

The role of alkaline/alkaline earth metal oxides in CO₂ capture: A concise review

ABSTRACT

Reducing the concentration of CO₂ from the atmosphere has attracted a lot of attention given the rapid level of industrialization in the world. Process Industries are one of the major contributors to this pollution in terms of the incessant release of CO₂ from flue gas streams. In recent times metal oxides have received a lot of attention as potential adsorbents for application in post-, pre-, and oxy-combustion conditions. Their basic sites plus a lower charge to radius ratio increase their ionic nature and site basicity and facilitate the capture of this pernicious gas from flue gas streams by reacting with CO₂ to form carbonates which when heated liberates an almost pure stream of CO₂ which can be sequestered, thereby, subsequently aiding the release of environmentally benign flue gas streams to the atmosphere. This work takes a concise review of these metal oxides that have been widely studied.

Keywords: CO₂ Capture technology, Carbonation, Capture capacity, Thermal stability, Regeneration heat, Structural properties.

1. INTRODUCTION

The rise in industrial activities in the world today has necessitated an increase in the world's energy demand. This energy demand is predominantly being met in the form of coal, petroleum, and natural gas. However, these fuels have been identified to have a deleterious effect on the environment due to the emissions such as CO₂, SO_x, NO_x, Mercury, and Particulate matter that result from the combustion of these fuels. Recently, major attention has been focused on CO₂ because they have been regarded as the major cause of global warming, ocean acidification, sea-level rise, and climate change. The need to curb these emissions has led to a renaissance in the research industry [1-3], to develop strategies that would significantly reduce CO₂ emissions both from the stationary sources

with high CO₂ concentrations (e.g. Process Industries, and Coal-fired Power plants) and directly from the air have attracted increasing attention worldwide. Nonetheless, this decrease in carbon-intensive fuel consumption has not been achieved as the CO₂ concentration on the earth has been steadily increasing as seen in **figure 1**, as of December 2019, CO₂ concentration in the atmosphere had reached 412 ppm accounting for about 31% increase of that in 1958 with reports prognosticating that the CO₂ concentration in the air would surpass 550ppm by 2050 [4] if no further drastic actions are taken to curb these CO₂ emissions. Although the supply of alternative energies such as biomass, solar, and wind is increasing, they are still inchoate and are still far from ready to replace fossil energy completely.

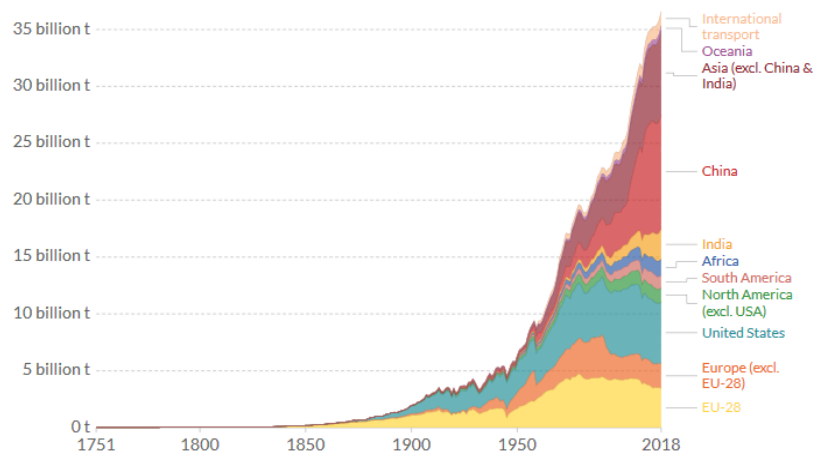


Fig. 1. Global carbon emission from 2006 – 2019, reproduced from [5]

Recently carbon capture, utilization, and sequestration (CCUS) have been touted as a viable option to mitigate these CO₂ emissions within a short term. This technology involves using various sorbents to capture the CO₂ from stationary sources such as Process Industries followed by recycling for utilization or storing underground. CCUS has the potential to lead to a closed carbon cycle especially if the captured CO₂ is utilized as a carbon source feedstock for industrial chemicals and fuels production. It offers a cost-competitive way to fill the gap between the ever-increasing energy demand and CO₂ emissions reduction campaign [6]. The various capture process that exists for CCUS includes physical absorption [7-8], chemical absorption [9-10], adsorption [11], and membranes [12]. Currently, absorption by amine-based solvents is the predominant technology commonly used in the industry [13-15], but the high energy cost of absorbent regeneration, high corrosion rate, high absorbent cost, associated with these absorbents has inspired research into other sorbents which can be used for carbon capture such as metal oxide. This work as depicted in figure 2 therefore aims to present a clear and concise review on some selected metal oxides in terms of their capture capacity, reversibility rate, carbonation kinetics and multi-cycle durability.

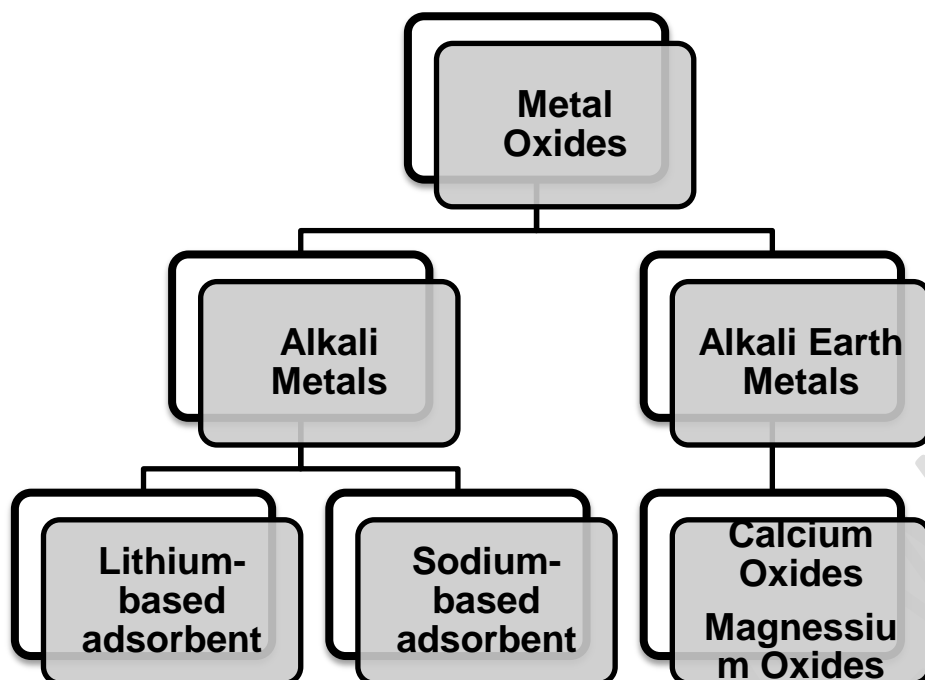


Fig.2. Classification of metal oxide adsorbents as discussed in this review.

2. METAL OXIDES

Metal oxides are regarded as promising chemisorbents for CO₂ capture due to their thermodynamic stability, abundance in nature, low cost of production, and reduced toxicity [16]. Coupled with the basic sites of some selected metal oxides that possess a lower charge to radius ratio which increases their ionic nature and site basicity [17], they exhibit good performance for CO₂ capture. In addition, with applicability within a wide range of temperatures from ambient conditions to temperatures of about 700⁰C [18], research into the use of metal oxides for CO₂ capture has become a hot area of research. The mode of operation of metal oxides follows a cyclic process of exothermic carbonation and endothermic calcination as depicted in **figure 3**. The metal oxide forms stable carbonates as the flue gas is passed through it, and this metal carbonates upon heating **releases** a pure stream of CO₂ gas which regenerates the oxides. Eventually, the generated pure CO₂ gas can either be sequestered underground or used for enhanced oil recovery [19].

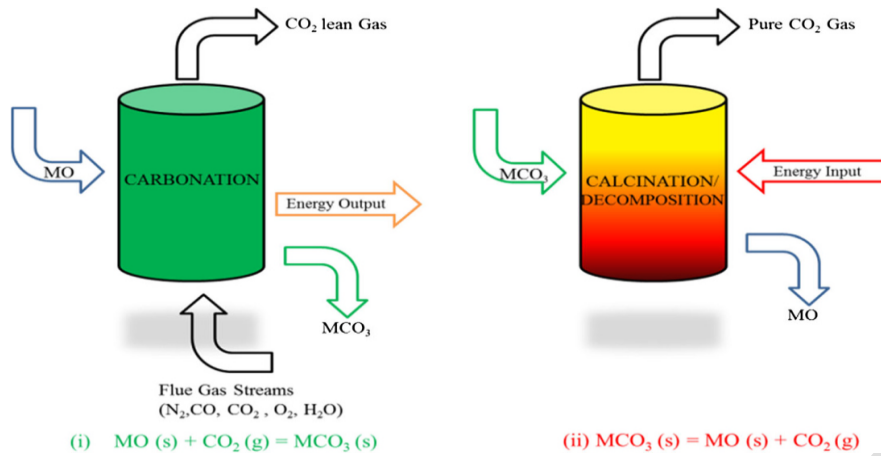


Fig. 3: Cyclic CO₂ capture process for metal oxides (MO) and metal carbonates (MCO₃) reproduced from [20]

However, the process efficiency of metal oxides for CO₂ capture is limited in process applications due to the effect of sintering [20] which reduces sorbent performance especially at high temperatures when metal oxides are repeatedly **cycled** for optimum functionality. This reduction is facilitated through a decrease in the pore sizes, consequent change in shapes of pores, and even closure of small pores during the heating process. Also, it is reported in the structure of metal oxides, that bimodal pore size distribution exists as an after effect of sintering; in this case, pores of larger sizes are identified [21]. Again, this is facilitated by the conversion of small pores to large pore sizes via the reduction in surface energy during the recycling process.

