CARBONATE LOOPING FOR INTERMEDIATE TEMPERATURE CO_2 CAPTURE: EVALUATING THE SORPTION EFFICIENCY OF MINERAL-BASED MGO PROMOTED WITH CACO$_3$ AND ALKALI NITRATES

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Abstract

This work focused on enhancing the CO_2 capture kinetics of magnesite-derived MgO via alkali nitrate and mineral $CaCO_3$ promoters for its application in the Carbonate Looping technology at intermediate temperatures (≤400°C). Alkali salts had a prominent role by shifting into molten state to offer a favorable carbonation pathway and allow a significantly higher CO_2 uptake than non-promoted MgO, while their synergy with $CaCO_3$ bestowed even better sorption activity. $MgCO_3$ and $CaMg(CO_3)_2$ were detected as the main carbonate products, with the latter exhibiting faster formation rate. The sorbent with $CaCO_3$ and alkali salts to MgO molar ratios of 0.05 and 0.20 respectively attained an uptake of 7.2 moles CO_2/kg of sorbent when exposed to a 30%CO_2 flow at 300°C with only 6% activity loss after 50 carbonation cycles, proving the applicability of the materials. Despite the cyclic sorption activity loss due to sintering and dewetting, alkali salts redistribution enabled a stable performance under proper conditions.

Keywords: Carbonate looping, CO₂ capture, MgO-based sorbent, molten salt promoter, In-situ XRD

1. Introduction

Global CO_2 emissions have been accelerating by the rampant exploitation of fossil energy sources, as demonstrated by their 2.6% annual increase between 2000 and 2014 [1]. The tremendous impact of the industrial sector on climate led to the development of Carbon Capture, Utilization and Storage (CCUS) technologies, which can reduce the contribution of the industry on the environmental disruption. Carbonate looping embodies an auspicious CCUS process, which employs a solid metal oxide to selectively adsorb CO_2 of industrial flue gases via an exothermic carbonation, followed by its endothermic calcination at a subsequent stage in a separate reactor to deliver a high-purity CO_2 stream ready for sequestration [2]. CaO comprises a widely-studied sorbent, since its fast sorption kinetics in the temperature range of 600-750°C have enabled its application for post-combustion CO_2 capture [2],[3] or the intensification of steam methane reforming process for high-purity H_2 generation [4]. Nevertheless, the elevated temperatures of its calcination (≥900°C) have shifted attention towards alternative sorbents with lower energy requirements [5]. MgO is an example of such material, which captures CO_2 (Eq. (1)) at intermediate temperatures (≤400°C), while other benefits include its theoretical sorption uptake (~25mol CO_2/kg MgO) and abundance in nature [6].

$$MgO_{(s)} + CO_{2(g)} \leftrightarrow MgCO_3, \Delta H_{298K} = -118kJ/mol \quad (1)$$
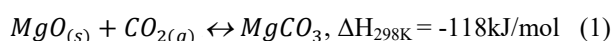
Nonetheless, the advantages of MgO are eclipsed by its intrinsically high lattice energy and facile formation of rigid carbonate layers while in contact with CO_2, which both lead to slow CO_2 sorption kinetics. The blockage of MgO sites can be evaded by using proper MgO precursors or promoters that secure a CO_2 sorbent with enhanced surface area. [6] But, this approach does not address the MgO lattice energy. As a solution to this problem, Zhang et al. [7] studied the addition of alkali nitrate promoters, which act as phase-transfer catalysts for MgO carbonation. These salts shift to a molten state in the temperature conditions where sorption occurs and dissolve both MgO and CO_2, thereby supporting their reaction and the generation of $MgCO_3$ nuclei. Through the years, the application of binary or ternary mixtures of alkali nitrates/nitrites was found to enhance solubility of reactants or cyclic stability and ensure a better CO_2 sorption activity. Harada et al. [8] firstly demonstrated a better sorption activity of MgO promoted with Li, Na and K nitrates with a molar ratio 30/18/52 compared to other works in the literature. Besides alkali nitrates, metal carbonates can also improve CO_2 uptake, by forming a kinetically more favoured mixed phase with MgO and CO_2 than $MgCO_3$. [9] Even if they remain unreacted, these compounds can also serve as carbonate seeds that facilitate the formation of $MgCO_3$ nuclei. [10]

The current infancy of carbonate looping with MgO has intensified research efforts on developing sorbents with high CO_2 uptake using various chemical reactants as MgO precursors or nitrate and carbonate promoters. Preparation methods also intend to improve the stability of MgO materials, since their sorption activity tends to gradually decrease over cycles. Nevertheless, the wide variety of chemical commodities and complex synthesis routes foster doubts on the economic feasibility of the process. Moreover, despite the existence of studies on the sorption mechanism and the reasons for the activity loss of these materials, [6] a thorough investigation is still required to demonstrate the influence of various

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77

parameters, such as the promoter content or the feed stream composition and temperature during sorption or desorption stages on the performance of sorbents.

Towards the direction of low-cost sorbents, this research focused on fabricating MgO-based materials derived from mineral magnesite and promoted with limestone and a mixture of Li, Na and K nitrates. Physicochemical properties were assessed via XRD, BET and SEM, while advanced *in-situ* XRD was used to examine the sorption mechanism. The applicability of sorbents was eventually proven by evaluating their sorption activity under continuous carbonation cycles via TGA, while employing various operating conditions.

