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New synthesis method for CaO-based synthetic sorbents with enhanced properties for high-temperature CO_2-capture

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Abstract

In this paper, a new synthesis method to obtain mixed $CaO/Ca_{12}Al_{14}O_{33}$ solids for high temperature CO_2 capture is presented. The modification of a pure phase $Ca_3Al_2O_6$ solid through a thermal treatment under controlled conditions leads to a high CO_2 absorption capacity material, with very promising long term stability during absorption/desorption cycles. The influence of the calcination temperature during the synthesis of the $Ca_3Al_2O_6$ powders, and the temperature and atmosphere applied during the thermal treatment was studied. Therefore, optimum conditions for high stabilization rate and high final CO_2 absorption capacity of the sorbent could be determined. Comparison with a natural sorbent (dolomite) over 150 carbonation/calcination cycles is also included, showing a substantial improvement of the synthetic solid CO_2-uptake at long term use, compared to that of natural sorbents.

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Keywords: CaO; sorbent; CO_2 capture

1. Introduction

Looping cycles for CO_2 capture, employing a CaO-based sorbent, represents an important new type of technology to separate efficiently CO_2 from combustion/gasification gases. This capture process based on the reversible carbonation reaction of CaO at high temperature - has been widely reported in the literature by various authors [1-5]. Thus, one of the key issues of this technology is the development of stable and efficient high temperature solid sorbent.

Ideally, a desirable CO_2 sorbent must present a large absorption capacity, fast kinetics at low CO_2 partial pressure, a low regeneration temperature and high chemical and mechanical stability. The most conventionally used sorbents are natural Ca-based materials - such as limestone ($CaCO_3$) and dolomites ($Ca,Mg(CO_3)_2$) since they show a high initial absorption capacity, good absorption and regeneration kinetics and are largely available at low price. However, natural sorbents show a rapid decay of the absorption capacity with carbonation/calcination cycles [6-7]. This loss of CO_2 capacity is due to a grain sintering mechanism occurring at elevated temperature, and to the loss of porosity caused by small pores volume reduction [6-8]. Thus, only a low residual conversion of approx. 8g CO_2/100g sorbent can be expected at long term use, as it was reported for limestone after 500 cycles [7]. Therefore,

the synthesis of CaO-based sorbents with small particle size and high specific surface area have been investigated over last years, in order to overcome the degradation of the absorption capacity during cycles [9-10].

The addition of a binder as support for fine CaO sorbent has been proposed by several authors to limit the sintering and increase the durability of the sorbent [11-13]. The most promising results were obtained by integration of CaO with mayenite ($Ca_{12}Al_{14}O_{33}$). Indeed, the calcium aluminate metal oxide provides a stable and inert framework for the active sorbent particles, which significantly improves the long-term chemical and mechanical properties of the sorbents [14-19].

In this study, a new synthesis route for a $CaO/Ca_{12}Al_{14}O_{33}$ sorbent by decomposition of $Ca_3Al_2O_6$ is for the first time reported. Synthesis and chemical stability of $Ca_3Al_2O_6$ was investigated at different temperature and gas compositions. The resulting CO_2-acceptor properties are evidenced. To determine the potential of $Ca_3Al_2O_6$ and mixed $CaO/Ca_3Al_2O_6$ materials as CO_2 acceptors, the chemical stability during carbonation/calcination cycles in severe calcination conditions was tested and compared to a natural sorbent (dolomite).