In general, The CO₂ adsorption capacity of metal oxide adsorbents depends mainly on available active sites (basic sites) accessible to CO₂ molecules. The reaction rate is largely dependent on the rate of CO₂ diffusion into the inner layer or pores and is the rate-determining step. Pore characteristics and chemical affinity determine the selectivity of the adsorbent. The energy requirement for regeneration is associated with the heat of adsorption. The poor cyclic capacity can be related to thermo-mechanical strength and drastic changes in morphology during multi-cycle operation. Hence, the physical, as well as chemical properties of the material such as surface area, pore volume, pore size distribution, chemical composition, particle size, surface geometry at the atomic scale, and stability, are very critical for better CO₂ capture characteristics [22]. As a guiding rule, metal oxides that can qualify for CO₂ capture must be; bountiful, react with CO₂ at low temperature, require low regeneration energy, should have suitable reaction kinetics, and must form a carbonate that is stable in the environment at ambient conditions. Below are some of these metal oxides that have been investigated and considered for CO₂ Capture:

2.1 ALKALI METAL BASED OXIDES

Porous oxides such as alkali and alkaline-earth metals have been reported as promising candidates for CO₂ capture. They are usually binary-metal oxides made up of a minimum of one alkaline element. These metal oxides possess long durability, good mechanical strength, wide availability, and low cost

since they are present as natural minerals and have high CO₂ absorption capacity at moderate working temperatures [23].

Recently attention has been drawn to lithium-based silicates (Li₄SiO₄, Li₈SiO₆, and Li₂SiO₃), lithium-based zirconates (Li₂ZrO₃, Li₆Zr₂O₇, and Li₈ZrO₆), lithium based- aluminate (Li₅AlO₄), lithium cuprate (Li₂CuO₂), lithium ferrite (LiFeO₂), lithium titanate (Li₄TiO₄), and sodium ceramics (Na₂ZrO₃, Na₂SiO₃, and Na₂TiO₃) due to their favourable characteristics. Also, the precursors of these compounds lithium oxide (Li₂O), lithium hydroxide (LiOH), and sodium hydroxide (NaOH) have also been studied for CO₂ adsorption but however have shown difficulty in regeneration, high reactivity, instability, and huge volume expansions during absorption [24]. Among these materials, Li₄SiO₄ has shown great promise given its higher CO₂ sorption capacity and cyclic stability. Additionally, the regeneration temperature of Li₄SiO₄ material is much lower when compared with the calcium-based CO₂ sorbents, indicating that lower energy consumption is required for its regeneration [25]. The efficacy of these sorbent materials is closely determined by temperature, pressure, CO₂ concentration, CO₂ flow rate, particle size, crystalline structure, and structural phase transitions during ceramic synthesis. A double sorption mechanism has been proposed for the sorption of these compounds, first beginning with chemical sorption of CO₂ over the surface of these ceramics which leads to the formation of an external layer of alkaline carbonate and subsequent diffusion of the alkaline element throughout the external layer formed in order to reach the surface and continue reacting with the CO₂ [26-27]. This diffusion process is one of the rate determining steps of this mechanism [28].

It has been reported by Romero-Ibarra et al [29] that a secondary lithium phase which depends on the initial composition of the lithium ceramic is also formed on the particle surface which can either reduce or increase the diffusion process depending on the composition of the external shell as depicted in **Fig.4** is composed of Li₂CO₃ and metal oxides or another lithium phase. According to their work, the presence of metal oxides reduces CO₂ chemisorption while the presence of Li₂CO₃ and another lithium phase, can either enhance or decrease the CO₂ chemisorption process depending on whether the secondary lithium phases have better lithium diffusion properties than Li₂CO₃ or not; although it should be noted that this only applies to cases where Li₂CO₃ is a solid.

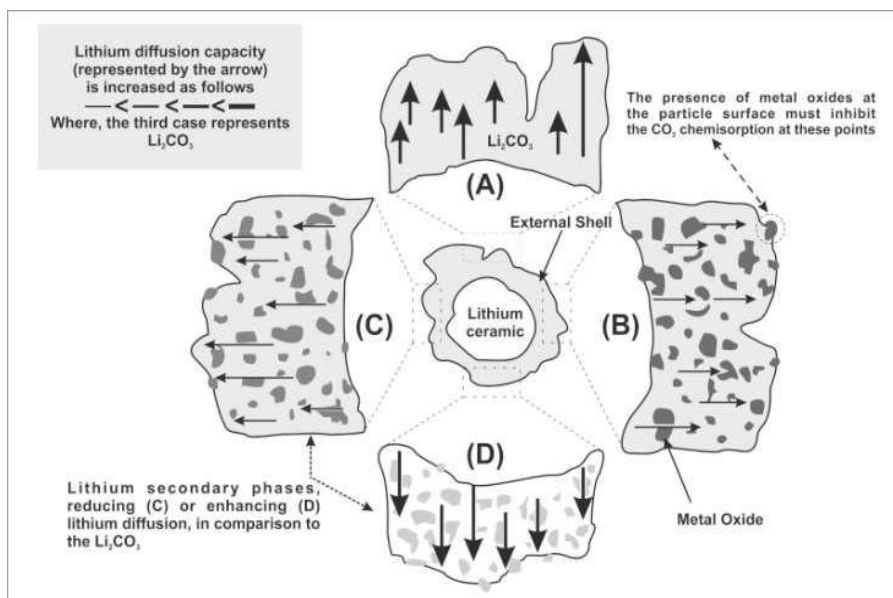


Fig 4: Possible compositions of external shell reproduced from [23]

A faster reaction rate has been reported for Na_2ZrO_3 when compared to synthetic adsorbents such as Li_2ZrO_3 and Li_4SiO_4 this has been attributed to the lamellar structure of Na_2ZrO_3 which enhances sodium mobility, unlike the more packed structure seen in Li_2ZrO_3 [30]. Alkaline ceramics have also been reported to show good selectivity in separation of CO_2 from flue gas with Li_2ZrO_3 showing no affinity for nitrogen at all leading to an infinitely large CO_2/N_2 selectivity ratio [31]. It has also been commonly reported that the presence of steam improves the performance of these ceramics by dissolution of the external shell ultimately leading to an increase in absorption rate, absorption capacity, and regeneration [32]. Several researches attest to this fact such as that carried out by Santillan-Reyes and Pfeiffer [33] who reported a beneficial effect of adding water when absorbing CO_2 over Na_2ZrO_3 at low temperature range.

Similarly Ochoa et al [34] investigated the effect of steam addition on stability, capacity, and regeneration properties of Li_2ZrO_3 , K-doped Li_2ZrO_3 , Na_2ZrO_3 , and Li_4SiO_4 under sorption enhanced steam methane reforming (SESMR) relevant conditions they reported that the presence of steam enhanced absorption/ desorption rate whereas a large decay was observed under dry conditions which was attributed to sintering.

The regeneration of these alkaline ceramics has also been studied although only Li_2ZrO_3 and Li_4SiO_4 have been extensively studied. Reports have it that they require significantly lower temperature than CaO based sorbents, and as a result require low regeneration energy. Although the desorption rate of unmodified lithium ceramics is low. Li_2ZrO_3 is the easiest to regenerate followed by Li_4SiO_4 [35] and Na_2ZrO_3 having a much lower regeneration rate than Li_4SiO_4 [36].

Li_2ZrO_3 and Li_4SiO_4 have also been proven to show good cyclic stability for a limited number of cycles (<100) with minimal loss of capacity, although not much study has been carried out regarding the stability of other alkaline ceramics. More studies are still required on this alkaline

ceramics to determine cheaper precursor sources for these alkaline ceramics as they are relatively expensive when compared to mineral based sorbents [37]. Studies are currently on-going as regards the modification of the different properties of this alkaline ceramics such as kinetics, efficiency, and working temperature. Promising among this modification alternatives are the use of dopants, preparation of solid solutions, development of novel synthetic routes to obtain ceramic with desirable properties, and use of eutectic mixture. Furthermore each of these ceramic would be scrutinized for their individual capture properties in the following sections that follows. Additionally a summary of their sorption properties is given in the table below.