2. Experimental

2.1. Sorbent preparation

MgO precursor comprised a calcined mineral magnesite (denoted as Mg) supplied from Grecian Magnesite S.A, while mineral limestone (denoted as LM) provided by A.G.E.T. Heracles was employed as Ca precursor after being subjected to calcination at 900°C for 2h under air to decompose to CaO. Table 1 presents the composition of minerals, which was defined by X-Ray Fluorescence analysis. For the alkali nitrates, chemical commodities of Merck, namely lithium nitrate (LiNO₃, ≥99.0%), sodium nitrate (NaNO₃, ≥99.5%) and potassium nitrate (KNO₃, ≥99.0%) were used. Acetic acid from Panreac Quimica SA was also applied (CH₃COOH, ≥99.7%).

Table 1: X-Ray Fluorescence analysis results.

%	MgO	CaO	Al_2O_3	SiO_2	Others	LOI
Mg	91.76	1.31	0.13	0.52	0.12	6.16
LM	0.45	56.80	0.04	0.06	0.02	42.63

Sorbents were crafted with a facile preparation protocol, starting with wet mixing of calcined magnesite and limestone in a solution of 12%$_{v/v}$ acetic acid by applying a molar ratio of $CH_3COOH/(Ca+Mg)$ of 3/1. The solution was stirred for 0.5h at 25°C, followed by solvent removal in a rotary evaporator at 80-85°C under reduced pressure and drying at 120°C for 12h. The obtained material was calcined at 450°C for 4h in air and then at 600°C for another 1 h in air with 5% CO_2 to obtain a MgO-$CaCO_3$ material. The applied CO_2 partial pressure intended to avoid decomposition of $CaCO_3$. The MgO-$CaCO_3$ material was immersed in an aqueous mixture of $LiNO_3/NaNO_3/KNO_3$ (with a molar ratio of 30/18/52). The obtained suspension was stirred for 1h, dried at 120°C for 12h and calcined at 450°C for 4h in air to obtain the final sorbent.

A parametric evaluation of the composition of sorbents was performed, including the molar ratios of alkali (Li+Na+K) salts to MgO (0.05, 0.10, 0.15, 0.20, 0.25) and $CaCO_3$ to MgO (0.05, 0.10, 0.20, 0.25). Materials were abbreviated as $MgCa_XA_Y$, with X and Y reflecting the aforementioned ratios. Two additional sorbents were prepared by skipping alkali salts or limestone addition and were denoted as $MgCa_{0.05}$ and $MgA_{0.10}$ respectively.

2.2. Characterization

Crystal structure of sorbents was examined via X-ray diffraction (XRD) with a BRUKER D8 ADVANCE apparatus with a CuKα radiation wavelength λ of 0.15406 nm. XRD spectra between 20 and 80° were recorded with a step of 0.02° and a scanning rate of 0.2s/point. MgO crystal size (d_{MgO}) was retrieved with the Scherrer equation (Eq. (2)) via the full width of half the maximum (β) of the peak with 2θ equal to ~42.7°. N_2 adsorption analysis at 77K defined the surface area (S_{BET}) and pore volume (V_p) via the multipoint BET method in a Autosorb-1 Quantachrome flow apparatus after dehydrating sorbents overnight at 250°C. Lastly, Scanning Electron Microscopy (SEM) was employed to examine the morphology of sorbents with a JEOL JSM-IT500 microscope.

$$d_{MgO} = \lambda/\beta \cos\theta \qquad (2)$$

2.2.1. Structure alterations assessment via in-situ XRD

Advanced *in-situ* XRD analysis was used to understand the structural modifications during carbonation cycles. Experiments were conducted through a BRUKER D8 ADVANCE diffractometer, coupled with a XRK-900 Anton-Paar cell, allowing operation at temperatures ranging from 25 to 900°C. Initially, the samples were treated for 10min at 450°C to release CO_2 and/or H_2O that were physisorbed from the atmosphere. The temperature was reduced to 325°C with a 40°C/min rate and the feedstock was altered to 100%CO_2 and maintained for 30min to perform the sorption step. Carbonation was succeeded by the temperature increase to 450°C under pure N_2 with a rate of 25°C/min, where the desorption step was carried out for 10min. The reactor cell was cooled down to 325°C to repeat sorption and the material underwent a total 20 sorption/desorption cycles. XRD spectra were recorded during sorption and desorption steps with a 2θ range of 28-45°, a step of 0.02° and a scanning rate of 0.2s/point. The chosen 2θ range enabled the supervision of changes of the main MgO and $MgCO_3$ peaks. Scherrer equation was used after each desorption to monitor the MgO size.

2.3. Evaluation of sorption performance

CO_2 sorption activity and stability were tested under continuous sorption/desorption cycles performed in a TGA apparatus (TG 209 F3 Tarsus, Netzsch). A sample of 10-15mg of each sorbent was placed in an Al-based crucible and subjected into a temperature and flow alteration program, by concurrently recording the mass changes over time. Sorbents were initially treated with a pure N_2 flow for 10min at 450°C to remove physisorbed CO_2 and/or humidity. Temperature was then reduced with a rate of 50°C/min and the gas feedstock was switched to a CO_2 containing stream to conduct carbonation for 30 min. Various temperatures (300 and 325°C) and gas feedstocks (100%CO_2 and 30% CO_2/N_2) were tested. Sorption was followed by heating to 450°C with 10°C/min rate to carry out desorption with pure N_2 or CO_2 flow. Cooling down was applied to repeat the carbonation stage and assess the stability over cycles.

