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Development of CaO-based Mixed Oxides as Stable Sorbents for Post-Combustion CO_2 capture via Carbonate Looping

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Abstract

A promising concept for post-combustion CO_2 capture is carbonate looping, in which CO_2 is captured at high temperature using calcium-based sorbents. The process suffers from degradation of the materials and decrease of CO_2 capacity after multiple calcination/carbonation cycles. In this paper, we report the development of stable synthetic and natural mixed CaO-based sorbents for post-combustion CO_2 capture from industrial plans flues gases. The promoted synthetic sorbents, synthesized via a sol-gel auto-combustion method, exhibited very stable performance for 100 consecutive sorption/desorption cycles and an increased CO_2 uptake capacity. Promising performance was also achieved with a natural sorbents consisting of industrial water-treated hydrated lime mixed with a kaolin and/or MgO binder.

Keywords: Carbonate looping; CO_2 sorption; CaO-based sorbents; Sol-gel auto-combustion method; Cyclic experiments

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1. Introduction

More than 85 % of the world energy demand is supplied today by fossil fuels, with approximately three-fourths of the increase in atmospheric CO_2 being attributed to fossil fuel combustion [1]. It is generally accepted that a reduction in greenhouse gases (GHG) emissions is necessary to prevent the increase of CO_2 concentration in the atmosphere and the negative global warming effects. Combustion of fossil fuels releases a huge amount of carbon as

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CO_2 into the atmosphere. The use of fossil fuels in large stationary emission sources, such as power plants and other processing industries, contributes to the increase of GHG emissions, with energy-related CO_2 release from fuel combustion representing about 80% of the anthropogenic GHG worldwide [2].

Removing CO_2 from power plant flue gases is a very challenging task, as existing processes for CO_2 separation from the gas mixture requires a significant fraction of the plants' energy output. The CO_2 capture technology closest to market is post-combustion 'scrubbing' using amine-based solvents, which has been used for industrial-scale separation of CO_2 for several decades [3,4]. However, the installation and operation of these systems translates to large energy penalties and high costs for CO_2 separation from the flue gas components, resulting in a significant decrease of the overall plant efficiency and thus leading to increased energy prices. New or improved processes for CO_2 capture, combined with advanced power systems and industrial process designs, could reduce CO_2 capture cost and energy requirements [5].

A promising concept for CO_2 separation from combustion flue gases is Carbonate Looping [6-8]. Carbonate looping is an ex-situ, post-combustion CO_2 capture technology in which CO_2 from the flue gases is captured by a CaO-based sorbent in the carbonator. After saturation, the material is regenerated at higher temperatures and CO_2 is removed as pure stream, ready to be sequestrated or used in other applications. CaO carbonation is a highly exothermic process and with proper heat integration of the process, this heat can be employed for the endothermic regeneration of the saturated sorbent rendering the whole technique nearly autothermal.

CaO-based materials are presumed to be promising sorbents for CO_2 capture due to their low cost, high CO_2 sorption capacity and fast carbonation/calcination kinetics [9]. The challenge, however, remains with respect to sorbent conversion and recyclability. The decrease in the CO_2 sorption capacity of CaO over multiple carbonation/calcination cycles has been widely reported [9-11]. The high calcination temperature used for regeneration has a deteriorating effect on the cyclic stability of these sorbents, which has been mainly attributed to the intense sintering of the CaO particles. Although a high initial capacity is important in order to minimize the amount of sorbent circulating between the two reactors, maintaining or recovering this high capacity after multiple cycles, plays an equally important role. Different approaches have been applied to improve the cyclic stability of the sorbents, including thermal pretreatment [12,13], incorporation of inert thermally resistant materials in the structure of CaO [14-19] and reactivation through water or steam hydration [20,21]. Different synthesis methods have also been employed in order to improve the stability of CaO, including precipitation, dry or wet mixing, flame spray pyrolysis and several modified sol-gel routes [14-16,22-26]. The sol-gel preparation route ensures a homogenous distribution between CaO and binder, resulting in a stable structure, and inhibits sintering during multi-cycle operation. LuO *et al.* [26] prepared La-doped CaO via sol-gel using citric acid or urea as gelation agent. Carbonation conversion higher than 80% was reported, with satisfactory stability for the material prepared with citric acid. However, the material deteriorated rapidly under higher temperatures of sorbent regeneration. Aggeli *et al.* [16] developed a CaO-$Ca_3Al_2O_6$ sorbent using triethanolamine as combustion agent in a modified sol-gel method. They reported a carbonation conversion of 84% which remained constant for over 40 carbonation/calcination cycles.

