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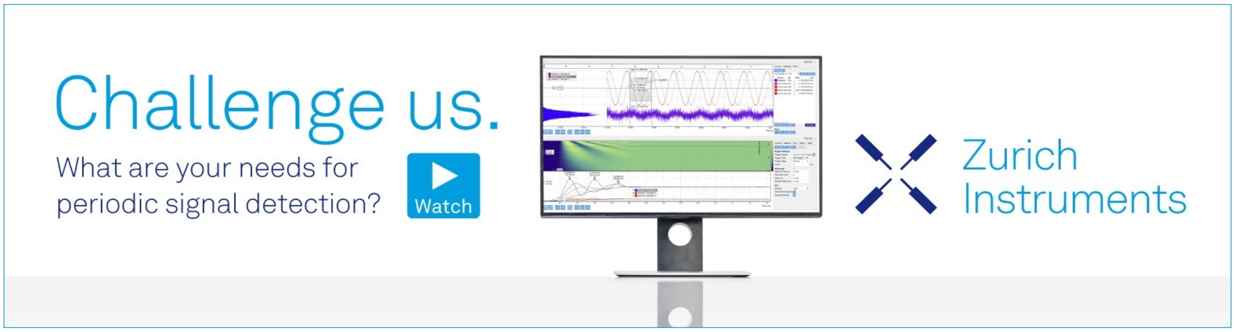

Mayenite-supported CaO for Thermochemical Storage Applications: Analysis of Dynamic Behavior Under Charging/Discharging Cycles

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Abstract. The possibility of storing solar thermal energy to decouple electricity production from the availability of the solar resource is a key factor in development of concentrating solar power (CSP) technologies. In this context, a challenging perspective is the storage of solar energy on a seasonal basis through thermochemical storage (TCS) systems, as well as the use of excess summer solar energy for stabilizing the annual electricity production, thus increasing the capacity factor of the CSP plant. In this paper, we report the experimental characterization of a material initially developed within the context of CO_2 capture technologies, namely calcium oxide supported on mayenite, which in previous investigations shown good sorption capacity and substantial cycling stability. The objective of this new experimental campaign is to test the performance of this material when adopted for thermochemical storage purposes. The tests confirmed that the material, synthesized through a SolGel method, remains stable over long term cycling, with a carbonation conversion higher than 80%. Furthermore, no physical/chemical interaction of the mayenite support with CO_2 was observed, confirming its inertia and suitability for TCS purposes.

INTRODUCTION

Among all renewable energy technologies, CSP stands out for the feature of dispatchability, which is the ability to produce electricity on demand, thanks to the possibility of efficiently storing the thermal energy collected by the solar plant. Presently, the commercial solutions for thermal storage in CSP plants are based on sensible heat systems, which are suitable for continuous power generation on a daily basis. Providing 24-h continuous supply of solar energy is a key step in the development of solar thermal power generation technology, but a more challenging objective is the realization of long-term storage systems that allow maximizing the solar plant capacity factor, stabilizing the seasonal production capacities of the CSP installations. Therefore, alternative storage options are currently under study to increase not only the energy density but also the duration of the thermal storage. Among the innovative concepts, thermochemical storage (TCS) systems, which use reversible chemical reactions to store thermal energy in the form of chemical energy, represent a very promising route. Such systems are potentially characterized by high energy density and capability of long-term thermal storage, due to the involved chemical reactions (and associated heat flows) which are activated only under given conditions of pressure and temperature and in the presence of specific reagents [1]. Thus, the TCS technology can be suitable for seasonal storage, provided that the reacting media are sufficiently stable and properly handled.