2. Experimental

2.1. Powder preparation

The starting oxide powders were synthesized through the citrate route [20]. Citric acid (CA) (Merck, >99.5%), ethylene glycol (EG) (Merck, >99.5%), aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Aldrich > 99%) and calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$, Aldrich >99%) were used as precursors. After dissolution of stoichiometric amounts of the metal nitrates in deionized water, citric acid monohydrate (CA) ($C_6H_8O_7.H_2O$, Merck GR for analysis >99.5%) was added in the molar ratio 2/1 to that of cations, to ensure that all the cations were complexed in the solution. After achieving complete dissolution, ethylene glycol (EG) ($C_2H_6O_2$ pro analysis Merck >99.5%) was added at a molar ratio EG/CA=3/2, and the solution was introduced in an oven preheated at 160°C for 6h to evaporate the superfluous water. Upon heating, the volume of the solution decreased by evaporation of superfluous water and no evidence of precipitation was observed. The resulting brown fluffy solid was further pulverized and calcined at 700°C for 6 h to burn off most of the organic residues. Finally, the powder was calcined at different temperatures and times to obtain single phase $Ca_3Al_2O_6$ materials. The solids were labelled C3A-T-t, where T means temperature in Celsius degrees (900, 1000 and 1100 ºC) and t means time in hours (6, 24 and 1 h). Prior further analysis, the powder was sieved under 100μm.

2.2. Powder characterization

The X-ray Diffraction (XRD) spectra of the sorbents were performed on an Inel XRG 3000 diffractometer with CuKα radiation. XRD tests results were retrieved and stored using commercial software (Inel Acquisition). The morphology and the elemental analysis of the powders were investigated by scanning electron microscopy (SEM, Hithachi S-4800 Field Emission).

2.3. Thermogravimetric experiments

Thermal stability, CO_2 sorption capacity and sorption/regeneration kinetics were studied using a thermogravimetric analyzer (TGA, CI electronics). The TGA tests were initiated in a N_2 atmosphere. Temperature was increased to the desired value at a rate of 10°C/min. After thermal stabilization, N_2, CO_2 and/or H_2O inlet flows were introduced after 5 minutes at the working temperature. The N_2/CO_2 ratio was controlled by mass flow controllers (Bronkhorst, EL-FLOW Digital series) whilst steam flow was controlled using a liquid flow controller (Bronkhorst, Liqui-flow). Both streams were combined using a controlled evaporation mixing system (Bronkhorst, CEM). The effects of CO_2 and steam partial pressures on the carbonation of the Ca-based sorbent were also investigated. A natural Ca-based sorbent (artic dolomite) was also tested in similar conditions for comparison purposes.

3. RESULTS

3.1. $Ca_3Al_2O_6$ characterization

The XRD patterns of the $Ca_3Al_2O_6$ powder after calcination at various temperatures and times are shown in Fig. 1. After calcination at $900^{\circ}C$ for 6h (C3A-900-6), CaO did not completely react with the aluminium and traces of $Ca_5Al_6O_{14}$ were detected in the powder, together with CaO and $Ca_3Al_2O_6$ phases. After calcination at $1000^{\circ}C$ for 6h (C3A-1000-6) the amount of $Ca_5Al_6O_{14}$ decreased. Single phase $Ca_3Al_2O_6$ (C3A) materials were finally obtained after calcination at $1000^{\circ}C$ for 24h (C3A-1000-24, see Fig. 1) and $1100^{\circ}C$ for 1 hour (C3A-1100-1) (not included in Fig. 1).

3.2. Chemical stability of $Ca_3Al_2O_6$ in CO_2/steam atmosphere

The thermal stability of pure $Ca_3Al_2O_6$ powders, (C3A-1000-24 and C3A-1100-1) was investigated by TGA in controlled atmosphere (20/30/50vol% of $CO_2/H_2O/N_2$) at $780^{\circ}C$ for 20 hours. These gas concentrations were chosen to simulate the typical CO_2 and steam concentrations applied during methane reforming. Thermal stability of the powder calcined at the lowest temperature (C3A-900-6) was also investigated to highlight the influence of the secondary phase ($Ca_5Al_6O_{14}$).

As illustrated in Figure 2, under those experimental conditions a weight increase was measured for the three different samples. The rate of weight increase was dependent on the calcination temperature. Powder calcined at $900^{\circ}C$ displayed the fastest weight increase but had a lower maximum weight increase (~16wt %) while the single phase C3A samples calcined at higher temperature showed a slower weight increase, but a weight uptake close to 20wt%.