Although synthetic sorbents exhibit in general higher sorption capacity and stability, natural materials like limestone or dolomite are of high interest due to their low cost and wide availability. Grasa and Abanades [27] investigated the multi-cycle stability of CaO-based sorbents derived from natural limestone. They showed that high temperatures and long duration during calcination accelerate the deactivation of the sorbent, leading to a residual conversion of ~8% after many hundreds of cycles. In order to reverse the deactivation of the natural materials, Manovic and Anthony [28] reactivated spent sorbents using steam hydration. After reactivation, the sorbent demonstrated significantly higher conversion and also better stability.

In this work, we report the development of stable synthetic and natural mixed CaO-based stable sorbents for post-combustion CO_2 capture from industrial plans flues gases. The synthetic materials consist of CaO-based mixed oxides with Al, Zr, La and Mg, prepared via sol-gel auto-combustion synthesis. Concerning the natural CO_2 sorbents, we investigated the effect of different pre-treatments on the sorption capacity and stability of an industrial hydrated lime. Mixing with inert minerals, such as kaolin and magnesia, was attempted in an effort to reduce sintering and degradation under consecutive sorption/desorption cycles.

2. Experimental

2.1. Sorbents preparation

Synthetic materials

Four CaO-based powders promoted with Al, Zr, La and Mg were prepared by sol-gel auto-combustion synthesis using citric acid as combustion agent. The starting material was $Ca(NO_3)_2 \cdot 4H_2O$ (J.T.Baker) and the corresponding precursor for each promoter ($Al(NO_3)_3 \cdot 9H_2O$ (Carlo Erba), $La(NO_3)_3 \cdot 6H_2O$ (Merck), $Mg(NO_3)_2 \cdot 6H_2O$ (J.T.Baker) and $ZrO(NO_3)_2 \cdot xH_2O$ (Acros)). All sorbents were prepared with a constant 66wt% concentration of free CaO. The required amounts of calcium nitrate and the precursor of each promoter were dissolved in distilled water under continuous heating and stirring. Subsequently, the required amount of citric acid was added to the aqueous solution in order to maintain a constant nitrate salts/combustion agent molar ratio of 3. The new solutions were heated on a heating plate to promote water evaporation. After gelation occurred, the formed gel was transferred to a preheated furnace at 300°C, where after a few minutes the gel was combusted in a self-propagating combustion manner. The as synthesized powders were then calcined at 900°C for 1.5 hour under air flow. The sorbents are denoted as Ca-X, where X refers to the promoter (Zr, La, Mg or Al).

Natural materials

Hydrated lime, $Ca(OH)_2$, provided by *CaO Hellas* was investigated as CO_2 sorbent. The effects of thermal pretreatment as well as hydration with water before the sorption/desorption tests on sorption capacity and stability of the natural sorbent were examined. The parent material was calcined at 900°C for 1.5 hour under air flow ($Ca(OH)_2$-C) in order to enhance the cyclic stability. The calcined sample was then hydrated with water at 70°C for 4 hours to increase the surface area and as a result the sorption capacity, and was finally recalcined at 600°C for 3 hours in order to decompose the formed $Ca(OH)_2$ during hydration. Lime after hydration was mixed with two natural binders, kaolin and magnesia obtained from *Prolat* and *Grecian Magnesite* respectively. Kaolin is a mineral composed mainly of Al_2O_3 and SiO_2 with a general formula of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, while the used magnesia was mainly MgO with less than 3% impurities. The mixed sorbents were prepared by wet mixing at 70°C under continuous stirring for 4 hours. The materials were filtered, dried overnight at 120°C and calcined at 900°C for 1.5 hr under air flow.