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The research in this field is currently focused on oxides- (mainly manganese and cobalt oxides subject to reversible redox reactions [2-3]) and hydroxides- (mainly Ca-based systems reversibly exchanging water [4-5]) based systems, but also carbonates-based systems have been proposed to store thermal energy in an efficient way [6-7]. For this latter class, the reaction usually considered is $CaCO_3 \rightleftharpoons CaO + CO_2$, with a reaction enthalpy of 177 kJ/mol and a turning temperature of about 900°C at 1 atm partial pressure of carbon dioxide. In a previous work performed by ENEA, a synthetic CaO system initially developed within the context of CO_2 capture technologies [8-10], namely calcium oxide supported on mayenite, was studied to characterize its performance when adopted for thermochemical storage purposes and assess its chemical stability under charging/discharging cycles [11]. The material confirmed sufficient stability over about four hours of charging/discharging cycles and good reaction kinetics, which justifies further investigations. In the present work, the system is tested over longer charging/discharging stability tests. Moreover, by employing thermogravimetric and morphological analyses, this work investigates the possible interaction of the mayenite support with CO_2, which may affect the overall loading capacity of the material and reaction kinetics.

MATERIALS AND METHODS

The Mayenite support ($Ca_{12}Al_{14}O_{33}$) and CaO/Mayenite powders were synthesized, with negligible variations in accordance with the scientific literature [12]. CaO supported on Mayenite was prepared by sol-gel method. The calcium precursor Calcium oxide (CaO, Acros Organics) and the nitrate salt of the support material ($Al(NO_3)_3$ $9H_2O$, Acros Organics) were mixed. A deionized water/2-propanol ($(CH_3)_2CHOH$, 99.5% Sigma-Aldrich) solution (188 mL, volumetric ratio 7.5:1) was added and stirred until all chemicals were homogenized. Then the mixture was heated at 80 °C under stirring, to evaporate the excess solvent. The wet gel obtained was heated at 300 °C for 1h (5 °C/min ramping-up rate). The dried material was ground via a mortar and placed in a muffle furnace at 500 °C for 1 h (5 °C/min ramping-up rate), then calcined at 1000 °C for 1 hour (5 °C/min ramping-up rate).

Inductively coupled plasma (ICP) chemical analysis was performed by MP-AES microwave plasma Atomic emission spectroscopy 4100 Agilent. The CaO/Mayenite ratio of 68/32 (%w/w) over fresh sample was obtained.

Pure Mayenite was synthesized similarly to the supported CaO/Mayenite system by adjusting the amounts of precursors.

The first set of fresh samples (labelled as M1, M2, M3) was further ground before processing by a mechanical treatment utilizing a Retsch MM200 Mixer-mill. A powder batch of 5 g was ground inside a plastic vial at 15 Hz for 5 min (ball to powder ratio 1:1).

X-ray diffraction (XRD) analysis was carried out over the fresh powder using a simultaneous 120° angular dispersion diffractometer (Italstructures, curved PSD detector from INEL) equipped with FeKa radiation.

The morphology of the powder was investigated by Scanning Electron Microscopy (SEM) using a SEM/EDX technique, performed with a FEI model inspect S, equipped with a Genesis EDX probe and a graphite sample holder.

Thermal analysis, consisting of TG and DSC experiments, was performed in a STA 409C/CD system (Netzsch, Germany), investigating the calcination reaction at a fixed temperature of 900°C and the carbonation reaction, which is the slowest step, at the three temperatures of 700/750/800°C. Both charging (calcination) and discharging (carbonation) cycles were carried out at a total pressure of 1 bar, under argon and carbon dioxide flows, respectively.

In a typical run, about 40 mg of the material was placed inside a compact alumina open crucible. The sample was heated up to 900°C at 10°C/min in Ar atmosphere at a constant total gas flow of 50 ml/min; subsequently, an isothermal step of 1 h was carried out to allow complete sample dehydration and calcination. Afterwards, 5 or more consecutive carbonation/calcination cycles were performed alternating CO_2 and Argon atmosphere (gas flow rates 50 ml/min). The carbonation reaction was explored at three different temperatures for 120 min.

Chemical/physical inertia of the pure Mayenite support was also investigated, by subjecting the material to the same TGA thermal cycling of the CaO/Mayenite samples.

Carbonation and de-carbonation enthalpies were determined through the integration of the area under the heat flow signal obtained from the DSC analyses, utilizing sigmoidal tangent peak integration.