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3. Results

3.1. Characterization

The obtained XRD spectra (Figure 1) clarified that the applied preparation protocol delivered sorbents with MgO as their main crystal phase. $CaCO_3$ peaks were also detected, proving that the calcination step after the organic acid treatment provoked the decomposition of the acetate compounds at their desired forms, without forming CaO. Alkali metals retained their nitrate forms, with the main peak of $NaNO_3$ overlapping with $CaCO_3$ and KNO_3 emerging in rhombohedral and orthorhombic crystal forms (existence of both structures was proven with Rietveld analysis). Increasing the loading of either $CaCO_3$ or alkali salts caused the augmentation of the intensities of their characteristic peaks. Regarding $LiNO_3$, even though it was not identified, its inclusion as part of a ternary mixture of salts rejects the proposition that it possibly disintegrated in other composites while calcining at 450°C during preparation. Thus, $LiNO_3$ either belongs to the amorphous phase of sorbent or it is composed of uniformly dispersed small crystallites. [9]
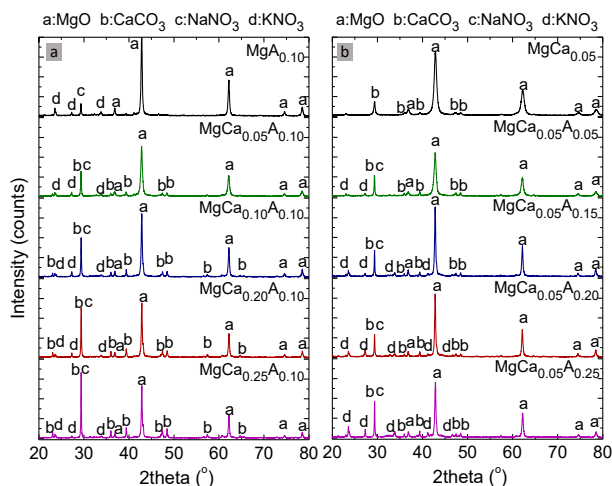

Figure 1: XRD spectra of sorbents with various (a) $CaCO_3$ and (b) alkali salt loadings.

Textural properties of prepared sorbents are summarized in Table 2. The calcined magnesite (Mg) was composed of a wide pore network, which was ideal for alkali nitrates to deposit and cause a notable reduction of both surface area and pore volume ($MgA_{0.10}$). The deposition occurred during the final calcination step while preparing the sorbents, where alkali salts shifted to their molten state, spread into the pores and eventually solidified after cooling down to ambient conditions. The change of physicochemical characteristics was milder with the addition only of $CaCO_3$ ($MgCa_{0.05}$), due to the ability of Ca^{2+} ions to incorporate in the MgO lattice and prevent a larger surface area reduction. [10] This effect enabled materials with both alkali nitrate and $CaCO_3$ promoters ($MgCa_{0.05}A_{0.10}$) to demonstrate better textural properties than the material only with alkali nitrates ($MgA_{0.10}$). Higher alkali salt contents led to higher

occupation of pores and further decrease of the surface area. Moreover, the larger ionic radius of Ca^{2+} compared to Mg^{2+} allowed a limited amount of former ions to enter the MgO lattice. Thus high $CaCO_3$ loadings provoked the generation of $CaCO_3$ crystallites which were deposited in the pores of MgO and reduced its available surface area. The inclusion of Ca^{2+} in the MgO lattice was also beneficial for the crystallite size, which was smaller in materials with both promoters than single alkali salts. However, a gradual growth of crystal size was observed while increasing either promoter amount.

Table 2: BET surface area (S_{BET}), pore volume (V_p) and MgO crystallite size (d_{MgO}) of sorbents.

Sorbent	S_{BET} (m²/g)	V_p (cm³/g)	d_{MgO} (nm)
Mg	110.2	0.35	22.3
$MgCa_{0.05}$	52.3	0.27	18.4
$MgA_{0.10}$	19.4	0.13	32.8
$MgCa_{0.05}A_{0.10}$	22.7	0.23	25.8
$MgCa_{0.10}A_{0.10}$	17.5	0.15	26.9
$MgCa_{0.20}A_{0.10}$	13.5	0.14	29.0
$MgCa_{0.25}A_{0.10}$	11.0	0.10	30.5
$MgCa_{0.05}A_{0.05}$	60.6	0.65	23.4
$MgCa_{0.05}A_{0.15}$	14.7	0.12	27.2
$MgCa_{0.05}A_{0.20}$	10.1	0.08	27.5
$MgCa_{0.05}A_{0.25}$	7.3	0.04	29.8

Regarding the nature of the pore network defined by the N_2 adsorption analysis, sorbents with both $CaCO_3$ and alkali nitrate promoters presented type IV adsorption isotherms (Figure 2) with a H_3 hysteresis loop at high partial pressures ($P/P_o \geq 0.8$). This adsorption behavior is found in sheet-like materials with slit-like mesopores, while the hysteresis loop disclosed the presence of capillary condensation. Higher promoter loadings reduced the volume of adsorbed N_2, which is evidence of their deposition to the pores of the sorbent.
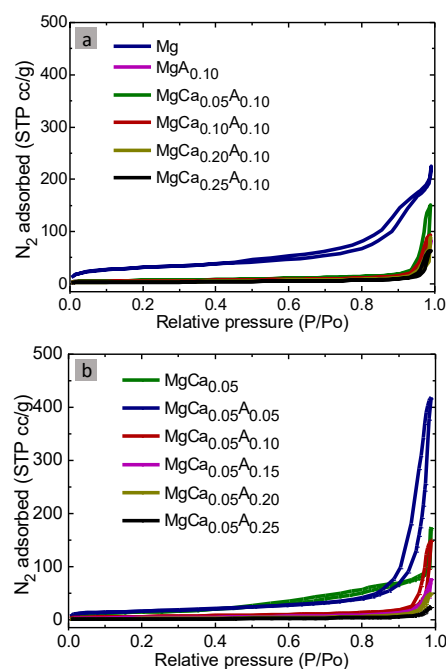

Figure 2: N_2 adsorption isotherms of sorbents with different (a) $CaCO_3$ and (b) alkali salt contents.