2.2. Sorbents characterization

X-ray diffraction (XRD) patterns were obtained with a Siemens D500 diffractometer using Cu-Kα radiation. An aluminum holder was used to support the samples in the measurements.

BET surface area and pore volume were measured by using nitrogen physisorption at 77K with an Autosorb-1 Quantachrome flow apparatus. Before the actual measurements, the samples were degassed at 250°C overnight.

2.3. Experimental procedure

The sorption capacity and stability of the CO_2 sorbents was tested in a SDT Q600 instrument for 50 and 100 consecutive sorption-desorption cycles for the natural and synthetic sorbents respectively. The CO_2 capacity of the sorbents was tested under 15% CO_2 flow in N_2 for 30 minutes at 650°C while desorption took place under 100% N_2 flow for 5 minutes at 850°C. The concentration of CO_2 flow was selected based on the realistic concentration of CO_2 in the outlet stream of power plant flue gases. Results are presented in terms of sorption capacity of the materials (mol CO_2/kg of sorbent) and CaO conversion. CaO conversion can be expressed as a function of the weight increase of the sorbent due to CO_2 absorption:

$$X(t),\% = \frac{MW_{CaO}}{MW_{CO_2}} * \%\text{weight increase}(t) * \frac{1}{w_{CaO}} \tag{1}$$

where MW_{CaO} and MW_{CO2} are the molecular weight of CaO and CO_2 respectively, and w_{CaO} is the weight fraction of free CaO present in the sorbent.

3. Results & Discussion

3.1. Characterization

3.1.1 Synthetic sorbents

The crystalline phases formed in the synthesized CO_2 sorbents were determined by X-ray Diffraction. Fig. 1 illustrates the X-ray diffraction patterns of all synthetic CaO sorbents. In the diffractrogram of pure synthesized CaO, reflections in angular positions characteristic of CaO and $Ca(OH)_2$ appear. Concerning the mixed oxides, characteristic reflections of CaO appear in all samples, accompanied by $Ca(OH)_2$ in Ca-Mg and Ca-Zr sorbents. Formation of mixed $Ca_3Al_2O_6$ and $CaZrO_3$ was observed in Ca-Al and Ca-Zr sorbents, respectively. On the contrary no mixed phase was formed between CaO and Mg or La, where the nitrate salts decomposed to MgO and La_2O_3 respectively.