Table 1: Absorption properties of alkaline ceramics

S/N	Ceramic Adsorbent	Calcination temperature (°C)	CO2 Uptake			Gas Composition	Ref.
			Ads. Cap. (wt%)	Temp	P (bar)		
1	Li ₄ SiO ₄	900	27.0	580	1	4% CO ₂	38
2	Li ₂ ZrO ₃	600	22.0	600	5	100% of CO ₂	39
3	Nano Li ₂ ZrO ₃	600	27.0	575	1	100% of CO ₂	40
4	K-Li ₂ ZrO ₃	-	22.0	550	1	100% of CO ₂	41
5	Y-Li ₂ ZrO ₃	700	29.9	500	1	100% of CO ₂	42
6	Promoted Li ₂ ZrO ₃	850	23.0	550	1	100% of CO ₂	43
7	Li ₄ SiO ₄ from rice husk	700	30.5	680	1	100% of CO ₂	44
8	Li ₄ SiO ₄ from diatomite	-	28.6	700	1	100% of CO ₂	45
9	Li ₂ CuO ₂	-	13.6	650	1	100% of CO ₂	46
10	Li ₂ CuO ₂	1000	40.2	875	1	100% of CO ₂	47
11	Li ₄ TiO ₄	-	27.0	900	1	CO ₂ /Ar	48
12	Li ₄ TiO ₄	600-1000	42.0	856	1	100% of CO ₂	49
13	Li ₈ SiO ₆	800	42.0	550	1	100% of CO ₂	50
14	Li ₈ SiO ₆	800	52.1	650	1	100% of CO ₂	51
15	Na ₂ ZrO ₃	850	47.5	70	1	100% of CO ₂	33
16	Na ₂ ZrO ₃	850	23.8	550	1	100% of CO ₂	52
17	Na ₂ SiO ₃	700	37.4	50	1	100% of CO ₂	53
18	Na ₂ TiO ₃	850	12.0	610	1	100% of CO ₂	54

2.1.1 Lithium Based Adsorbents

Lithium based sorbents has being considered for use in CO₂ capture due to its ionic mobility and it's affinity for CO₂ [55]. These compounds are quite promising and have being thoroughly investigated for their CO₂ adsorption properties. Notably among them are LiFeO₂ [56], Li₂CuO₂ [57], Li₂ZrO₃ [58], Li₈SiO₆ [59], and Li₄SiO₄ [60-62].

A. Lithium Orthosilicates (Li₄SiO₄)

Attention has being drawn to Lithium orthosilicates due to their high theoretical CO₂ sorption capacity (36.7 wt %, approximately 8.34 mmol CO₂/ Li₄SiO₄ g) and good cyclic stability[17]. Research shows that Li₄SiO₄ are high temperature CO₂ absorbers and can absorb different concentrations of CO₂ within the temperature range of 450-700⁰C but suffers from high decomposition temperature (>800⁰C) which may require more heat and costly equipment ultimately increasing capital and operational cost.

The chemisorption sorption process is limited by the rate of the formation and growth of the crystals with double-shell structure consisting of Li₂CO₃ and Li₂SiO₃ as depicted in Fig.5. The reaction occurs mainly due to the lithium ion mobility in the ceramics; they diffuse from the core of the particles to the surface and react with CO₂ to form Li₂CO₃. The diffusion of CO₂ in the solid Li₂CO₃ is recognised as the rate limiting step:

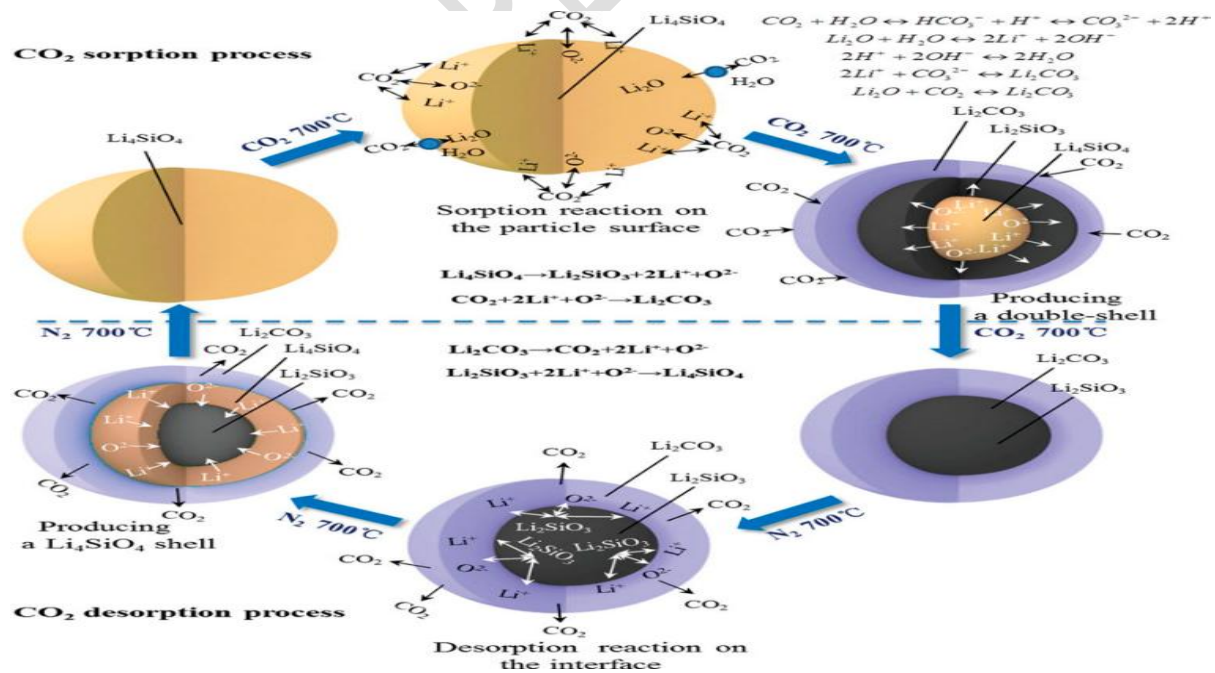
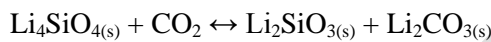


Fig 5: Double-shell mechanism of Li₄SiO₄ material for CO₂ absorption and regeneration [63].

In a research done by Rodriguez et al [64], where they evaluated the CO₂ chemisorption capacity as a function of CO₂ flow rate and sorbent particle size they revealed that the CO₂ capture rate is controlled by CO₂ diffusion through the Gas-film system, whereas at high CO₂ flows it is controlled by the CO₂ chemisorption reaction rate. After formation of the carbonate oxide external shell, the whole CO₂ capture process is controlled kinetically by lithium diffusion. Li₄SiO₄ also finds application in Sorption-enhanced Hydrogen production which mainly consists of sorption enhanced steam methane reforming or sorption enhanced steam ethanol reforming. In these processes, in-situ CO₂ removal with Li₄SiO₄ material as the CO₂ acceptor shifts the reaction equilibrium to hydrogen production, and exothermal absorption of CO₂ by the Li₄SiO₄ material provides heat for reforming, thus high hydrogen yield can be achieved. [65]. Despite their excellent CO₂ sorption capabilities at high temperatures, Li₄SiO₄ face certain constraints such as slow capture kinetics and poor stability–recyclability which limits their application. The slow capture kinetics is due to the formation of a lithium carbonate shell which limits CO₂ diffusion, thus limiting kinetic performance. Poor stability occurs as a result of sintering which reduces the cyclic stability necessary for practical applications.

A lot of research has been done aimed at improving the reaction kinetics of this lithium ceramics by altering the synthesis routes and reducing the particle size of this ceramics since one of the limiting steps is the diffusion process, which may be avoided or at least reduced by the synthesis of smaller particles [66]. Various methods such as solid-state reaction method, sol-gel method, Precipitation method, combustion method etc. have been developed for the synthesis of Li₄SiO₄ sorbents. The solid-state reaction method is easy and the most commonly used technique to synthesize Li₄SiO₄ sorbents [67]. In Sol-gel method the lithium and silicon precursors are mixed in a liquid phase, followed by the formation of a three-dimensional gel network by the gelatinized particles and finally the drying and calcination of the gel to obtain the Li₄SiO₄ sorbent. Sol-gel method facilitates the formation of relatively homogeneous material at lower temperatures [68]. In precipitation method, the silicon source is first mixed with a solution of lithium source and the mixture suspension is stirred, dried and calcined at high temperatures to produce Li₄SiO₄ sorbent [69-74]. In combustion method, the silicon source is mixed with the lithium solution and the fuel (i.e., citric acid, urea, and glycine) followed by vaporization, during which it begins to foam and swell and finally burns itself (autoignition) due to strong exothermic reaction. The charred ash is grinded and calcined at high temperatures to produce Li₄SiO₄ sorbents [75-76].