Theodoros Papalas, Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus
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The hysteresis loop was different in the parent materials Mg and $MgCa_{0.05}$, since it was more representative for pores of irregular size or micropores. This proves that the immersion of MgO-$CaCO_3$ in the solution of alkali nitrates during sorbent preparation is a fundamental step to define the textural and morphological characteristics of the final sorbents. This was also proven by employing SEM analysis (Figure 3). Mg and $MgCa_{0.05}$ consisted of small grains resembling spheres, while the sorbents promoted with alkali nitrates displayed a flower-like morphology. During the alkali salt deposition, MgO was hydrated to $Mg(OH)_2$, which consisted of flake grains. Magnesium reverted back to its oxide form during calcination by retaining the flake grains, which agglomerated via an Ostwald ripening process [9]. Eventually, sorbents with both $CaCO_3$ and alkali salts had a morphology similar to $MgCa_{0.05}A_{0.10}$ (Figure 3d) despite the loading of each promoter.
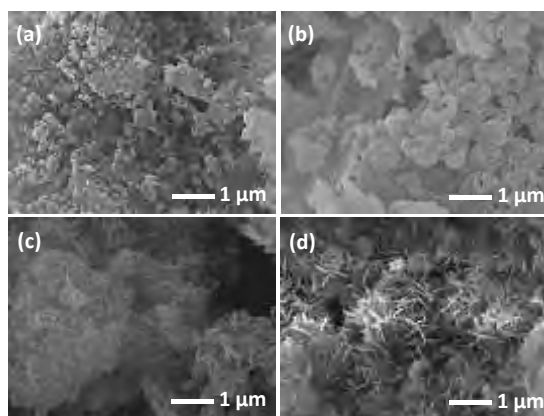

Figure 3: SEM analysis of (a) Mg, (b) $MgCa_{0.05}$, (c) $MgA_{0.10}$ and (d) $MgCa_{0.05}A_{0.10}$.

3.2 Evaluation of sorption performance

3.2.1. Role of each promoter on sorption mechanism

The mass alterations of calcined magnesite (Mg), or materials with either one ($MgCa_{0.05}$, $MgA_{0.10}$) or both promoters ($MgCa_{0.05}A_{0.10}$) were examined via TGA while heating to 450°C under a 100%CO_2 flow as an initial step of evaluating the effect of each promoter in the sorption activity (Figure 4a). It was observed that only $MgA_{0.10}$ and $MgCa_{0.05}A_{0.10}$ demonstrated notable weight increase at temperatures above 200°C due to the attained CO_2 uptake. The weight of both sorbents followed a sigmoidal curve, since the increase rate was initially slow and gradually enhanced. Temperatures higher than ~375°C eventually caused the desorption of the captured CO_2 and the weight reduction to its initial value. On the other hand, Mg and $MgCa_{0.05}$ remained inert during the whole experiment. These results establish alkali nitrates as essential promoters to enhance the CO_2 capture kinetics. This is in accordance to their role as phase-transfer catalysts that shift to a molten state, dissolving MgO and CO_2 and facilitating their reaction, [7] while the sigmoidal curve made clear that the generation of carbonate products follows a nuclei formation and growth mechanism. [10]
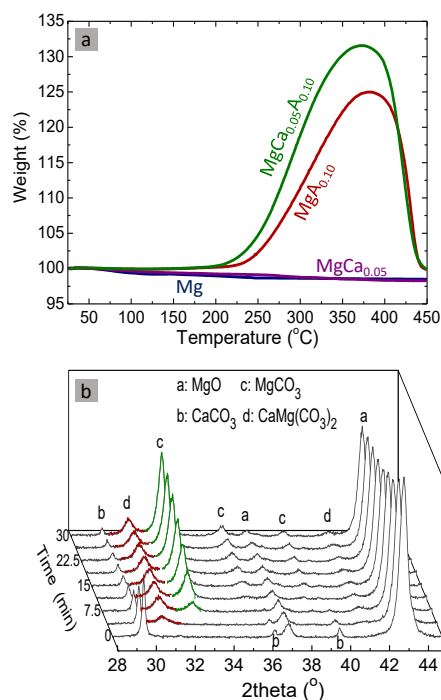

Figure 4: (a) Weight vs temperature of Mg, $MgCa_{0.05}$, $MgA_{0.10}$ and $MgCa_{0.05}A_{0.10}$ while heating to 450°C and (b) *in-situ* XRD of $MgCa_{0.05}A_{0.10}$ during carbonation at 325°C with 100%CO_2.

The addition only of the $CaCO_3$ promoter did not have a beneficial effect, while it seems that its synergy with alkali nitrates allowed for a more efficient sorption activity compared to the addition only of molten salts. *In-situ* XRD was employed to understand the role of $CaCO_3$ by carrying out a sorption step for 30min under a 100%CO_2 stream (Figure 4b). It was found that carbonation proceeded via the formation of both $MgCO_3$ and $CaMg(CO_3)_2$, which proves that $CaCO_3$ also dissolved in the molten phase and enabled the generation of the mixed carbonate phase. Furthermore, the reflection peak of $CaMg(CO_3)_2$ emerged faster than $MgCO_3$, which was expected due to the lower equilibrium CO_2 partial pressure for the formation of mixed carbonates at a specific temperature. [9] The formation kinetics of each carbonate are controlled by a driving force term, which is calculated as the difference between the applied CO_2 partial pressure and the equilibrium CO_2 partial pressure ($P_{CO2} - P_{CO2,eq}$). Since $P_{CO2,eq}$ is lower for $CaMg(CO_3)_2$, its formation is kinetically more favored than $MgCO_3$. This explains the faster appearance of $CaMg(CO_3)_2$ at 325°C.