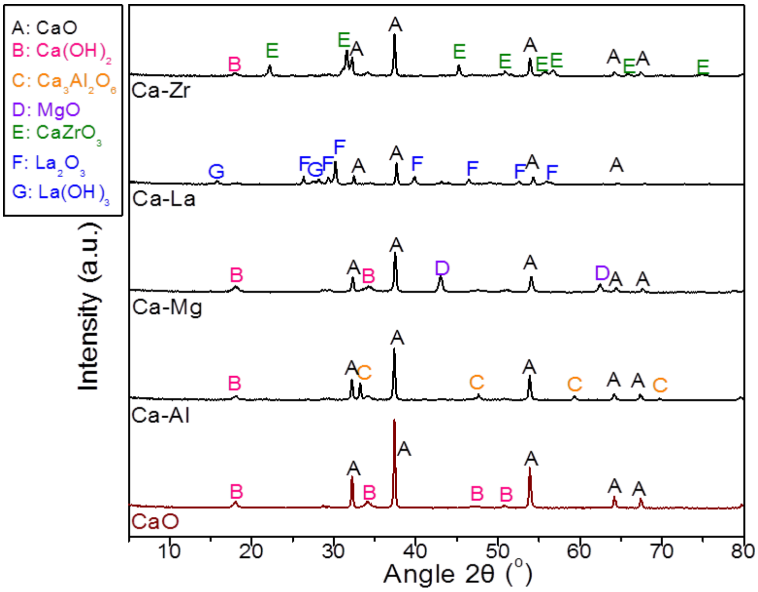

Fig. 1. X-ray diffraction patterns of the synthetic sorbents

The textural properties of the synthetic CaO-based sorbents are presented in Table 1. Comparing the four promoted sorbents prepared with the same combustion agent, it can be observed that the nature of the dopant affects the surface area of the final material. Surface areas ranging from 28 m^2/g for Mg-doped CaO to 9 m^2/g for La-doped CaO were recorded.

Table 1. BET surface area and pore volume of the synthetic CaO sorbents

Sorbent	Surface area (m^2/g)	Pore volume (cm^3/g)
CaO	12.22	0.130
Ca-Mg	28.37	0.112
Ca-La	8.78	0.138
Ca-Zr	15.28	0.051
Ca-Al	11.93	0.062

3.1.2 Natural sorbents

The X-ray diffraction patterns of the natural CaO-based sorbents are presented in Fig 2. The as delivered industrial material ($Ca(OH)_2$) is composed of almost pure calcium hydroxide, with only a small reflection corresponding to calcium carbonate. After thermal pre-treatment at 900°C ($Ca(OH)_2$-C), $Ca(OH)_2$ was almost completely decomposed to CaO with minor $Ca(OH)_2$ reflections. When the calcined sample was subjected to water treatment ($Ca(OH)_2$-W), only reflections at the angular positions of $Ca(OH)_2$ appear. The addition of kaolin to the CaO lattice leads to the formation of a mixed phase $Ca_3Al_2Si_2$, together with pure Al_2O_3 and SiO_2 that were also observed in the diffractrogram of pure kaolin (not shown). In the case of the use of MgO as binder, the XRD patterns reveals the existence of only CaO and MgO crystalline phases, without any formation of mixed components.

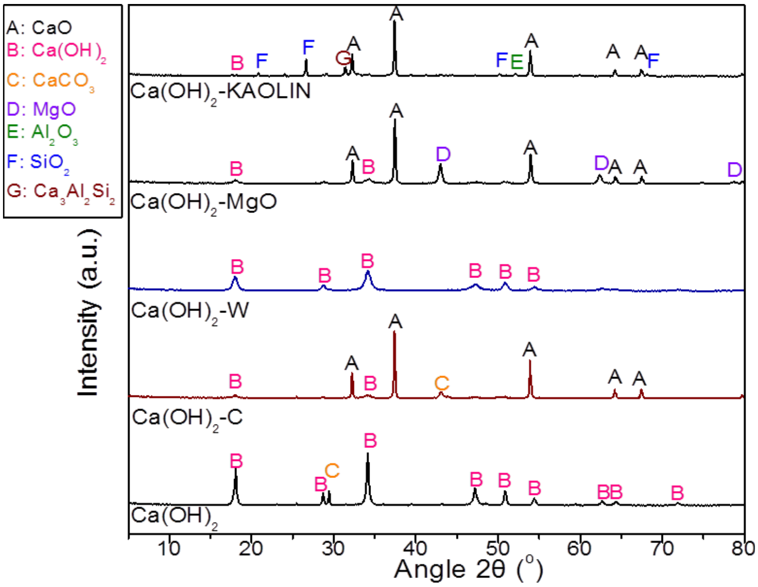

Fig. 2. X-ray diffraction patterns of the natural sorbents

The surface area and pore volume of all the natural CaO-based sorbents is presented in Table 2. Thermal pre-treatment of the sorbent has, as expected, a negative effect on the textural characteristics of the material. On the other hand, hydration of the calcined sample leads to an increase in surface area and porosity by 27% and 83% respectively compared to the parent material ($Ca(OH)_2$). Concerning the mixed materials, the nature of the binder seems to affect the textural properties of the final sorbent in a different way. The introduction of kaolin in industrial hydrated lime severely decreases the surface area, from $17m^2/g$ to $3m^2/g$, even though pure kaolin has similar surface area as the hydrated lime (~$13m^2/g$). On the contrary, the use of MgO greatly increases the surface area to ~$23m^2/g$ which can be partly attributed to the high surface area of pure MgO ($70m^2/g$). It is interesting to note that the highest surface area among the synthetic sorbents was measured again for the Mg-doped CaO sample.