The CaO conversion in the carbonation reaction, X_{CaO}, was calculated according to the following equation:

$$X_{CaO} = \frac{\Delta m \frac{PM_{CaO}}{PM_{CO2}}}{m\, x_{CaO}} \tag{1}$$

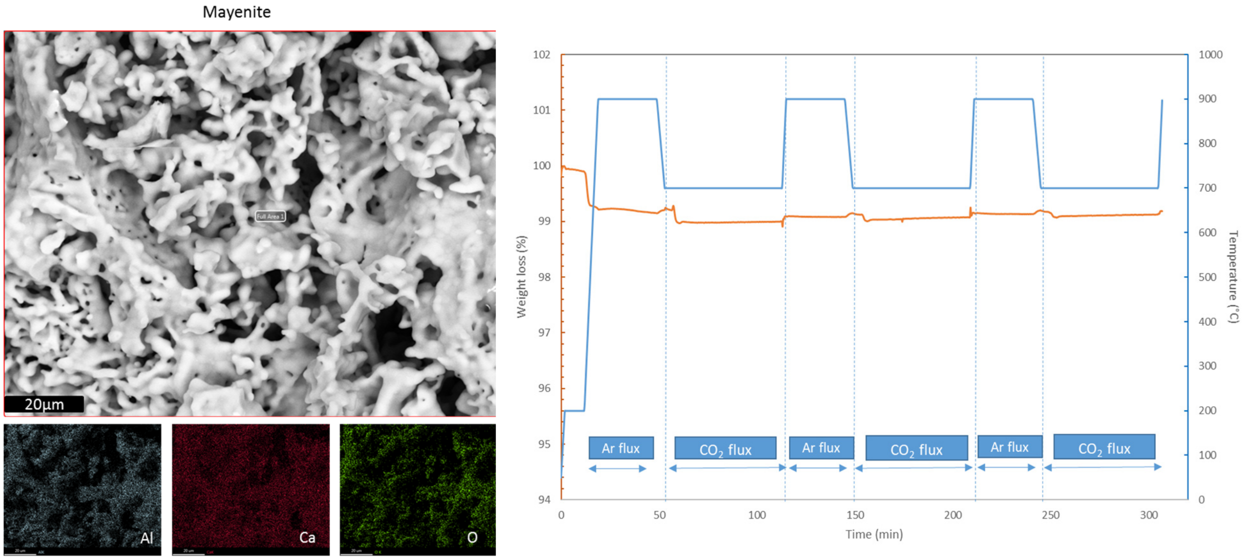
where Δm is the sample mass increase during the carbonation step, PM is the molecular weight, m is the initial mass of the sample and x_{CaO} is the weight fraction of CaO in the sample.

RESULTS AND DISCUSSION

Morphological and phase characterizations were carried out over fresh powder samples.

Regarding pure Mayenite, morphological analysis reveals a coarse porous nature, showing macroporosity with an average pore size of 10 µm, as depicted in Fig. 1a.

Chemical/physical inertia of the pure Mayenite support toward carbon dioxide was investigated testing pure Mayenite to thermal cycling, as shown in Fig. 1b. Apart from an initial weight loss ascribable to atmospheric moisture and carbon dioxide, no weight change was detected over time, and consequently no CO_2 uptake. Weight oscillations within ±0,2% are attributable to the instrumental background noise and buoyancy effect produced by the switch of the carrier gas.