The structures and properties of the synthesized lithium silicates is largely a function of the synthesis method adopted, type of raw material used and the synthesis temperature (synthesis temperature affect the micro structure which can in turn affect the sorbent performance) [72]. Normally the lithium is sourced from lithium nitrate, lithium carbonate, lithium acetate and lithium hydroxide. The silicon source is derived from raw materials like natural silicon containing minerals, biomass ashes, fly ashes, zeolite based materials, organosilicone compounds, silica powder and its different forms like fumed silica, amorphous silica gel, colloidal silica, aerosol silica, silica sol and quartz powder [77-81]. Research also shows that the addition of dopants such as Al, Fe, Na, K and Cs increases the CO₂ uptake of lithium orthosilicate. In an experiment carried out by Walther-Dari et al [82] using steel

metallurgical slags as silica source with and without addition of 10-30wt% K_2CO_3 , he observed that the CO_2 Capture efficiency improved with the addition of K_2CO_3 because of the formation of a eutectic phase between K_2CO_3 and Li_2CO_3 , which facilitated CO_2 diffusion into the material bulk. The best capture capacity value (104mg CO_2 /g material) was obtained using the material produced from steel metallurgical slag with 20wt% K_2CO_3 . Also Olivares-Marin et al. [83] reported that K-doped Li_4SiO_4 obtained using fly ash as source of SiO_2 exhibited a capacity of 101 mg g^{-1} under optimum conditions (at 600 $^{\circ}C$ with 40 mol % K_2CO_3).

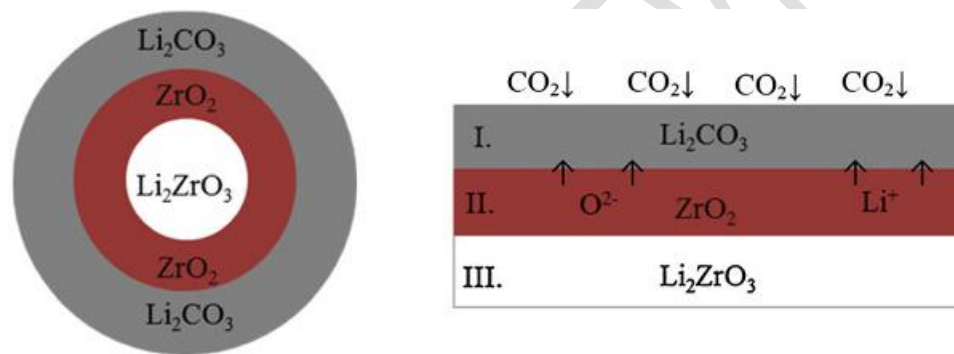
Further studies are focused on decreasing the precursor particle size or choosing more sintering-resistant precursors to result in a smaller product grain size. Such is evident by the recent research done by Rajesh Belgamwar et al. [84], they synthesized lithium silicate nanosheets (LSN) which showed a high CO_2 capture capacity (35.3wt% CO_2 capture using 60% CO_2 Feed gas close to the theoretical value) with ultra-fast kinetics and enhanced stability at 650 $^{\circ}C$. Their work showed that the nanosheet morphology of the lithium silicon nanosheets allow for efficient CO_2 diffusion to ensure reaction with the entire sheet as well as providing extremely fast CO_2 capture kinetics (0.22 $g\ g^{-1}\ min^{-1}$). It was also reported that the LSNs were stable for at least 200 cycles without any loss in their capture capacity or kinetics and neither formed a carbonate shell unlike conventional lithium silicates which are known to rapidly lose their capture capacity and kinetics within the first few cycles due to thick carbonate shell formation and also due to the sintering of sorbent particles. In a similar report by Wang et al. [44] who synthesized Li_4SiO_4 -based adsorbent using rice husk ash as silicon source, he reported that the adsorbent showed better CO_2 sorption capacity (32.4 wt%) and cyclic stability compared with pure Li_4SiO_4 (22.1 wt%), due to high pore volume and high surface area.

B. Lithium metazirconates (Li_2ZrO_3)

The pioneering work of Nakagawa and Ohasi in 1998[85], where they investigated the capture of CO_2 using Li_2ZrO_3 at high temperatures of (400-700 $^{\circ}C$) and reportedly captured about 4.5mol/kg (28wt%) was what sprung up massive interest in lithium zirconates as possible CO_2 capture adsorbents plus unlike other sorbents that had a limited CO_2/N_2 selectivity, lithium zirconate does not absorb nitrogen at all and would result to infinitely large CO_2/N_2 selectivity. Lithium zirconates also showed good stability over carbonation/calcination cycles. Furthermore, lithium zirconates have been used in the CO oxidation, showing complete conversion to CO_2 between 450 and 600 $^{\circ}C$ and subsequent capture of CO_2 that was produced [86]. Similarly to lithium silicates Li_2ZrO_3 also suffers from a slow reaction rate due to the formation of Li_2CO_3 shell which prevents the mobility or access of Li ions to CO_2 , hence Ultimately reducing the reaction rate almost making them impossible for industrial use [87], the mechanism for CO_2 adsorption on Li_2ZrO_3 is as depicted in **Fig. 6**

Recent studies have shown that adding dopants such as Iron, Potassium, Sodium and Yttrium to Li_2ZrO_3 increases the CO_2 adsorption rate. These dopants change the melting point of the system to produce a liquid eutectic mixed-salt molten shell on the outer surfaces which offers much less resistance to CO_2 diffusion and consequently increasing absorption rate [88]. Presence of iron improved the kinetics of lithium zirconates and this can be explained based on partial iron reduction,

implying an oxygen release, which promoted the CO₂ chemical transformation to carbonate ions. Presence of Potassium as a dopant increases the CO₂ diffusion rate (which is usually the rate limiting step) towards the inner unreacted particles by forming a eutectic mixture with Li₂ZrO₃ at 500⁰C. Presence of Yttrium as a Dopant on the other hand shifts the rate limiting step for CO₂ sorption to the diffusion of ions in the ZrO₂ formed during the adsorption process and did not increase the CO₂ sorption kinetics of Li₂ZrO₂ [89]. For Lithium–sodium based zirconates, experiment show that sodium increased the absorption kinetics and the higher the lithium content in the mixture the faster the regeneration kinetics [90].



Reaction at



Fig 6: Proposed mechanisms for CO₂ sorption on Li₂ZrO₃ reproduced from [20]

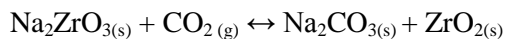
2.1.2 Sodium based sorbents

The CO₂ capture properties of certain sodium based compounds were first reported by Lopez-Ortiz et al. who stated that Na₂ZrO₃, Na₂SbO₃, and Na₂TiO₃ could absorb CO₂ in the temperature range of 600-700⁰C. Observed that the reactivity followed the order Na₂ZrO₃ > Na₂SbO₃ > Na₂TiO₃, Na₂ZrO₃ exhibited better absorption rate and inferior regeneration performance compared to Li₄SiO₄ and Li₂ZrO₃. The following sections that follow give an insight on this ceramics.

A. Sodium Meta Zirconate (Na₂ZrO₃)

With a CO₂ adsorption capacity of 23.75wt% and a lower cost compared to lithium based oxides Na₂ZrO₃ has gained attention as a good CO₂ adsorbent. They can operate at higher temperature plus a

higher reaction rate has also been observed compared to other lithium based adsorbents [91]. Though Na_2ZrO_3 is able to absorb CO_2 even at room temperature the best temperature for CO_2 Absorption on Na_2ZrO_3 is said to be 600°C [92].



According to the work of Alcerra-Corte et al. who studied the kinetics for the chemisorption of CO_2 on Na_2ZrO_3 particles in the temperature range of $150\text{-}700^\circ\text{C}$, a fast kinetics was observed between 550 and 700°C , however at low temperatures, kinetics was relatively low and was attributed to the sintering effect as well as diffusion problems. It was also concluded that sodium diffusion was the rate limiting step for the process. Jimenez et al [93] suggested that the rate limiting step for the CO_2 sorption kinetics of Na_2ZrO_3 at a similar temperature and partial pressure of $0.4\text{-}0.8\text{atm}$ was the surface reaction. Further studies have also revealed that the presence of steam favours the kinetics of the reaction and regeneration because steam increases the mobility of alkaline ions and therefore accelerates the reactions. In another study done by Santillan-Reyes at a temperature of $30\text{-}70^\circ\text{C}$ it was reported that Na_2ZrO_3 was able to absorb 5.8mmol/g of CO_2 in the presence of water, therefore enabling its CO_2 application in low temperature condition.

In 2007 Zhao et al. [94] synthesized nanosized Na_2ZrO_3 with well-controlled crystal phase using a soft-chemical route. It was reported that monoclinic Na_2ZrO_3 showed much faster CO_2 capture rate than hexagonal Na_2ZrO_3 even at low CO_2 partial pressures (0.025 bar). Thus, a higher CO_2 capture rate is obtained for Nanosized Na_2ZrO_3 due to the dual effect of its crystal size and structure showing that reducing particle size can help increase the kinetics of the reaction.