Table 2. BET surface area and pore volume of the natural CaO sorbents

Sorbent	Surface area (m^2/g)	Pore volume (cm^3/g)
$Ca(OH)_2$	13.63	0.099
$Ca(OH)_2$ -C	5.04	0.041
$Ca(OH)_2$-W	17.24	0.181
$Ca(OH)_2$-MgO	23.25	0.427
$Ca(OH)_2$-KAOLIN	3.22	0.023

3.2 Sorbent evaluation in TGA

3.2.1 Synthetic sorbents

The performance of the four promoted CaO sorbents is presented in Fig. 3. The performance of pure CaO prepared by the same method using citric acid as combustion agent is also included for comparison reasons. All of the doped sorbents, except Ca-La, exhibit a very stable performance during the first 70 cycles, unlike the pure CaO prepared with citric acid which deactivates very fast in the first 20 cycles. In addition to stability, they also show an improved initial sorption capacity of over 9 moles CO_2/kg of sorbent due to the dispersion of the dopant through the CaO structure. Although a wide range of surface areas was observed, all the promoted sorbents (with the exception of Ca-La) achieved very high CaO conversions (>80%) that could be attributed mainly to the nature of the dopants and the formed structure of the final materials during combustion synthesis. The Al-promoted CaO shows the highest sorption capacity, followed by Mg and Zr with similar initial value and finally La. At around 70 cycles Ca-Mg demonstrates a decrease of capacity, while the Ca-Al and Ca-Zr sorbents continue to be stable even after 100 sorption/desorption cycles.

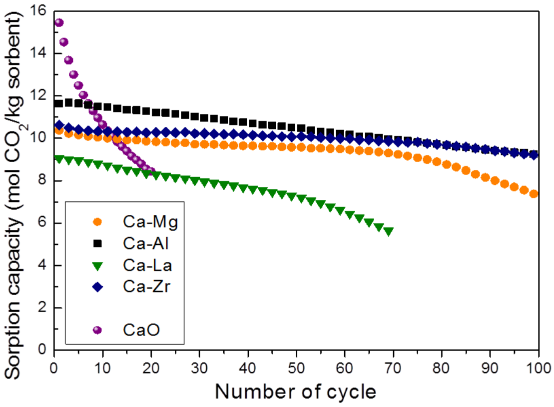

Fig. 3. CO_2 sorption capacity of the synthetic CaO-based sorbents as a function of the number of cycle

To summarize, the results for all investigated synthetic sorbents are tabulated in Table 3. We can generally observe that the different CaO-based synthetic sorbents exhibit different initial sorption capacity depending on the promoter and the type of the combustion agent used in the synthesis, as described above. Among the different dopants, Zr leads to the synthesis of the most stable sorbent, followed closely by Al. Moreover, Al exhibits the highest initial sorption capacity..

Table 3. Initial and final capacity and deactivation after 100 cycles of the synthetic sorbents

	Ca-Al	Ca-Mg	Ca-La	Ca-Zr
Initial capacity (mol CO_2/kg sorbent)	11.64	10.37	9.05	10.63
Final capacity (mol CO_2/kg sorbent)	9.23	7.29	5.64	9.17
Deactivation after 100 cycles (%)	20.7	29.7	37.7[1]	13.7

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[1] Deactivation after 70 cycles