After 20 hours under thermal treatment in CO_2 and steam-rich atmosphere (balanced in N_2), the CO_2 and steam flows were switched off and powders were cooled down to room temperature under N_2 flow prior to XRD analysis. When exposed to nitrogen, the weight of the powder decreased swiftly and finally came back to the initial weight value. XRD diffraction patterns of C3A-900-6 and C3A-1000-24 after thermal treatment are shown in Figure 3, where no C3A can be detected.

In both powders, the initial C3A phase has been replaced by a mixture of CaO (C) and $Ca_{12}Al_{14}O_{33}$ (also mentioned as C12A7), with traces of $CaCO_3$. In addition to those three compounds, C3A-900-6 showed a significant amount of $Ca_5Al_6O_{14}$ (also mentioned as C5A3).
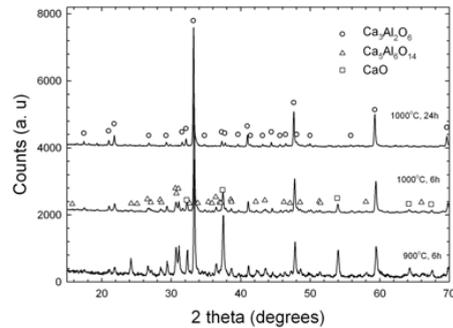

Fig. 1: X-ray diffractions of $Ca_3Al_2O_6$ powders after calcination at various temperatures.

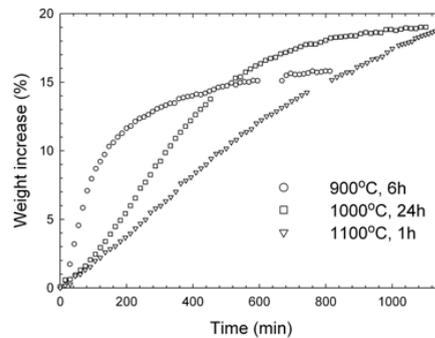Fig. 2: Effect of calcination temperature on thermal stability of $Ca_3Al_2O_6$ at $780^{\circ}C$ in $20\%CO_2/30\%H_2O/50\%N_2$ atmosphere.
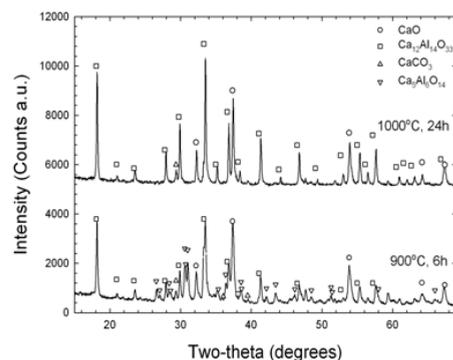

Fig. 3: X-ray diffractions of C3A powders (C3A-900-6 and C3A-1000-24) after decomposition in a CO_2/steam atmosphere followed by regeneration in N_2 atmosphere.

As evidenced by TGA (Fig. 2) and XRD (Fig. 3) studies, C3A powders are unstable in the presence of CO_2 and steam at elevated temperature, and decompose according to the following reaction:

$$Ca_3Al_2O_6 + CO_2 + H_2O(g) \quad \Rightarrow \quad 9/7\ CaCO_3 + 1/7\ Ca_{12}Al_{14}O_{33} + H_2O(g) \quad (1)$$

Considering (1), a maximum CO_2-uptake of 21g (CO_2)/100g $(Ca_3Al_2O_6)$ is expected, which is in good agreement with the maximum weight increase reported in Fig.2 for single phase powders C3A-1000-24 and C3A-1100-1. On the other hand, since $Ca_5Al_6O_{14}$ phase is still present in C3A-900-6 after 20 hours exposure in 50vol% of CO_2/steam at 780°C. It is assumed that the C5A3 phase is stable and inert in those conditions, and does not contribute to the total CO_2-sorption. Therefore, despite better decomposition kinetics during the thermal treatment in CO_2/steam mixture for C3A-900-6 powders, single phase C3A-1000-24 powders are preferred, and will be used for further investigation.