B. Sodium meta-silicate (Na_2SiO_3)

Na_2SiO_3 has been reported to show a low CO_2 adsorption rate $1\text{-}2\text{wt}\%$ at temperatures ranging from room temperature to 130°C , following a two-step process first: Superficial chemical sorption and Sodium Diffusion Process, with sodium diffusion process being recognised as the rate determining step [95].

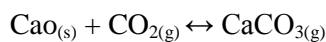
The CO_2 absorption rate has also been observed to increase with decreasing particle size of Na_2SiO_3 and can be attributed to an increase in surface area [96]. Conditions of thermal humidity has also been known to increase CO_2 adsorption rate enabling Na_2SiO_3 absorb up to 16.39 mmol of CO_2/gm of ceramic, much more than that absorbed under dry conditions. Synthesis method also affects the CO_2 capture capacity. CO_2 absorption capacity of Na_2SiO_3 is governed by the combined effect of water vapour and surface area, in a recent research carried out by Rodriguez- Mosqueda et al. [97], involves the synthesis of Na_2SiO_3 using solid-state reaction and combustion method. They reported that Na_2SiO_3 sample prepared by the combustion method presented a surface area 3 times larger than the solid-state reaction sample. He also performed different water vapor sorption experiments. The experiment showed that, The Na_2SiO_3 sample prepared by the combustion method captured up to 8.5 mmol of CO_2 per gram of ceramic (efficiency of 52%), a considerably high CO_2 amount among different materials. Also, the presence of water vapor strongly favored the CO_2 chemisorption on

Na_2SiO_3 . Thus, the recent results support the potential of Na_2SiO_3 as a CO_2 Capture sorbent at moderate or environmental temperatures.

2.2 ALKALI EARTH METALS

2.2.1 Calcium Oxide (CaO)

Focus has been placed on CaO as possible adsorbents for CO_2 due to its availability and its ability to absorb CO_2 at high temperatures. It has a high CO_2 Capture (up to 17.8mmol CO_2 Per gram of sorbent) and can operate at high temperature ($>600^\circ\text{C}$).



In a study conducted by Abanades group [98-99] on the cost of calcium oxide for capturing CO_2 , they reported that it would cost 0.0015 dollars per mole of CO_2 captured with CaO, compared to the cost of activated carbons (0.25 dollars), zeolites (0.20 dollars) and hydrotalcites (4.00 dollars) per mole of CO_2 . Thus, this shows CaO is relatively inexpensive.

CaO has been reported to have regeneration issues, as the ability of CaO to regenerate the carbonate decreases strongly with the increasing number of cycles. It is known to have poor attrition resistance which is quite common with natural sorbents [100-101].

Research such as that done by Baker et al proves that the amount of CO_2 adsorbed dropped significantly as CaO was cycled up to 40 times and he attributed this decreased capacity to a loss of pore volume and sintering, baker also reported that carbonation initially occurred very rapidly, however the reactivity of the sorbent subsequently decreased over time due to the formation of a carbonate shell through which the rate of reaction was controlled by diffusion process. Although current research suggests that KMnO_4 -doped CaO-based sorbent has the potential to reverse this trend as Li et al. [102] reported a better cyclic carbonation rate and conversion over 100 cycles compared with the pristine sorbent. The Dopants are able to achieve this by controlling the surface area and pores to a specific range. In a related experiment Reddy and Smirniotis [103] investigated the role of alkali metals as dopants for CaO the results were in the order of $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$, which indicates a possible relationship between sorption properties and increase of the atomic radii of the alkali metals.

CaO has a tendency to react with SO_2 and CO_2 at the same time to form both CaCO_3 and CaSO_4 (sulphation) this sulphation process increases with increasing number of cycles which may necessitate the need for desulphurization of flue gas before CO_2 Capture in post combustion applications. The reaction mechanism of this sorbents also follows a two-step mechanism, where the first step involves kinetically-controlled rapid chemical reaction at the beginning followed by the diffusion of CO_2 through the product layer formed in the first step to reach unreacted CaO core this is the slowest step in the process and is dependent on the pore size of the sorbents.

Skorfa et al [104] performed an analysis between synthetic and natural based CaO based sorbents he posited that natural sorbents derived from industrial hydrated lime presented promising results; the

preparation procedure seems not to significantly affect activity and stability. They also carried out some tests using the most promising synthetic Ca-Zr, and Ca-Al and natural pure CaO derived from Ca(OH)₂ direct calcination and MgO- doped Ca(OH)₂, were tested in a fixed bed reactor under realistic flue gas feed composition, and discovered that the natural sorbents presented inferior results. Several modifications has being done to improve the properties of this calcium based compounds which includes modification of precursors, use of dopants, Preparation of Nano Sorbents, reactivation through steam/water hydration.

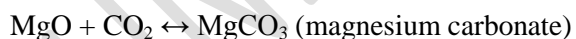
Calcium silicate has also being investigated and reports shows that it starts to absorb CO₂ At 400⁰C with about 28.72% sorption efficiency using 15% CO₂ and the rest Nitrogen. However the CO₂ Capture capacity also drastically decreases from large number of cycles and could be attributed to sintering of the material which leads to the loss of specific surface area [105].

Table 2: Sorption Properties of CaO based sorbents

S/N	Ceramic Adsorbent	Calcination temperature (°C)	CO ₂ Uptake			Gas Composition	Ref.
			Ads. Cap	Temp (Ads)	P (bar)		
1	CaO- based mesoporous silica	950	80	580	-	100% of CO ₂	106
2	Mesoporous Nano crystalline CaO	700	22	600	1	100% of CO ₂	107
3	CaO-MgO	800	53	575	-	100% of CO ₂	108
4	CaO / Ca ₁₂ Al ₁₄ O ₃₃	850	41	550	1	20% of CO ₂	109
5	NiO-CaO-Ca ₁₂ Al ₁₄ O ₃₃	700	56	500	1	15% of CO ₂	110

2.2.2 Magnesium Oxide (MgO)

MgO has being considered for CO₂ capture given its high abundance, cost effectiveness, low toxicity, and thermodynamic stability of the products of the reaction.

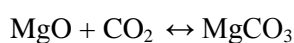
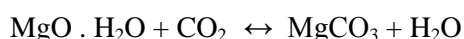
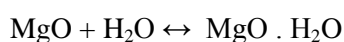


It finds application in both pre and post combustion due to its low regeneration temperatures and has being reported to have good selectivity for CO₂ over N₂ in the presence of steam. The disadvantages of MgO as an adsorbent include low kinetics, poor thermal as well as mechanical stability [111-112]. Mayorga et al [113] reported a sorption capacity of 0.13mmol/g(0.57wt%) for MgO under moderate temperature and dry environment. Studies have also shown that the presence of water catalysed the reaction kinetics, together with surface properties of MgO (such as surface area, Particle size and Porosity).

Research also shows that mesoporous MgO is a better CO₂ adsorbent than non-porous commercial MgO due to high surface area and a narrow pore size distribution the role of porosity was clearly

shown by Bhagiyalakshmi et al [114] on carbon templated mesoporous MgO, who showed that the mesoporosity enhanced CO₂ adsorption up to 1.81mmol/g (8 wt %) at 298k and 2.27mmol/g(10wt%) at 373k whereas non porous MgO only displayed 0.23-45mmol/g(1-2wt%) of adsorption at 298k under atmospheric pressure. Investigations has also being carried out to improve CO₂ adsorption capacity using K₂CO₃ modified MgO, as both MgO and K₂CO₃ can adsorb CO₂ in the presence of water vapour at low temperatures. The modified materials absorbs CO₂ effectively over a temperature range of 50-100⁰C and can be regenerated around 150-400⁰C.

From H₂O:- According to the reaction



Although water catalyzes the reaction but the formation of MgCO₃ layer resists the mobility of CO₂ molecules to come in contact with the unreacted MgO, this means that water vapour alone cannot lead to the complete carbonation conversion of MgO therefore besides the amount of steam, surface properties of MgO such as surface area, Particle size, and Porosity are also very crucial parameters for the carbonation process.

So far, the role of water vapour, porosity, surface area and particle size with the carbonation yield has been established but factors such as carbonation kinetics, sorbent reversibility and durability are still not completely resolved and thus need to be investigated more.