3.2.2 Natural sorbents

In order to improve the capacity and stability of the as received natural $Ca(OH)_2$ sorbent, different pre-treatments, namely high temperature calcination at 900°C and hydration at 70°C, were applied. Fig. 4 shows the sorption capacity of the as-received hydrated lime, as well as the sorption capacity after calcination and hydration, as a function of sorption/desorption cycles. The untreated natural sample exhibits a relatively high initial CO_2 sorption capacity, which however decreases rapidly with the number of cycles. When the initial sample is first calcined, the initial capacity reduces significantly, as a result of the reduced surface area that occurs after the thermal treatment. On the contrary, treatment with water improves the sorption capacity compared to the parent material, an effect which can again be attributed to the surface area and the increase that was recorded upon hydration. However, the water-treated sample displays similar deactivation with the original material and quickly loses its sorption capacity. On the contrary, the calcined material exhibits low deactivation, surpassing the capacity of the parent and the water-treated material after 7 and 22 sorption/desorption cycles, respectively. The calcined sorbent retained a good capacity for the whole duration of the experiment and overall demonstrated high stability for 50 consecutive sorption/desorption cycles.

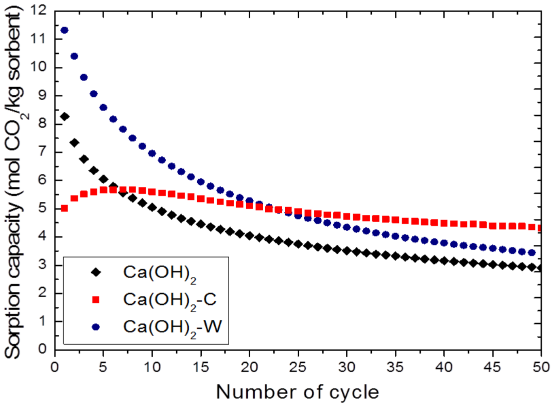

Fig. 4. Effect of thermal pretreatment and hydration in the performance of hydrated lime

In an attempt to increase stability with high sorption capacity, the water-treated $Ca(OH)_2$ sample, which had the highest initial capacity, was mixed with kaolin and MgO respectively in order to stabilize the CaO structure and prevent deactivation after multiple cycles. Fig. 5a and 5b present the CaO conversion and CO_2 sorption capacity of the mixed natural sorbents respectively. Both mixed sorbents display a lower carbonation conversion, although the incorporation of the binder in the CaO structure would be expected to lead to increased conversion due to better dispersion of CaO in the final material. Stability though benefits, with major increase with the use of binders compared to the parent material. No significant difference can be observed between MgO or kaolin, with both mixed sorbents exhibiting initial CaO conversion around 45% and deactivation of ~35% after 50 sorption desorption cycles. Comparing the sorption capacity, the mixed sorbents exhibit reduced values due to the lower conversion and lower free CaO concentration in the sorbent, reaching however almost the same capacity with $Ca(OH)_2$-W over time due to the increased stability.