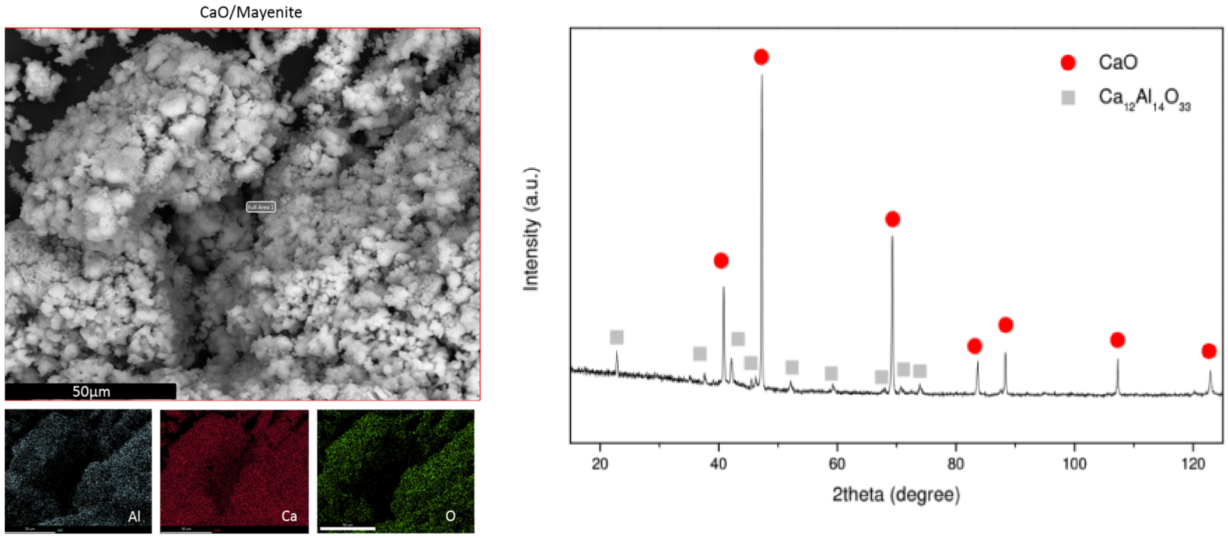


(a) (b)

FIGURE 1. a) SEM image of pure Mayenite, b) TGA analysis of pure Mayenite under charging/discharging cycles (blue line: normalized weight pattern; black line: temperature program).

Regarding CaO/Mayenite system, SEM image for CaO supported on Mayenite (Fig. 2a) shows porous aggregates with dimensions of 50-100 µm, composed by smaller (5-10µm) particles. Elemental EDX mapping analysis of Ca and Al shows the homogenous distribution of CaO on the Mayenite support (Fig. 2a).

Figure 2b shows the XRD patterns for CaO/Mayenite system as–prepared. The characteristic peaks of CaO and $Ca_{12}Al_{14}O_{33}$ are detected. CaO exhibits a polycrystalline nature with a preferential orientation along the (200) axis. The possible presence of $CaCO_3$ or $Ca(OH)_2$ formed by powder exposure to the atmosphere is below detection limit.



(a) (b)

FIGURE 2. (a) SEM/EDX analysis for CaO supported Mayenite; (b) XRD patterns for CaO supported Mayenite

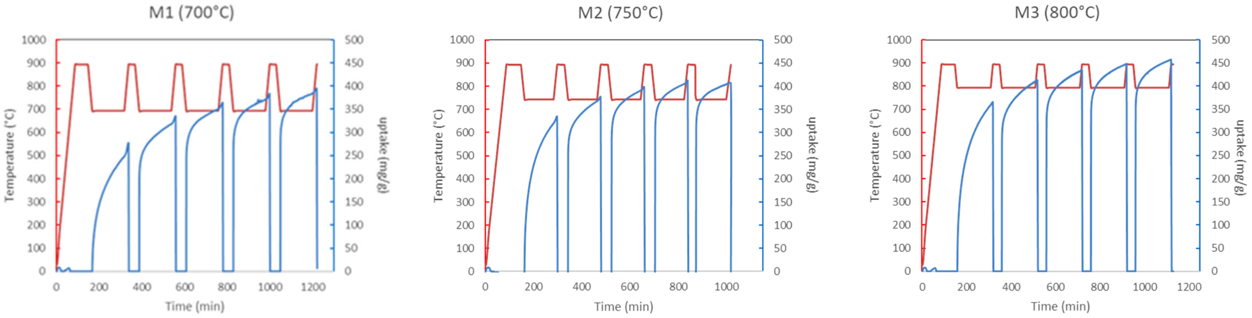
The CO_2 capture capacity was investigated on three fresh samples (M1, M2 and M3), which were subjected to different thermal cycles. The weight variations of the samples as a function of time during cyclic experiments (5 consecutive cycles) are shown in Fig. 3. The de-carbonation reaction is always complete in the time interval considered. The effect of temperature on carbon dioxide uptake is explored by varying the carbonation temperatures at 700, 750 and 800 °C, as reported respectively in Fig. 3a), 3b), 3c).