After complete decomposition of the C3A phase, the formed $CaCO_3$ is decomposed when the atmosphere is switched back to $N_2(g)$ as predicted by the thermodynamic stability curve of CaO [21] and the weight comes down to its initial value. No reaction of the solid with steam could directly be observed during those experiments. However, as evidenced further in this paper, presence of steam together with the CO_2 is necessary to decompose the C3A phase and is therefore reported in the equation (1).

3.3. Effect of the temperature on decomposition of $Ca_3Al_2O_6$

Fig.4 shows the influence of the temperature on the decomposition rate of the C3A-1000-24 powder in 50/50vol% CO_2/steam atmosphere. As it can be observed, for all the experiments an initial CO_2-uptake increase with time is detected, followed by the further stabilisation of the total CO_2 uptake. A maximum decomposition rate was observed at 780°C. At 700°C and 780°C, a maximum weight increase close to 20wt% was measured while at 600°C, the maximum CO_2-uptake could not be reached because of the slow kinetic. At 850°C, the kinetic of decomposition decreases as well as the maximum CO_2-uptake (~14.5%). Therefore, an optimum temperature can be established at around 800°C, considering both the rate of CO_2-uptake increase at the initial stage and the final absorption capacity. Finally the powder was treated at 900°C in the same atmosphere for 12 hours but no weight increase was observed on the TGA.
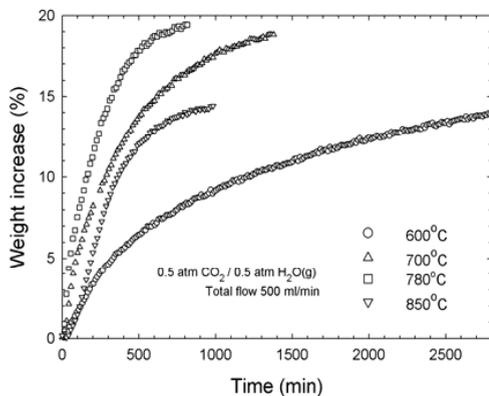

Fig. 4: Effect of temperature on the decomposition of C3A-1000-24 in 50vol%CO_2/$H_2O(g)$ atmosphere.
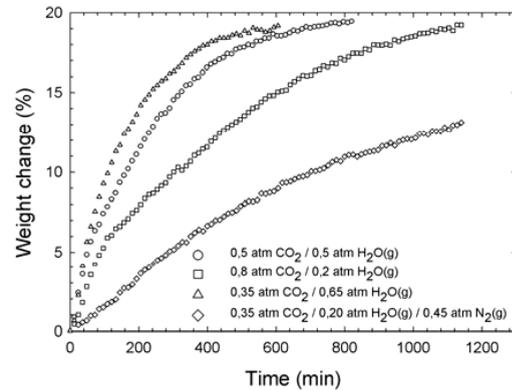

Fig. 5: Effect of partial pressure of CO_2 and $H_2O(g)$ at 780°C on stability of $Ca_3Al_2O_6$ calcined at 1000°C for 24h.

The equilibrium shift towards the formation of $CaCO_3$ at high temperature seems to be the driving force for the decomposition of C3A into $CaCO_3$ and C12Al7, in agreement with (1). The calcination temperature as a function of the equilibrium CO_2 partial pressure can be calculated from an equation proposed by Barker et al [21]. According to this equation, at P_{CO2}=0.5, the calcination temperature of $CaCO_3$ is 853°C. Therefore, when the C3A material was exposed to a CO_2/H_2O mixture at 850°C, the decomposition reaction is not total even after 20 hours, whilst at 900°C no decomposition of CA3 was detected.