Regarding the beneficial effect of $CaCO_3$, it can be seen that except from a higher sorption capacity (Figure 4a), CO_2 uptake of $MgCa_{0.05}A_{0.10}$ began at relatively lower temperatures (~200°C) compared to $MgA_{0.10}$ (~220°C). Even though the formation of $CaMg(CO_3)_2$ nuclei would justify the faster CO_2 sorption kinetics at 325°C, carbonation of the samples at 275°C with *in-situ* XRD (not shown for brevity) revealed that CO_2 capture occurs only via the $MgCO_3$ formation. The absence of $CaMg(CO_3)_2$ was possibly due to its slow formation kinetics and inadequate $CaCO_3$ solubility in the molten

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alkali nitrates, with both elements having the potential of improving only with the application of higher temperatures [8]. This implies that CaMg(CO$_3$)$_2$ is not available at ~200°C, where the weight increase started in TGA. Thus, the enhanced sorption of MgCa$_{0.05}$A$_{0.10}$ was associated with the ability of CaCO$_3$ to act as a carbonate seed that facilitates the formation of the first MgCO$_3$ nuclei. [10] Approaching higher temperatures enabled also the CaMg(CO$_3$)$_2$ generation and retained the CO$_2$ capture of MgCa$_{0.05}$A$_{0.10}$ faster than MgA$_{0.10}$.

3.2.2. Effect of promoters loading on sorption activity

Sorbents with different CaCO$_3$ and alkali salt loadings were subjected to a carbonation cycle in order to assess the impact of each promoter. Figure 5 displays the weight alterations of the sorbents as a function of time. Regarding CaCO$_3$, all sorbents exhibited similar weight increase during the first ~2.5min, implying that sorbents with higher CaCO$_3$ loadings attained higher conversion of MgO. This is ascribed to the fast and more apparent formation of CaMg(CO$_3$)$_2$. However, the MgCa$_{0.20}$A$_{0.10}$ and MgCa$_{0.25}$A$_{0.10}$ materials displayed lower BET surface area (Table 2) and thus the formed carbonates limited the CO$_2$ diffusion and blocked the MgO sites more easily. This resulted in a lower mass increase rate after ~2.5min of sorption compared to MgCa$_{0.05}$A$_{0.10}$ and MgCa$_{0.10}$A$_{0.10}$, while the similar uptake of the latter sorbents inferred that the harmful effect of CaCO$_3$ is evident only after surpassing a specific amount.
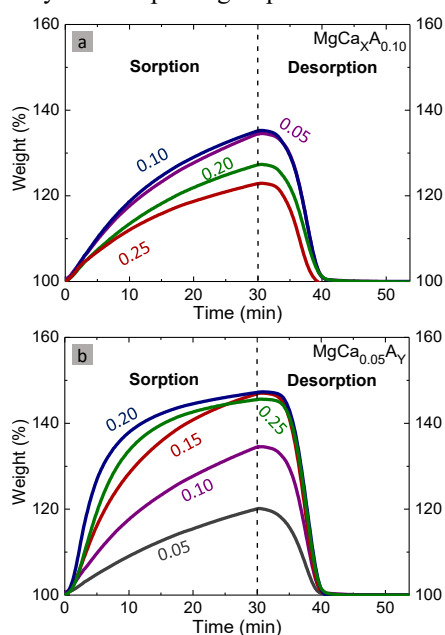

up to 0.15, proving that the lower alkali nitrate amounts did not attain an adequate coating and thus exploitation of the MgO surface. Raising the molar ratio to 0.20 did not alter the sorption capacity attained after the 30min of reaction, but instead profoundly improved the CO$_2$ capture rate in the first minutes of sorption. Nuclei carbonates were formed and grown rapidly in the first 10min and the material secured most of its maximum permitted uptake. The slower weight increase in the remaining time (t>10min) was attributed to the hindered CO$_2$ diffusion through the carbonate products. [8]

Further increase of alkali salts content (MgCa$_{0.05}$A$_{0.25}$) led to the formation of thick molten salt layers which impeded the efficient contact between MgO and CO$_2$ and thus decreased the CO$_2$ capture rate in the initial minutes of carbonation. [12] Regarding the relation of the performance of molten salt promoted sorbents with surface area, it is clear that the two parameters do not have a direct connection with each other. [8] However, it was seen that the surface area decreased drastically with the increase of the alkali salt to MgO ratio from 0.05 to 0.15, while further increase of the latter resulted in milder reduction of the surface (Table 2). A similar behavior was demonstrated from the CO$_2$ uptake after 30min of reaction. Hence, BET surface functions mostly as an indicator of the maximum alkali salt loading allowed to prevent the deterioration of CO$_2$ capture.

3.2.3. Effect of operating conditions on sorption activity

Based on the aforementioned results, MgCa$_{0.05}$A$_{0.20}$ was considered a promising sorbent due to its high sorption rate and thus it was tested under 50 continuous sorption/ desorption cycles under different temperature or gas feedstock composition conditions for the sorption stage. MgCa$_{0.05}$A$_{0.10}$ was also tested under the same conditions to clarify the role of molten promoters (Figure 6).
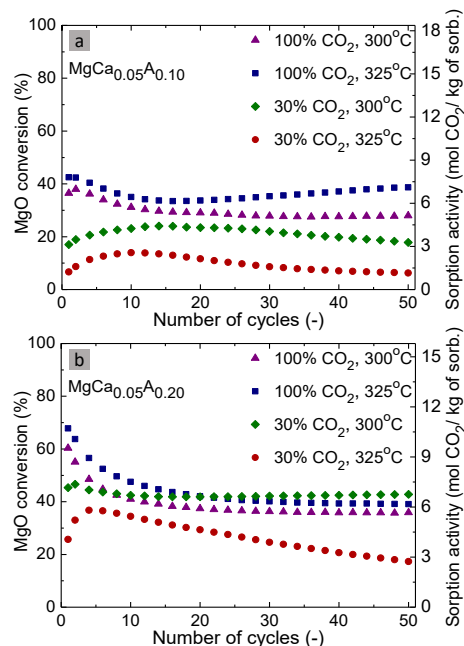
Figure 5: Weight vs time of sorbents with varying (a) CaCO$_3$ and (b) alkali salt loadings (sorption: 325°C, 100%CO$_2$, 30min; desorption: 450°C, 100%N$_2$, 10min).