Table 3: Sorption properties of various MgO based sorbents

S/N	Ceramic Adsorbent	Calcination temperature (°C)	CO ₂ Uptake			Gas Composition	Ref.
			Ads. Cap.	Tem p	P (bar)		
1	Mg/K-SBA-15	300	3.6	20	-	-	115
2	Mg/K-SBA-16	300	2.0	20	1	-	115
3	Mg/K-MCM-48	300	2.5	20	1	-	115
4	Na ₂ CO ₃ -MgO	400	15.0	380	-	100% of CO ₂	116
5	Mesoporous MgO	800	10.0	100	1	100% of CO ₂	117
6	MgO/TiO ₂	150	2.1	25		-	118

3 OUTLOOK AND CONCLUSION

The potential of metal oxides in ameliorating CO₂ emissions within the purview of sustainable chemical and energy production has being firmly established, with a lot of research on-going on the

application of this metal oxides in Sorption Enhanced Steam Methane/Methanol Reforming in which these oxides are able to catalyse the conversion of CO to CO₂ and subsequently capturing the CO₂ produced in the process, Also there application as Dual functional materials in reactive capture of CO₂ in which these metal oxides are combined with a hydrogenation catalyst for CO₂ capture and conversion has sparked off alot of interest in this materials. These materials, though auspicious quite sadly face certain challenges which must be addressed before they can be employed commercially. It is highly recommended in order to scale –up the application of these sorbents that more studies should be done in terms of capture capacity, reversibility rate, carbonation kinetics, multi-cycle durability plus an In-depth analysis of the performance of these adsorbents under real life flue gas conditions, because research shows that some of these sorbents tend to lose their capture capacity in the presence of sulphur and Nitrogen oxides which are typical components of real life flue gas streams.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

REFERENCES

- [1] Maroto-Valer, M. M., Song, C. S., and Soong, Y. (2002). Environmental challenges and greenhouse gas control for fossil fuel utilization in the 21st century. New York, NY: Kluwer Academic/Plenum Publishers
- [2] Brovkin, V., Sitch, S., Von Bloh, W., Claussen, M., Bauer, E., and Cramer, W. (2004). Role of land cover changes for atmospheric CO₂ increase and climate change during the last 150 years. *Global Change Biol.* 10, 1253–1266. doi:10.1111/j.1365-2486.2004.00812.x
- [3] Song, C. S. (2006). Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catal. Today* 115, 2–32. doi:10.1016/j.cattod.2006.02.029
- [4] Smith, M. R. and Myers, S. S. (2018). Impact of anthropogenic CO₂ emissions on global human nutrition. *Nat. Clim. Change* 8, 834–839. doi:10.1038/s41558-018-0253-3
- [5] Hannah Ritchie, Max Roser, CO₂ and Greenhouse Gas Emissions, Our World Data. (2020). <https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions> (accessed October 8, 2020).
- [6] Markewitz, P., Kuckshinrichs, W., Leitner, W., Linssen, J., Zapp, P., Bongartz, R., et al. (2012). Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂. *Energy Environ. Sci.* 5, 7281–7305. doi:10.1039/C2EE03403D
- [7] Little, R.J., Versteeg, G.F., Van Swaaij, W.P.M (1991).: Physical absorption into non-aqueous solutions in a stirred cell reactor. *Chem. Eng. Sci.* 46, 3308–3313

- [8] Chiesa, P., Consonni, S.P (1999): Shift reactors and physical absorption for low-CO₂ emission IGCCs. *J. Eng. Gas Turbines Power* 121, 295–305
- [9] Bishnoi, S., Rochelle, G.T (2000): Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chem. Eng. Sci.* 55, 5531–5543
- [10] Rochelle, G.T (2009): Amine scrubbing for CO₂ capture. *Science* 325,1652–1654
- [11] Harlick, P.J.E., Tezel, F.H. (2004): An experimental adsorbent screening study for CO₂ capture from N₂. *Microporous Mesoporous Mater.* 76, 71–77
- [12] Powell, C.E., Qiao, G.G. (2006): Polymeric CO₂/N₂ gas separation membranes for the capture carbon dioxide from power plant flue gases. *J. Membr. Sci.* 279, 1–49
- [13] Rochelle, G. T. (2009). Amine scrubbing for CO₂ capture. *Science* 325, 1652–1654. doi:10.1126/science.1176731
- [14] Rochelle, G. T. (2016). “Conventional amine scrubbing for CO₂ capture,” in Absorption-based post-combustion capture of carbon dioxide. Editors P.H.M. Feron (Cambridge, UK: Woodhead Publishing), Chap. 3, 35–67
- [15] Tontiwachwuthikul, P. and Idem, R. (2013). “Recent progress and new developments in post-combustion carbon-capture technology with reactive solvents,” in Recent progress and new developments in post-combustion carboncapture technology with reactive solvents, Editors P. Tontiwachwuthikul and R. Idem, Future Science Book Series, pp. 2–8.
- [16] M. Pardakhti, T. Jafari, Z. Tobin, B. Dutta, E. Moharreri, N.S. Shemshaki, S. Suib, R. Srivastava, (2019) Trends in Solid Adsorbent Materials Development for CO₂ Capture, *ACS Appl. Mater. Interfaces.* 11 34533–34559. doi:10.1021/acsami.9b08487.
- [17] Z. Yong, V. Mata, A.E. Rodrigues, (2002) Adsorption of carbon dioxide at high temperature - A review, *Sep. Purif. Technol.* 26 195–205. doi:10.1016/S1383-5866(01)00165-4.
- [18] S. Wang, S. Yan, X. Ma, J. Gong, (2011) Recent advances in capture of carbon dioxide using alkali-metal-based oxides, *Energy Environ. Sci.* 4 3805–3819. doi:10.1039/c1ee01116b.
- [19] Sally M. Benson, David R. Cole; (2008) CO₂ Sequestration in Deep Sedimentary Formations. *Elements*; 4 (5): 325–331. doi: <https://doi.org/10.2113/gselements.4.5.325>
- [20] Kumar, S., Saxena, S.K. (2014): A comparative study of CO₂ sorption properties for different oxides. *Mater Renew Sustain Energy* 3, 30. <https://doi.org/10.1007/s40243-014-0030-9>
- [21] Inamuddin, Abdullah M. Asiri, Erc Lichtfouse (2019) sustainable agriculture reviews 38: Carbon Sequestration Vol.2 Materials and chemical methods. Pg 77 <https://doi.org/10.1007/978-3-030-29337-6>
- [22] Hayder A. Alawan, Alaa H. Alminshid, (2021) CO₂ capturing methods: Chemical looping combustion (CLC) as a promising technique Pg1-5. <https://doi.org/10.1016/j.scitotenv.2021.147850>
- [23] Lakshminarayana Kudinalli Gopalakrishna Bhatta, L. Kudinalli Gopalakrishna Bhatta, Seetharamu Subramanyam, S. Subramanyam, Madhusoodana D. Chengala, M. D. Chengala, Sharon Olivera, S. Olivera, & Krishna Venkatesh, K. Venkatesh. (2015). Progress in hydrotalcite like compounds and metal-based oxides for CO₂ capture: a review. *Journal of cleaner production*, 103, 171-196. doi: 10.1016/j.jclepro.2014.12.059
- [24] Mosqueda, H. A.; Vazquez, C.; Bosch, P.; Pfeiffer, H. (2006) Chemical Sorption of Carbon Dioxide (CO₂) on Lithium Oxide (Li₂O) *Chem. Mater*, Pg 18 <https://doi.org/10.1021/cm060122b>
- [25] Xianyao Yan 1, Yingjie Li , Xiaotong Ma 1, Jianli Zhao 1 and Zeyan Wang, (2019), Performance of Li₄SiO₄ Material for CO₂ Capture: A Review, Pg 1-2. doi:10.3390/ijms20040928
- [26] Dunstan, M. T., Donat, F., Bork, A. H., Grey, C. P., & Müller, C. R. (2021). CO₂ Capture at Medium to High Temperature Using Solid Oxide-Based Sorbents: Fundamental Aspects, Mechanistic Insights, and Recent Advances. *Chemical Reviews*, 121(20), 12681-12745.