3.4. Effect of CO_2 and steam partial pressures on decomposition of $Ca_3Al_2O_6$

The influence of the partial pressure of CO_2 and steam on the decomposition rate of C3A-1000-24 was investigated by exposing the materials to different partial pressures of CO_2 and steam at 780°C (Fig. 5). When the material was exposed to 100% CO_2 or 100% steam, no weight change could be detected, whilst in diluted atmosphere (45/35/20vol% of $N_2/CO_2/H_2O$) the maximum weight increase was 13% after 20 hours. When increasing the steam partial pressure (35/65vol% CO_2/H_2O) or the CO_2 partial pressure (80/20vol% CO_2/H_2O), the decomposition rate and the total absorption capacity increased, and a maximum weight uptake of ~19.5% was achieved after 9 and 19 hours, respectively. Introduction of steam and CO_2 at high temperature showed to be necessary to achieve the decomposition of CA3, and a higher decomposition rate was observed at high steam partial pressure. Previous reports have shown the influence of steam on the CO_2-uptake for CaO-based sorbents [22,23], but mechanisms are not yet fully understood. However, steam hydration of CaO increases both pore area and pore volume, consequently improving the long-term conversion to $CaCO_3$ over multiple cycles [23]. Thus, diffusivity of CO_2 through the product layer is improved and the reaction kinetics enhanced. Such mechanism most certainly plays a role in the thermal behaviour of the C3A powders studied in the present work.

3.5. Morphology of the powder

Fig. 6 shows the SEM image of the CA3-1000-24 powder before and after treatment at 780°C in 50/50vol% CO_2/steam. Although the general morphology of the particles is not modified by the thermal treatment, as shown by images (a) and (c), their surface changes, (see (b) and (d)), due to formation of nanoparticles (200-500 nm). The elemental analysis by EDX of the particles cross section showed that those nanoparticles are mainly constituted of CaO that had evolved on the surface of larger C12A7 particles during the thermal treatment.

Those nanoparticles are homogeneous in size and uniformly distributed on the surface of the C12Al7 particles, forming a thin CaO external layer (500nm – 1um). Therefore, the surface morphology and composition - and consequently the sorbent behaviour- have critically changed due to the formation of those CaO nanoparticles during the thermal treatment.
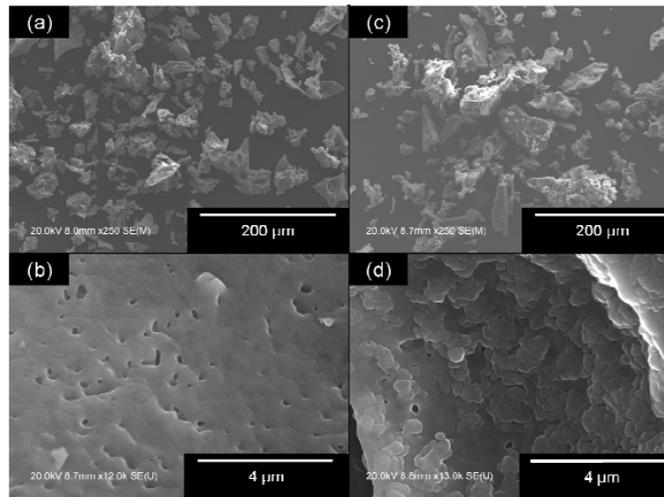

Fig. 6: SEM image of C3A-1000-24 powder; before (a,b) and after exposure to 50/50vol.% CO_2/steam atmosphere (c,d).

3.6. Stability during carbonation/regeneration multi-cycles analysis

Because of the accessible CaO formed during decomposition of C3A, this material has a clear potential as high temperature CO_2 acceptor. In order to determine the performance of this new CO_2-sorbent, the stabilised calcium aluminate material was repeatedly exposed to a mixture of 50/50vol.% CO_2/steam at 780°C for 10 min, heated to 870°C for regeneration with a 10 °C/min heating ramp and finally cooled to 780°C in 50%N_2/50%$H_2O(g)$ with a 3°C/min cooling ramp. Figure 7a shows the absorption profiles for the first, the 10th and 70th cycles together with the temperature profile. It can be observed an initial increase of CO_2-uptake, followed by a plateau and, finally, a weight loss corresponding to a release of CO_2 when the material is heated up to 870°C. The absorption and regeneration kinetics remain unchanged after the 70th cycle. The CO_2 absorption capacity increases from 14 to 18wt% during the first 20 cycles and keeps constant around 19wt% for over 150 cycles afterwards (Figure 7b).