Concerning the influence of the molten promoter loading, even though the higher alkali nitrate amounts reduced the surface area of the sorbents in the same way as CaCO$_3$, they generally provoked an enhancement of the sorption kinetics. This effect was widely evident while increasing the molar ratio of alkali salts to MgO

Figure 6: Sorption activity of (a) MgCa$_{0.05}$A$_{0.10}$ and (b) MgCa$_{0.05}$A$_{0.20}$ while applying various sorption conditions (sorption: 30min; desorption: 450°C, 100%N$_2$, 10min).

Theodoros Papalas, Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus 54124, Greece

It was evident that the CO_2 uptake activity of both materials deteriorated during cyclic operation with sorption tested at either 325 or 300°C with 100%CO_2. Liquid phase sintering was identified as one of the main reasons for this performance, which is related to the gradual disappearance of pores and densification of solid grains during their exposure at high temperatures. This is related to the $MgCO_3$ phase, which has a low Tammann temperature (180°C) and thus is prone to sintering. The spreading of molten alkali nitrates into the pores intensify this phenomenon by pulling solid grains together via a capillary force, which is reinforced due to the solution of solid reactants in the molten salts. [13] The $MgCa_{0.05}A_{0.20}$ sorbent exhibited higher loss of activity than $MgCa_{0.05}A_{0.10}$ when tested with 100%CO_2, which was expected since the higher alkali salt content of the former could lead to accelerated densification, according to the theory of liquid phase sintering.

The existence of sintering was verified by evaluating $MgCa_{0.05}A_{0.10}$ over 20 carbonation cycles in *in-situ* XRD (Figure 7). It was proven that the crystallite size of MgO displayed a constant augmentation during cyclic operation. Besides the crystal size, the I_{MgCO3}/I_{MgO} ratio achieved at the end of the sorption step of each cycle was also assessed as a means of testing the MgO conversion attained with *in-situ* XRD analysis. It was found that the ratio presented an initial reduction followed by a tendency of stabilization, while similar behavior was also exhibited in TGA (Figure 6). Hence, except from sintering, there is another counteracting phenomenon which may have a beneficial role in the stability of sorbents, as discussed more thoroughly later.
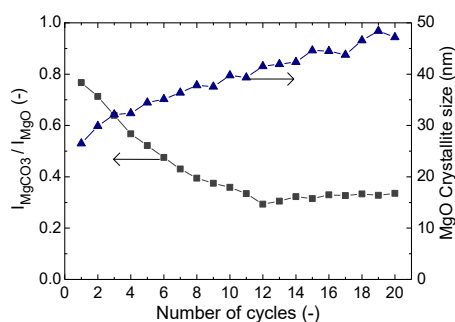

Figure 7: I_{MgCO3}/I_{MgO} ratio after sorption step and MgO crystal size after desorption step of $MgCa_{0.05}A_{0.10}$ for each cycle.

The reduction of CO_2 concentration of gas feedstock from 100% to 30% by retaining 325°C as default temperature had an expected detrimental effect on the performance of sorbents due to the weakening of the carbonation kinetic driving force ($P_{CO2} - P_{CO2,eq}$). Self-reactivation was witnessed in the first carbonation cycles due to alkali salt and solid grain rearrangement during the formation and decomposition of carbonates. [14]. These transformations portend the densification of grains caused by the liquid phase sintering [13] and thus the maintenance of their effect for a number of cycles with the reduced CO_2 concentration (30%) implies that sintering progresses with a slower rate than with the 100%CO_2 flow. This was supported by employing SEM

analysis on spent sorbents (available for $MgCa_{0.05}A_{0.20}$ at Figure 8) after their evaluation under the two different sorption conditions. The initial flower-like structure (Figure 3d) was replaced with agglomerated grains with no visible small pores when sorption was tested with the 100% CO_2 flow (Figures 8a). However, sintering was less severe with 30%CO_2, with SEM analysis revealing a visible pore network (Figures 8b). Hence, sintering rate seems to depend on the gas feedstock composition and thus the MgO conversion.
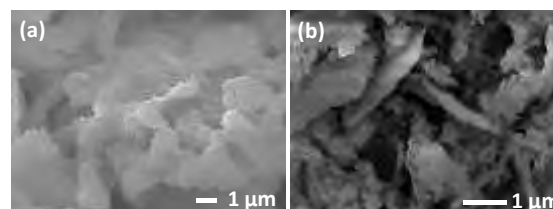

Figure 8: SEM analysis of spent $MgCa_{0.05}A_{0.20}$ with sorption tested with (a) 100%CO_2 or (b) 30%CO_2.