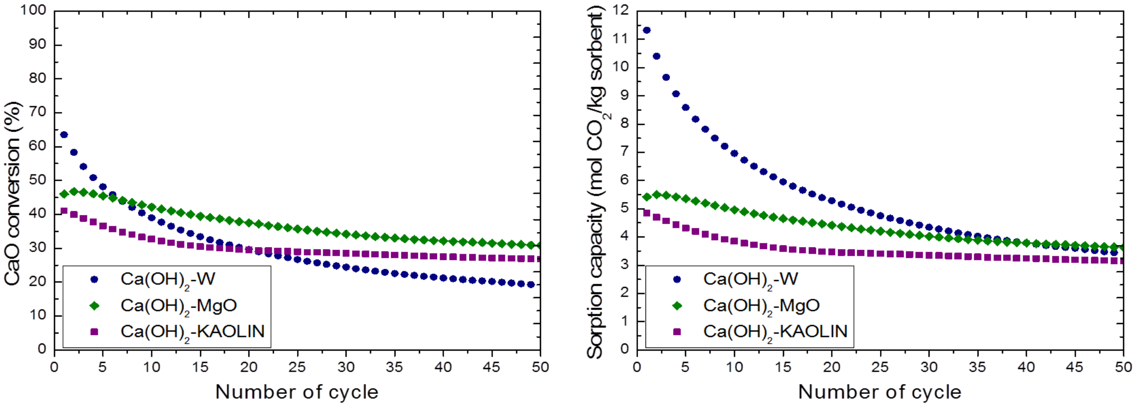

Fig. 5. CaO conversion (**a**) and CO_2 sorption capacity (**b**) of the natural CaO-based mixed sorbents as a function of the number of cycle

Table 4 summarizes the results for the natural sorbents. It can be observed that water treatment of the industrial hydrated lime greatly increases the initial CO_2 sorption capacity, but unfortunately with no positive effects on stability which remains at similar levels as the original mineral. When the hydrated lime is however mixed with kaolin and MgO binders, stability greatly increases and deactivation reduces by almost half, in expense to the initial CO_2 sorption capacity due to the lower content of CaO in the materials. Another reason for the lower sorption capacity of the doped sorbents was the lower initial conversion compared to the initial material. Overall, thermal pre-treatment of the pure parent mineral at high temperature was found to stabilize the structure of the formed CaO and led to the development of the natural sorbent with the lowest deactivation, < 20% after 50 sorption/desorption cycles. Still, comparing with the corresponding results for the synthetic sorbents presented in Table 3, it becomes clear that all the synthetic CaO-based sorbents exhibited almost twice the initial sorption capacity of the natural sorbent and a very stable performance with much lower deactivation after the same number of sorption/desorption cycles.

Table 4. Initial and final capacity and deactivation after 50 cycles of the natural sorbents

	$Ca(OH)_2$	$Ca(OH)_2$-C	$Ca(OH)_2$-W	$Ca(OH)_2$-MgO	$Ca(OH)_2$-KAOLIN
Initial capacity(mol CO_2/kg sorbent)	8.27	5.36	11.32	5.50	4.84
Final capacity (mol CO_2/kg sorbent)	2.90	4.31	3.44	3.63	3.15
Deactivation after 50 cycles (%)	64.9	19.6	69.6	34.0	34.9

4. Conclusions

In this work, a series of stable synthetic and natural mixed CaO-based sorbents for post-combustion CO_2 capture from industrial plans flues gases was developed. All the synthetic sorbents, prepared using sol-gel auto-combustion synthesis using citric acid as combustion agent and doped with Al, Zr, Mg and La, appeared promising and exhibited high initial sorption capacity (>9 mol CO_2/kg of sorbent) and satisfying stability (less than 30% deactivation after 100 sorption/desorption cycles), with the exception of the La-doped sorbent which exhibited poorer stability. The nature of the dopant seems to affect the crystallographic structure of the sorbents, leading to variations in initial capacity and cyclic stability. No correlation between initial CO_2 sorption capacity and surface area of the sorbents was found. The most promising sorbents both in terms of capacity and stability were found to be the Al- and Zr-promoted materials due to the formation of the more thermally resistant mixed $Ca_3Al_2O_6$ and $CaZrO_3$ respectively.

The low cost of natural sorbents renders them attractive for this application. Industrial hydrated lime demonstrated, as expected, inferior behaviour compared to the synthetic materials both in terms of stability and initial capacity. Calcination of the parent material at high temperature reduces the surface area and leads to lower initial capacity, however greatly increases stability. The calcined sample demonstrated less than 20% deactivation for 50 consecutive sorption/desorption cycles. Treatment with water was found to increase the initial sorption capacity with no effect however on the stability of the material. In order to improve the stability of the lime after water hydration, two mixed samples with kaolin and MgO binders were prepared. Both mixed sorbents exhibited an increased stability compared to the initial material, with however lower initial capacity due to lower carbonation conversion and lower CaO concentration in the sorbent.

Acknowledgments

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