Mg^{2+} ions concentration in solution was chosen on the base of the desired $Mg(OH)_2$ deposited amount: the initial moles of Mg^{2+} in the solution are those that theoretically should be precipitated in case of complete precipitation according to the stoichiometric reaction:

$$Mg(NO_3)_2 + 2NH_4OH \rightarrow Mg(OH)_2 + 2NH_4NO_3 \quad (2)$$

The molar ratio $Mg(NO_3)_2{\cdot}6H_2O$:NH_4OH on the final solution was 1:100.

2.2. Impregnation

A physical mixture of $Mg(OH)_2$ and EG (weight ratio $Mg(OH)_2$/EG = 1) was prepared according to an impregnation method reported in literature [22]: a specific amount of $Mg(OH)_2$ (obtained by the precipitation reaction reported in Section 2.1) was soaked in 200 ml of ethanol and sonicated for 30 min. The same amount of EG was charged in the flask and soaked with the solution. The excess ethanol was eliminated by evaporation in about 1 h and the remaining product was oven-dried at 120 °C overnight.

2.3. Thermogravimetric analysis

A thermogravimetric analysis (TGA) was performed (TG-9600, Ulvac Shinku-Riko Inc.) to evaluate the behavior of the heat storage materials obtained to cyclic dehydration/hydration reactions representative of the CHP operation cycle. In this experiment the sample was first dried at 110 °C in inert atmosphere (Ar 100 ml/min) for 60 min to remove the physically adsorbed water and then subjected to the dehydration/hydration cycles. In a single cycle the temperature was increased by 10 °C/min to the desired dehydration temperature (T_d = 350 °C) and $Mg(OH)_2$ dehydration reaction proceeded over 120 min. After the complete dehydration reaction,