Even though the effect of sintering was not severe, the sorbents displayed a higher loss of activity during cyclic operation when carbonation was executed at 325°C with the 30%CO_2/N_2 flow. During the continuous loop of magnesium between oxide and carbonate forms, the pore network undergoes consecutive shrinkages and expansions because of the different molar volumes of reactants MgO and $CaCO_3$ (11.2 and 36.9cm^3/mol respectively) and products $MgCO_3$ and $CaMg(CO_3)_2$ (28.5 and ~42.9cm^3/mol respectively). The extent of the alterations of pore network are more pronounced when a high MgO conversion is achieved. Furthermore, the formation of carbonates causes molten alkali nitrates to lose their contact with the magnesium compound due to their lower affinity with $MgCO_3$ compared to MgO [10] and to form aggregated clusters. [14] Even though the molten salts can re-spread and regain their contact with MgO after the CO_2 desorption step, there is a risk that part of the surface will eventually be left uncoated, leading to the gradual CO_2 uptake loss with cycles. The dewetting possibility should probably be higher with milder morphological transformations of the pore network and thus lower chance for alkali salts to re-coat efficiently the MgO surface. Since the application of the 30%CO_2/N_2 stream led to lower MgO carbonation and milder morphological transformations, it is inferred that dewetting is the main reason behind the severe loss of activity of sorbents when tested under these conditions.

The aforementioned proposition that an extended MgO carbonation can limit the dewetting possibility and enable alkali salt redistribution to bestow its beneficial effect of high CO_2 uptake agrees with the stable performance of sorbents when exposed to a 100%CO_2 flow. It was noticed that $MgCa_{0.05}A_{0.10}$ even displayed a self-reactivation behavior in subsequent carbonation cycles (Figure 6). The comparison of textural properties between $MgCa_{0.05}A_{0.10}$ and $MgCa_{0.05}A_{0.20}$ showed that the former had higher BET surface (Table 2), indicating the potential existence of larger uncoated MgO surface

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from alkali nitrates after their transition to molten state. Although the uncoated surface does not contribute to the uptake of the first cycles, [9] it is believed that molten salts gradually dewet the sintered MgO to spread on the originally uncoated surface and bestow higher activity and even a self-reactivation ability to MgCa$_{0.05}$A$_{0.10}$.

In an effort to improve the activity of sorbents, the carbonation temperature was reduced to 300°C, which led to a more pronounced MgO carbonation and a better overall CO$_2$ capture performance, especially for the MgCa$_{0.05}$A$_{0.20}$ material (Figure 6). The latter attained an initial sorption capacity of 7.2 moles CO$_2$/kg of sorbent when exposed to a 30%CO$_2$ flow for 30min, while its activity reduced only by 6% after 50 carbonation cycles. This performance is promising, since the MgCa$_{0.05}$A$_{0.20}$ material would attain a sufficient CO$_2$ sorption activity in the flue gases of a water gas shift reactor in coal integrated gasification combined cycles, where CO$_2$ content can reach up to 40%. The better activity when carbonation was performed at 300°C instead of 325°C with the 30%CO$_2$ flow was expected because of the different ways that temperature can affect the performance of molten salt promoted MgO. In terms of kinetics, low temperatures would limit the beneficial influence of the Arrhenius parameter, but would bolster the kinetic driving force (P$_{CO2}$ − P$_{CO2,eq}$) due to the reduction of P$_{CO2,eq}$. Due to the nature of the sorption mechanism, temperature also plays a role on the solubility of solid and gas reactants, while it is known that CO$_2$ solubility is enhanced with lower temperatures. [6] It has also been mentioned that the application of a stream with P$_{CO2}$ lower than 0.5bar requires the reduction of the carbonation temperature in order to achieve sufficient CO$_2$ trapping in the molten phase. [8] These factors contributed to the enhancement of the MgO conversion and secured an adequate salt spreading and a stable sorption activity, notably for MgCa$_{0.05}$A$_{0.20}$.

Except from a relatively low CO$_2$ concentration during sorption, a realistic carbonate looping operation requires calcination to be carried out under pure CO$_2$, in order for the gas outlet to be comprised of a pure CO$_2$ stream ready for sequestration and isolation. Thus, the activity of MgCa$_{0.05}$A$_{0.10}$ and MgCa$_{0.05}$A$_{0.20}$ was tested with calcination performed under a pure CO$_2$ flow (Figure 9). Both sorbents displayed inferior performance in contrast to the operation of calcination with a 100%N$_2$ flow. Since the temperature of calcination remained the same, the presence of CO$_2$ decreased the rate of desorption and increased rate for sintering. However, the MgCa$_{0.05}$A$_{0.10}$ material maintained its self-reactivation ability, which limited its activity loss to 28%. MgCa$_{0.05}$A$_{0.20}$ displayed a faster decrease of its sorption activity followed by a tendency of stabilization near the end of the 50 sorption/ desorption cycles. The reduction rate of CO$_2$ uptake was slower compared to the application of the 30%CO$_2$/N$_2$ stream for carbonation (Figure 6), where dewetting was recognized as the main reason for the activity loss. MgO conversion was also high enough to ensure an alkali salt re-spreading with limited chance for dewetting. Hence, it is implied that calcination in pure CO$_2$ affects mainly sintering rather than the alkali salt rearrangement.
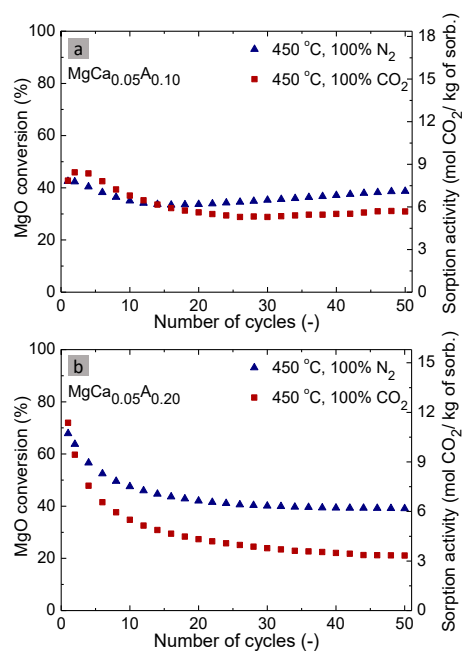

Figure 9: Sorption activity of (a) MgCa$_{0.05}$A$_{0.10}$ and (b) MgCa$_{0.05}$A$_{0.20}$ while applying various desorption conditions (sorption: 325°C, 100%CO$_2$, 30min; desorption: 10min).