Similar trends for the carbonation step are detectable in all experiments: the weight gain gradually increases from the first to the fifth cycle. It could be noted that CO_2 uptake in the first cycle is ~5% lower than in the second one. Such a phenomenon is unusual because typically sorbents are known to lose activity with increasing numbers of calcination/carbonation cycles, due to sintering and occlusive phenomena in the pores. However, these findings are in accordance with previous results reported for CaO supported over Mayenite. The material undergoes a gradual activation operated by the thermal effect called self- reactivation [13].

As clearly observable in Fig. 3, the carbonation reaction involves two stages [14]: an initial fast stage, which is kinetically controlled, and a second stage, usually much slower, controlled by diffusion of CO_2 through the newly formed $CaCO_3$ layer. The shift between these stages is hardly observed in the first cycle, for all the 3 temperature courses. In fact, focusing on the shape of the carbonation curves for the first cycles, it could be remarked that it is qualitatively different from the other ones.

During the following cycles, the typical features of carbonation processes with a marked transition between the fast stage and slow stage can be observed for all experiments.

It can also be seen that the higher is the temperature, the faster the material reaches the self-reactivation.



(a) (b) (c)

FIGURE 3. TGA results for cyclic carbonation-calcination tests during cycle number 1-5 at 700 °C (a), 750 °C(b) and 800 °C (c). The uptake is expressed in mg/g (calculated on total sample weight).

To better highlight the temperature response of the carbonation step, a comparison between the analyses reported in Fig. 3 was conducted, taking into account the 5th cycle for each cyclic test. In Fig. 4, the calculated CaO conversion over time for the three different temperature levels is reported. Independently of the temperature level, the typical feature of the carbonation reaction is clearly observable, with the reaction rate dramatically dropping after the first minutes of the test. From the same Figure, it can be noted that the maximum CaO conversion attained in the last carbonation steps is favoured by higher temperatures and, for temperatures below 800°C, 100% conversion is not attained. This is clearly linked to the reaction kinetics being favoured at higher temperatures, but also the reactivation phenomenon probably plays a role: Fig. 3a shows that the reactivation phenomenon is slower at lower temperatures and, as a consequence, the activity of the material after 5 cycles is different depending on the temperature used in the calcination steps. Further investigations are undoubtedly required to fully understand the kinetic limiting factor affecting the carbonation reaction yield at temperature lower than 800°C. Obviously, in order to maximize the carbonation reaction extent and consequently increase the system storage capacity (energy released per mass unit), the latter temperature might be considered for practical applications.

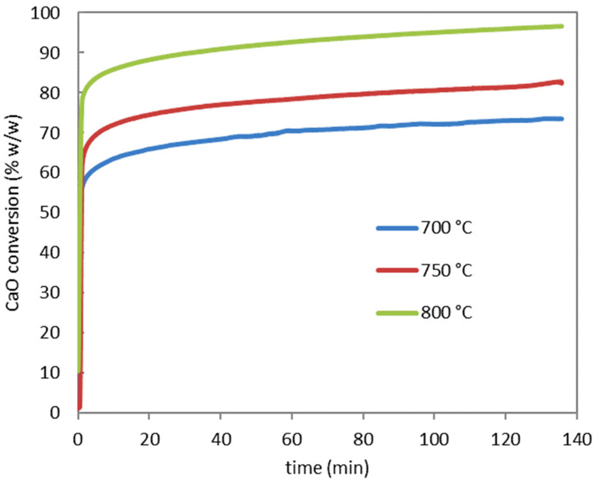


FIGURE 4. CaO conversions versus time profile at carbonation temperature of 700°C (M1), 750°C (M2), 800°C (M3) at 5th cycle

In order to check the material stability under cyclic thermal treatments, a specific test consisting of 14 cycles was conducted at a calcination temperature of 900°C and a carbonation temperature of 750°C, which are values that may be relevant for a TCS system coupled with a gas-based central receiver CSP system. The carbonation step, in analogy with the tests previously mentioned, has a standard duration of 120 min.