For comparison, the absorption capacity of natural dolomite during multi-cycles in the same conditions is included in Figure 7 b). Dolomite shows a large decay of its CO_2-uptake from 44wt% during the first cycle down to 16wt% at 70th cycles and finally stabilizes around 10wt% above 150 cycles, as reported previously [6]. The synthetic sorbent shows a slight increase of the absorption capacity during the 20 first cycles, which might be attributed to a completion of the decomposition of the $Ca_3Al_2O_6$ starting material. After 20 cycles, the absorption and regeneration kinetics are stable, and the total absorption capacity of the material remains close to 20g CO_2/100g sorbent for 150 carbonation/calcination cycles in severe regeneration conditions, without deterioration of the reaction kinetics. The improved chemical stability of the sorbent might be attributed to a limited sintering of the CaO nanoparticles, due to the layered structure of the sorbent. Indeed, the homogeneous dispersion of the CaO particles on the surface of the C12A7 particles limits the agglomeration of these CaO particles even at elevated temperature and high CO_2 partial pressure. Additionally, because of the small size and high accessibility of the CaO particles, the sorbent also shows a high reactivity and a conversion level above 90% of the total amount of CaO available.
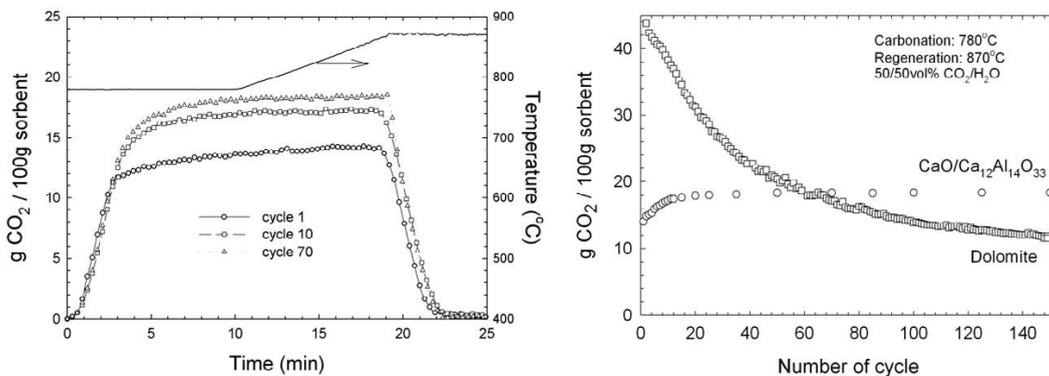

Fig. 7: Chemical stability of the synthetic CO_2 sorbent during multi-cycling under severe calcination conditions (carbonation at 780°C, regeneration 870°C in 50/50vol% CO_2/$H_2O(g)$); a) (left): Carbonation/regeneration cycles (1st, 10th and 70th); b) (right): Absorption capacity for the decomposed $Ca_3Al_2O_6$ after thermal treatment and for a dolomite sorbent.

3.7. Mixed sorbent CaO/Ca₃Al₂O₆

To improve the total CO_2-capacity of the sorbent, mixed $CaO/Ca_3Al_2O_6$ powders were prepared according to the synthesis method described previously. Biphasic materials with different CaO-to-$Ca_3Al_2O_6$ ratios were obtained after calcination at 1000^oC for 24h, as evidenced by XRD analysis (Fig. 8) and thermally treated at 800^oC in 50/50vol% H_2O/CO_2 for 24 hours prior to TGA analysis.
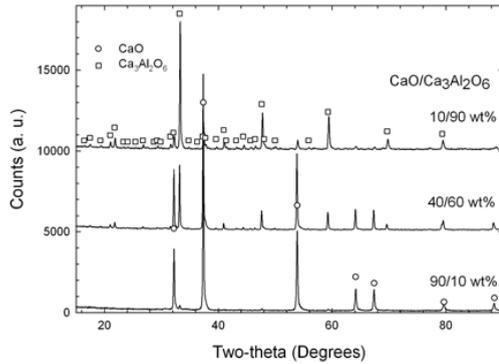
Fig. 8: X-ray diffractions of mixed $CaO/Ca_3Al_2O_6$ powders calcination at 1000^oC for 24h.