3.3. Comparison with high temperature CaO sorbents

The cyclic performance of MgCa$_{0.05}$A$_{0.20}$ was compared (Figure 10) with two CaO-based sorbents from previous works [2], [3]. These included a synthetic material (Ca-Zr-66) composed of 66%$_{w/w}$ CaO/CaZrO$_3$, which was synthesized via a sol-gel auto-combustion method and a mineral sorbent (LM_W30Mg) prepared by wet mixing calcined limestone and magnesite with a weight ratio of 70/30. It should be noted that the different temperature applied to achieve adequate sorption with CaO (650°C) and MgO (300°C) does not enable a direct comparison between sorbents. The ΔT (350°C) signifies limited MgO carbonation kinetics and CO$_2$ diffusion through formed carbonates, while higher operating temperatures cannot be employed for MgO due to thermodynamic restrictions of the reaction. However, a comparison can still be accepted in terms of stability and CO$_2$ uptake.

CaO-based sorbents gradually lose their activity over cycles due to the severe sintering. The incorporation of synthetic CaZrO$_3$ promoter in Ca-Zr-66 enabled CaO to withstand sintering more efficiently than CaO promoted with mineral-derived MgO (LM_W30Mg). Despite the better performance, the high cost of synthetic materials intensifies the necessity for high-stability sorbents using low-cost precursors. This is attained in the intermediate-temperature MgCa$_{0.05}$A$_{0.20}$ material, whose stability is similar to Ca-Zr-66, despite its mineral nature, and thus would lead to a higher sorption capacity compared to LM_W30Mg after the 50 carbonation cycles. However, the carbonation extent after 30min of reaction was lower than the high-temperature sorbents. This signifies that despite the enhanced sorption kinetics, future research could focus more on further exploiting the available MgO content in limited but realistic sorption durations.
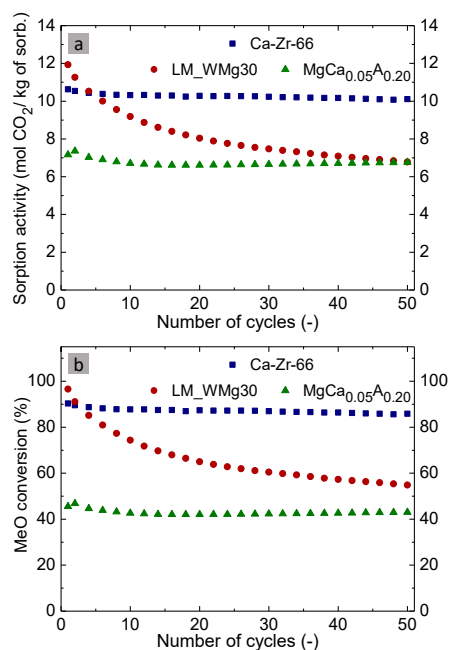
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Figure 10: (a) CO$_2$ uptake and (b) MeO conversion of the sol-gel synthesized 66%$_{w/w}$ CaO/CaZrO$_3$ (Ca-Zr-66), the mineral sorbent (LM_WMg30) derived by wet mixing calcined limestone and magnesite with a 70/30 weight ratio (Me: Ca; sorption: 650°C, 15%CO$_2$, 30min; desorption: 850°C, 5min, N$_2$) and the sorbent (MgCa$_{0.05}$A$_{0.20}$) of this study (Me: Mg, sorption: 300°C, 30%CO$_2$, 30min; desorption: 450°C 10min, N$_2$).

4. Conclusions

This study focused on the preparation of low-cost MgO sorbents based on mineral magnesite and reinforced with adequate CO$_2$ capture kinetics via limestone and Li, Na and K nitrates. Alkali nitrates successfully upgraded the sorption kinetics of magnesite via their transition into a molten state and the provision of an alternative pathway for MgO carbonation. CaCO$_3$ either acted as a carbonate seed to facilitate the generation of the first MgCO$_3$ nuclei or it reacted with MgO and CO$_2$ to form CaMg(CO$_3$)$_2$. The beneficial effects of CaCO$_3$ were apparent principally with the application of a low molar ratio of CaCO$_3$ to MgO of 0.05 in order to avoid the hindering of the CO$_2$ diffusion through the formed carbonates. The alkali salts to MgO ratio was another important parameter, since an increase up to 0.20 was profitable in terms of enhanced sorption kinetics, while higher ratios disabled the effective contact of CO$_2$ and MgO. The sorbent with the aforementioned composition attained an uptake of 7.2 moles CO$_2$/kg of sorbent when carbonation was performed with 30%CO$_2$ for 30min at 300°C and a negligible activity loss after 50 carbonation cycles. Sorbents were found prone to sintering which reduced their cyclic activity. Alkali salt rearrangement was also denounced for activity changes, which had a detrimental effect by dewetting the surface with limited MgO carbonation. However, high MgO conversions attained a beneficial salt rearrangement and enhanced stability under realistic operating conditions. This work highlighted mineral MgO as a low-cost CO$_2$ sorbent for carbonate looping in relatively mild temperature conditions.

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