Fig. 5 shows the final CaO conversion obtained in each cycle, for a total test duration corresponding to 40 h: the curve starts with a conversion value of 65%, then gradually increases approaching 80% CaO conversion and, finally, appears to be reaching a plateau in correspondence of the 10th cycle. The initial trend, lasting about 500 min, is attributed to the self-reactivation mechanism previously mentioned. These results suggest promising material stability and resistance regarding carbonation/calcination cycling that could ensure technical viability in operational TES systems.

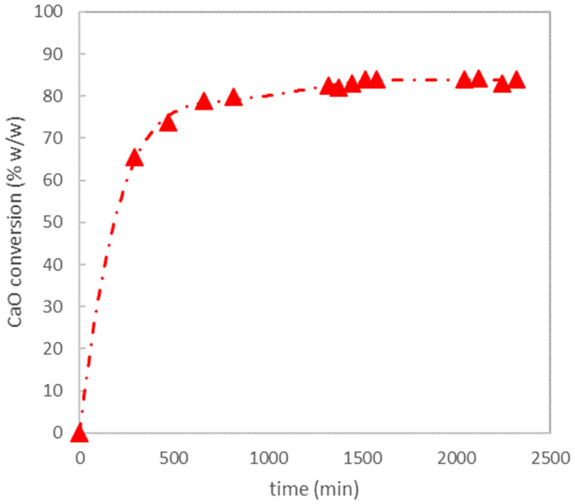


FIGURE 5. CaO conversion versus time during cycling between 900°C (calcination-30 min) and 750°C (carbonation-120 min).

The cycled sample was successively subjected to morphological analysis that showed some agglomeration and a partial voids occlusion after thermal cycling. Generally, this behaviour is ascribed to sintering that occurs when $CaCO_3$ thickness of the product layer grows and sticks grains together, but it is also generally accompanied by CaO conversion decline [13], which is not observed here. In fact, the SEM image (Fig. 6) confirms that the powder preserves the particle agglomerates with sizes around 1 µm, perfectly compatible with the substantial stability observed in the thermal tests. This confirms the effectiveness of the material stabilizing action provided by the mayenite support.

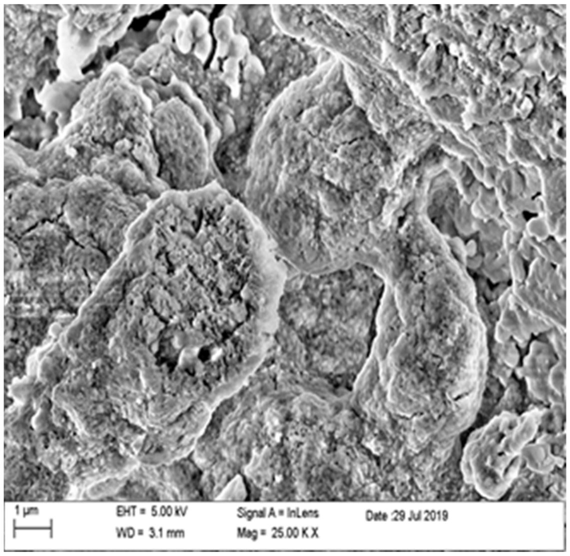


FIGURE 6. SEM image of a cycled sample (carbonation reaction temperature: 750 °C) at a magnification of 25 KX.

Finally, since the purpose of the present experimental campaign is to verify the viability of the material as a heat storage medium, an additional test was performed reducing the duration of the carbonation step (20 min in place of 120 min), thus limiting the analysis to the conditions characterized by the higher (and more easily exploitable) heat fluxes: indeed, even if calcium oxide keeps capturing carbon dioxide during the entire duration of the carbonation step (Fig. 7), high exothermic heat flows are observed only during the first 20 minutes in the given experimental conditions. Such higher flows correspond to the initial fast carbonation stage already mentioned, and the measured heat release is consistent with the partial weight gain. The supported sorbent was subjected to several charge/discharge cycles limiting the carbonation reaction to 20 min and the faster calcination step to 10 min.