Fig.9 shows the long-term stability of mixed CaO/C3A materials with various weight ratios during TGA multi-cycling in severe calcination conditions (regeneration at 925^oC in 85/15vol% CO_2/H_2O). High-temperature and high CO_2 concentrations were chosen to evaluate the sintering process of CaO particles and the thermal stress endured by the sorbent. Sorbent with 60 and 40wt% CaO have a higher total capacity (53 and 43g CO_2/100g sorbent respectively). Their absorption capacity is stable for a few cycles, but since the absorption kinetics decreases continuously during cycling due to sintering of CaO particles, the sorbents finally show an abrupt decay of their properties after only 10 and 20 cycles. However, sorbents with 10 and 20wt% CaO show exceptionally stable absorption capacities (21 and 29g CO_2/100g sorbent respectively) even after 115 sorption/regeneration cycles under severe conditions without significant loss of reactivity.

4. Conclusions

The $CaO/Ca_{12}Al_{14}O_{33}$ sorbent, synthesized via decomposition of $Ca_3Al_2O_6$ during thermal treatment in a steam/CO_2 mixture, shows remarkable properties as CO_2 acceptor. The evolution of the $Ca_3Al_2O_6$ crystalline phase under different conditions revealed that a new preparation route can be assessed to obtain CO_2-sorbents with high CO_2-capacity and excellent chemical durability. The influence of the process parameters (temperature and atmosphere composition) on the decomposition reaction was successfully determined. Thereby, the optimum calcination temperature during the synthesis of $Ca_3Al_2O_6$ and the adequate temperature and CO_2/steam partial pressures to obtain the
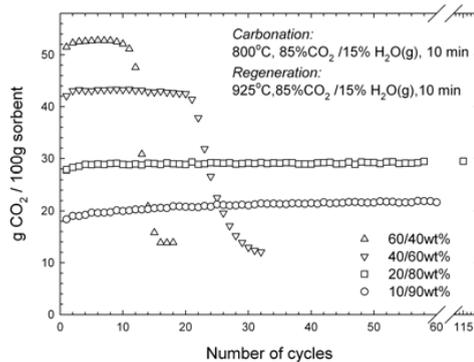
Fig. 9: Evolution of the absorption capacity during long-term multi-cycling in severe calcination conditions for mixed CaO/C3A with different CaO-to-C3A weight ratios.

$CaO/Ca_{12}Al_{14}O_{33}$ material were established.

The new sorbent presents a high CO_2 absorption capacity - up to 20g CO_2/100g sorbent - with a total conversion of 90%, during more than 140 carbonation/calcination cycles at 870^oC with 50vol% steam in CO_2. These exceptional properties are attributed to the formation of CaO nanoparticles on the surface of larger Ca/Al mixed-oxides particles during the thermal treatment. The experiments evidenced limited grain growth and absence of sintering of the CaO particles, even under severe calcination conditions. Additionally, the total absorption capacity of the sorbent could be increased up to 30g CO_2/100g sorbent by increasing the CaO-to-Ca3Al2O6 weight ratio in the initial composition without loss of reactivity and durability. Therefore, the clearly improved stability during

absorption/regeneration cycles compared to natural sorbents shows that the CaO/Ca$_{12}$Al$_{14}$O$_{33}$ material obtained via decomposition of Ca$_3$Al$_2$O$_6$ has a great potential for applications in high temperature CO$_2$ sorption processes [24].

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