- [27] Ida, J. I.; Xiong, R.; Lin, Y. S. (2004) Synthesis and CO₂ Sorption Properties of Pure and Modified Lithium Zirconate. *Sep. Purif. Technol.*, 36, [https://doi.org/10.1016/S1383-5866\(03\)00151-5](https://doi.org/10.1016/S1383-5866(03)00151-5)
- [28] Essaki, K.; Nakagawa, K.; Kato, M.; Uemoto, H. (2004) CO₂ Absorption by Lithium Silicate at Room Temperature. *J. Chem. Eng. Jpn.*, Pg 37, DOI:[10.1252/jcej.37.772](https://doi.org/10.1252/jcej.37.772)
- [29] Romero-Ibarra, I., Ortiz-Landeros, J., Pfeiffer, H., (2013). Microstructural and CO₂ Chemisorption Analyses of Li₄SiO₄: Effect of Surface Modification by the Ball Milling Process. *Thermochimica Acta.* 567,118 ,124. <https://doi.org/10.1016/j.tca.2012.11.018>
- [30] Boon, J., Cobden, P. D., van Dijk, H. A. J., van Sint, M. A., (2014). High-temperature pressure swing adsorption cycle design for sorption-enhanced water-gas shift. *Chem. Eng. Sci.* 122, 219-231. doi: <http://dx.doi.org/10.1016/j.ces.2014.09.034>
- [31] Xiong, R., Ida, J., Lin, Y. S., (2003). Kinetics of carbon dioxide sorption on Potassium doped lithium zirconate. *Chem. Eng. Sci.* 58, 4377-4385. (DOI: 10.1016/S0009-2509(03)00319-1)
- [32] Pfeiffer, Heriberto. (2010). Advances on Alkaline Ceramics as Possible CO₂ Captors. ACS Symposium Series. 10.1021/bk-2010-1056.ch015.
- Pfeiffer, H., (2010). Advances on Alkaline Ceramics as Possible CO₂ Captors. In: Yun- Hang, H. (Ed.), (2010) Advances in CO₂ Conversion and Utilization. ACS Symposium Series, vol. 1056. American Chemical Society, Washington DC, USA.(DOI: 10.1021/bk-2010-1056.ch015)
- [33] Santillan-Reyes, G. G., Pfeiffer, H., (2011). Analysis of the CO₂ capture in sodium zirconate (Na₂ZrO₃). Effect of the water vapor addition. *Int. J. Greenhouse. Gas Control.* 5, 1624-1629. (DOI: 10.1016/j.ijggc.2011.09.009)
- [34] Ochoa-Fernandez, E., Zhao, T., Rønning, M., Chen, D. (2009). Effects of Steam Addition on the Properties of High Temperature Ceramic CO₂ Acceptors. Special Issue: Recent Developments in CO₂ Emission Control Technology. *J. Environ. Eng.* 135, 397-403.
- [35] Xiao, Q., Liu, Y., Zhong. Y., Zhu, W., (2011). A citrate sol-gel method to synthesize Li₂ZrO₃ nanocrystals with improved CO₂ capture properties. *J. Mater. Chem.* 21, 3838-3842.DOI: <https://doi.org/10.1039/C0JM03243C>
- [36] López- Ortiz, A., Rivera, N. G. P., Rojas, A. R., Gutierrez, D. L., (2010). Novel Carbon Dioxide Solid Acceptors Using Sodium Containing Oxides. *Separ Sci Technol.* 39, 3559- 3572.DOI: 10.1081/SS-200036766
- [37] Yang, W., Kim, Y., Liu, P. K. T., Sahimi, M., Tsotsis, T. T., (2002). A study by in situ techniques of the thermal evolution of structure of a Mg-Al-CO₃ layered double hydroxide. *Chem. Eng. Sci.* 57, 2945-2953.DOI: 10.1021/ie900371r
- [38] Seggiani, M., Puccini, M., Vitolo, S., 2011. High-Temperature and Low Concentration CO₂ Sorption on Li₄SiO₄ Based Sorbents: Study of the Used Silica and Doping Method Effects. *Int. J. Greenh. Gas Control.* 5, 741-748.(DOI: 10.1016/j.ijggc.2011.03.003)
- [39]Ochoa-Fernandez, E., Rusten, H. K., Jakobsen, H. A., Ronning, M., Holmen, A., Chen, D. (2005). Sorption enhanced hydrogen production by steam methane reforming using Li₂ZrO₃ as sorbent: Sorption kinetics and reactor simulation. *Catalyst Today.* 106, 41-46.(DOI: 10.1016/j.cattod.2005.07.146)
- [40] Ochoa-Fernandez, E., Rønning, M., Grande, T., Chen, D., (2006). Nanocrystalline Lithium Zirconate with Improved Kinetics for High-Temperature CO₂ Capture. *Chem. Mater.* 18, 1383- 1385. DOI: 10.1021/cm052075d
- [41] Xiao, Q., Tang, X., Zhong Y., Zhu, W., (2012). A Facile Starch-Assisted Sol-Gel Method to Synthesize K-Doped Li₂ZrO₃ Sorbents with Excellent CO₂ Capture Properties. *J. Am. Ceram. Soc.* 95, 1544-1548.(DOI: 10.1111/j.1551-2916.2012.05090.x)
- [42] Iwan, A., Stephenson, H., Ketchie, W. C., Lapkin, A. A., (2009). High temperature sequestration of CO₂ using lithium zirconates. *Chem. Eng. J.* 146, 249-258.(DOI: 10.1016/j.ces.2008.06.006)

- [43] Ochoa-Fernandez, E., Rønning, M., Grande, T., Chen, D., (2006). Synthesis and CO₂ Capture Properties of Nanocrystalline Lithium Zirconate. *Chem. Mater.* 18, 6037-6046.(DOI: 10.1021/cm061515d)
- [44] Wang, K., Zhao, P., Guo, X., Li, Y., Han, D., Chao, Y., (2014). Enhancement of Reactivity in Li₄SiO₄ based Sorbents from the Nano-Sized Rice Husk Ash for High-Temperature CO₂ Capture. *Energ. Convers. Manage.* 81, 447-454.(DOI:http://dx.doi.org/10.1016/j.enconman.2014.02.054)
- [45] Yun, S. S., QingMing, J., LiHong, J., QinChao, L., YaMing, W., JinHui, P., (2012). Preparation and kinetic analysis of Li₄SiO₄ sorbents with different silicon sources for high temperature CO₂ capture. *Chinese Science Bulletin.* 57, 2475-2479.(DOI: 10.1007/s11434-012-5188-x)
- [46] Palacios-Romero, L. M., Pfeiffer, H., (2008). Lithium Cuprate (Li₂CuO₂): A New Possible Ceramic Material for CO₂ Chemisorption. *Chem. Lett.* 37, 862-863.(DOI: 10.1246/cl.2008.862)
- [47] Matsukura, Y., Okumura, T., Kobayashi, R., Oh-ishi, K., (2010). Synthesis and CO₂ Absorption Properties of Single-phase Li₂CuO₂ as a CO₂ Absorbent. *Chem. Lett.* 39, 966-967.
- [48] Ueda, S., Inoue, R., Sasaki, K., Wakuta, K., Ariyama, T., (2011). CO₂ Absorption and Desorption Abilities of Li₂O-TiO₂ Compounds. *ISIJ International.* 51, 530-537.
- [49] Togashi, N., Okumura, T., Oh-Ishi, K., (2007). Synthesis and absorption property of Li₄TiO₄ as a novel CO₂ absorbent. *J. Ceram. Soc. Jpn.* 115, 324-328.
- [50] Romero-Ibarra, I. C., Duran-Munoz, F., Pfeiffer, H., (2014). Influence of the K-, Na- and KNa-carbonate additions during the CO₂ chemisorption on lithium oxosilicate (Li₈SiO₆). *Greenhouse Gas Sci Technol.* 4, 145-154.(DOI: 10.1002/ghg)
- [51] Duran-Munoz, F., Romero-Ibarra, I. C., Pfeiffer, H., (2013). Analysis of the CO₂ chemisorption reaction mechanism in lithium oxosilicate (Li₈SiO₆): a new option for high temperature CO₂ capture. *J. Mater. Chem. A.* 1, 3919-3925.(DOI: 10.1039/c3ta00421j)
- [52] Martínez-dlCruz, L., Pfeiffer, H., (2012). Microstructural Thermal Evolution of the Na₂CO₃ Phase Produced during a Na₂ZrO₃-CO₂ Chemisorption Process. *J. Phys. Chem. C.* 116, 9675-9680. (DOI: dx.doi.org/10.1021/jp301917a)
- [53] Rodríguez-Mosqueda, R., Pfeiffer, H., (2013). High CO₂ Capture in Sodium Metasilicate (Na₂SiO₃) at Low Temperatures (30-60 °C) through the CO₂-H₂O Chemisorption Process. *J. Phys. Chem. C.* 117, 13452-13461.(DOI: dx.doi.org/10.1021/jp402850j)
- [54] Sanchez-Camacho, P., Romero-Ibarra, I. C., Duan, Y., Pfeiffer, H., (2014). Thermodynamic and Kinetic Analyses of the CO₂ Chemisorption Mechanism on Na₂TiO₃: Experimental and Theoretical Evidences. *J. Phys. Chem. C.* 118, 19822-19832.(DOI: dx.doi.org/10.1021/jp504922e)
- [55] Gómez-Garduño, N., & Pfeiffer, H. (2019). Thermokinetic evaluation of iron addition on lithium metazirconate (Fe-Li₂ZrO₃) for enhancing carbon dioxide capture at high temperatures. *Thermochimica Acta*, 673, 129-137. <https://doi.org/10.1016/j.tca.2019.01.017>
- [56] Drage, T. C., Snape, C. E., Stevens, L. A., Wood, J., Wang, J., Cooper, A. I., Dawson, R., Guo, X., Satterley, C., Irons, R., (2012). Materials challenges for the development of solid sorbents for post-combustion carbon capture. *J. Mater. Chem.* 22, 2815-2823.
- [57] Spigarelli, B. P., Kawatra, S. K., (2013). Opportunities and challenges in carbon dioxide capture. *Journal of CO₂ Utilization.* 1, 69-87.(DOI:http://dx.doi.org/10.1016/j.jcou.2013.03.002).
- [58] Smith, K., Ghosh, U., Khan, A., Simioni, M., Endo, K., Zhao, X., Kentish, S., Qader, A., Hooper, B., Stevens, G., (2009). Recent developments in solvent absorption technologies at the CO₂CRC in Australia. *Energy Procedia.* 1, 1549-1555.
- [59] Songolzadeh, M., Ravanchi, M. T., Soleimani, M., (2012). Carbon Dioxide Capture and Storage: A General Review on Adsorbents. *World Academy of Science, Engineering and Technology.* 70, 225-232.
- [60] Figueroa, J. D., Fout, T., Plasynski, S., McIlvried, H., Srivastava, R. D., (2008). Advances in CO₂ capture technology-The U.S. Department of Energy's Carbon Sequestration Program. *Int. J. Greenh. Gas Control.* 2, 9-20.(DOI: 10.1016/S1750-5836(07)00094-1)