Such "short cycles" have been performed on a material previously subjected to ten regular cycles, which exhibited a stable CaO conversion vs. time profile.

Obviously, the overall amount of cycled carbon dioxide is lower in shorter tests (0.35 vs 0.45 g of CO_2 per g of material) as can be observed in Fig. 7, but, from a technological point of view, the released heat flux may be significant only during the early stage of the carbonation reaction. From Fig. 7 it is evident that, after an initial conversion decay, the amount of carbon dioxide exchanged during carbonation/calcination cycle reaches a plateau. The inset highlights that after 20 min, the exothermal heat flow has dramatically reduced.

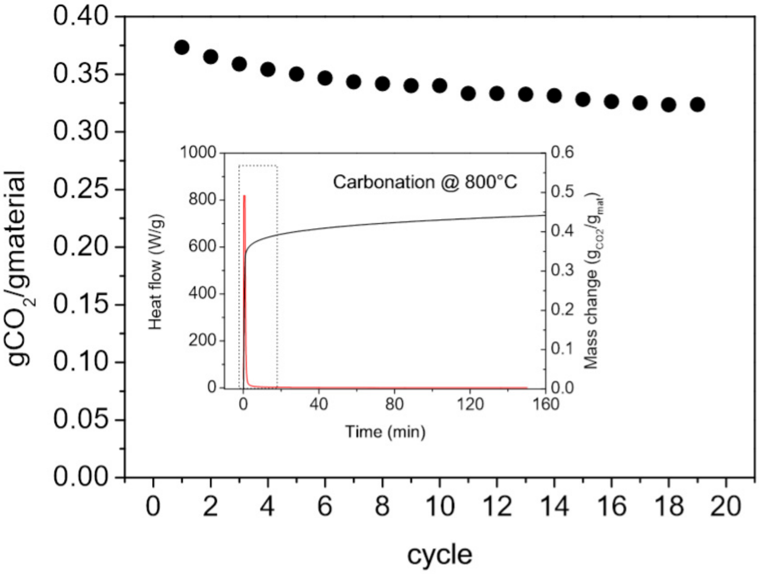


FIGURE 7. The amount of carbon dioxide cycled by the CaO-mayenite sample reducing the carbonation time to 20 min and calcination to 10 min.

As a future perspective, in order to improve the effectiveness of the discharging step, a more comprehensive investigation into the material preparation will be performed, by varying the CaO load on the inert support to identify the best compromise between the system reactivity and stability.

The objective is to enhance the carbonation reaction rate to make it comparable with the calcination kinetics, to recover all the stored thermal energy.

CONCLUSIONS

The purpose of the work is to synthesize and test a supported thermochemical storage material based on the $CaO/CaCO_3$ reacting system, which, even presenting a high reaction enthalpy, is typically subject to gradual deactivation under cyclic thermal treatments. Therefore, a supported material was synthesized, using Mayenite as inert media, recently adopted in literature within CO_2 capture technology; the novel system was prepared by a simple SolGel method, and its experimental characterization demonstrates good physical and kinetic properties. In particular, the powder remained stable over more than 40 h, with a carbonation conversion higher than 80%. Furthermore, no physical/chemical interaction of the mayenite support with CO_2 was observed, confirming its inertia and suitability for this application.

Regarding the storage thermal efficiency, the following considerations can be done:

- the relatively high temperature level of the carbonation reaction potentially leads to high heat losses towards the ambient and consequently to low thermal efficiencies of the thermal storage. This can be overcome through the use of a proper insulation systems;

- on the other hand, a high temperature level of the carbonation reaction guarantees high exergetic efficiencies of the overall CSP/TES system, alligning the temperatures of the charging and discharging steps.

To summarize, the proposed system seems promising for TCS applications and further investigation into the preparation protocol will be performed in the future to improve the carbonation reaction rate. As a future activity, new batches of material will be prepared, even varying the CaO load on the inert support, to identify the best compromise between the system reactivity and stability.

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