- [61] Rusten, H.K.; Ochoa-Fernández, E.; Lindborg, H.; Chen, D. (2017); Jakobsen, H.A. Hydrogen production by sorption-enhanced steam methane reforming using lithium oxides as CO₂-acceptor. *Ind. Eng. Chem. Res.*, 46, 8729–8737. <https://doi.org/10.1021/ie070770k>
- [62] Yu Zhang, Yanshan Gao, Heriberto Pfeiffer, benoit Louis, Luyi Sun, Dermot O'Hare, Qiang wang (2019) Recent advances in lithium containing ceramic based sorbents for high-temperature CO₂ capture. *Journal of Materials chemistry A* 7(14). Pg 1-3. DOI: [10.1039/C8TA08932A](https://doi.org/10.1039/C8TA08932A)
- [63] Zhang Q., Han D., Liu Y., Qian Y., Zhu Z. (2013) Analysis of CO₂ sorption/desorption kinetic behaviors and reaction mechanisms on Li₄SiO₄. *AIChE J.* ;59:901–911.
- [64] Rafael Rodríguez-Mosqueda and Heriberto Pfeiffer (2010):_Thermokinetic Analysis of the CO₂ Chemisorption on Li₄SiO₄ by Using Different Gas Flow Rates and Particle Sizes *The Journal of Physical Chemistry A* 114 (13), 4535-4541 DOI: 10.1021/jp911491t
- [65] Qi Zhang, Chen Shen, Sai Zhang, Yongqiang Wu (2016) Steam methane reforming reaction enhanced by a novel K₂CO₃-Doped Li₄SiO₄ sorbent: Investigations on the sorbent and catalyst coupling behaviors and sorbent regeneration strategy February 2016___International Journal of Hydrogen Energy 41(8)DOI:10.1016/j.ijhydene.2015.12.116
- [66] Pfeiffer H, Bosch P, Bulbulian S. (1998) Synthesis of lithium silicates. *J Nucl Mater*; 257:309 17.
- [67]Kato M, Yoshikawa S, Nakagawa K.(2002) Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations. *J Mater Sci Lett.* ;21:485–7. <http://dx.doi.org/10.1023/A:1015338808533>
- [68] Subha PV, Nair BN, Hareesh P, Mohamed AP, Yamaguchi T, Warriar KGK, Hareesh US. (2014) Enhanced CO₂ absorption kinetics in lithium silicate platelets synthesized by a sol–gel approach. *J Mater Chem A*.;2:12792–8. <https://doi.org/10.1039/C4TA01976H>
- [69] Izquierdo MT, Turan A, Garcia S, Maroto-Valer MM. (2018); Optimization of Li₄SiO₄ synthesis conditions by a solid state method for maximum CO₂ capture at high temperature. *J Mater Chem A.* 6:3249–57. <https://doi.org/10.1039/C7TA08738A>
- [70] Wang K, Wang X, Zhao P, Guo X. (2014) High-temperature capture of CO₂ on lithium based sorbents prepared by a water-based sol–gel technique. *Chem Eng Technol.*;37:1552–8.
- [71] Cruz, D., Bulbulian, S., Lima, E., & Pfeiffer, H. (2006). Kinetic analysis of the thermal stability of lithium silicates (Li₄SiO₄ and Li₂SiO₃). *Journal of Solid State Chemistry*, 179(3), 909-916. <https://doi.org/10.1016/j.jssc.2005.12.020>
- [72] Wu X, Wen Z, Xu X, Wang X, Lin J. (2009) Synthesis and characterization of Li₄SiO₄ nano-powders by a water-based sol–gel process. *J Nucl Mater.* 2009;392:471–5. doi:10.1016%2Fj.jnucmat.2009.04.010
- [73] Bretado, M. E., Guzmán Velderrain, V., Lardizábal Gutiérrez, D., Collins-Martínez, V., & Ortiz, A. L. (2005). A new synthesis route to Li₄SiO₄ as CO₂ catalytic/sorbent. *Catalysis Today*, 107–108, 863–867. <https://doi.org/10.1016/j.cattod.2005.07.098>
- [74] Ortiz AL, Bretado MAE, Velderrain VG, Zaragoza MM, Gutierrez JS, Gutierrez DL, Collins-Martinez V. (2014) Experimental and modeling kinetic study of the CO₂ absorption by Li₄SiO₄.*Int J Hydrog Energy.* 2014;39:16656–66.
- [75] Choudhary A, Sahu BS, Mazumder R, Bhattacharyya S, Chaudhuri P. (2014) Synthesis and sintering of Li₄SiO₄ powder from rice husk ash by solution combustion method and its comparison with solid state method. *J Alloys Compd*;590:440–5.
- [76] Rao GJ, Mazumder R, Bhattacharyya S, Chaudhuri P. (2017) Synthesis, CO₂ absorption property and densification of Li₄SiO₄ powder by glycine-nitrate solution combustion method and its comparison with solid state method. *J Alloys Compd*;725:461–71.
- [77] Niu M, Li X, Ouyang J, Yang H. (2016) Lithium orthosilicate with halloysite as silicon source for high temperature CO₂ capture. *RSC Adv.*;6:44106–12. <https://doi.org/10.1039/C6RA05004B>

- [78] Wang K, Zhao P, Guo X, Han D, Chao Y.(2015) High temperature capture of CO₂ on Li₄SiO₄ based sorbents from biomass ashes. *Environ Prog Sustain Energy*.34:526–32. <https://doi.org/10.1002/ep.11986>
- [79] Olivares-Marin M, Drage T, Maroto-Valer MM. (2010) Novel lithium based sorbents from fly ashes for CO₂ capture at high temperatures. *Int J Greenh Gas Control*.;4:623–9. <https://doi.org/10.1016/j.ijggc.2009.12.015>
- [70] Zhao M, Fan H, Yan F, Song Y, He X, Memon MZ, Bhatia SK, Ji G. (2018) Kinetic analysis for cyclic CO₂ capture using lithium orthosilicate sorbents derived from different silicon precursors. *Dalton Trans*. 2018;47:9038–50. <https://doi.org/10.1039/C8DT01617H>
- [81] Pan Y, Zhang Y, Zhou T, Louis B, O'Hare D, Wang Q. (2017) Fabrication of lithium silicates as highly efficient high-temperature CO₂ sorbents from SBA-15 precursor. *Inorg Chem*.;56:782134. <https://doi.org/10.1021/acs.inorgchem.7b00559>
- [82] Walther-Darío Bejarano-Peña, Brenda Alcántar-Vázquez, Rosa-María Ramírez-Zamora, (2021) Synthesis and evaluation in the CO₂ capture process of potassium-modified lithium silicates produced from steel metallurgical slags, *Materials Research Bulletin*, Volume 141,2021, 111353, ISSN 0025 5408, <https://doi.org/10.1016/j.materresbull.2021.111353>.
- [83] Olivares-Marin, M., Drage, T.C., Maroto-Valer, M. M., (2010). Novel lithium-based sorbents from fly ashes for CO₂ capture at high temperatures. *Int. J. Greenh. Gas Control*. 4, 623- 629.(DOI: 10.1016/j.ijggc.2009.12.015)
- [84] Rajesh Belgamwar, Ayan Maity, Tisita Das, Sudip Chakraborty, Chathakudath P. Vinod and Vivek Polshettiwar, (2021) Lithium silicate nanosheets with excellent capture capacity and kinetics with unprecedented stability for high-temperature CO₂ capture, 2021, Pg 1-5, <https://doi.org/10.1039/D0SC06843H>
- [85] Nakagawa, K., Ohashi, T.J.(1998): A novel method for CO₂ capture from high temperature gases. *J. Electrochem. Soc.* 145,1344–1346 (1998)
- [86] Wang, K., Guo, X., Zhao, P., Wang, F., Zheng, C., (2011). High Temperature Capture of CO₂ on Lithium-Based Sorbents from Rice Husk Ash. *J. Hazard. Mater.* 189, 301-307.(DOI:10.1016/j.jhazmat.2011.02.040)
- [87] Nair, Supriya, and Rajeev Raghavan (2021). "Synthesis and CO₂ sorption kinetics of lithium zirconate." *Thermochimica Acta* 706 : 179074. <https://doi.org/10.1016/j.tca.2021.179074>
- [88] Gómez-Garduño, Nayeli & Pfeiffer, Heriberto. (2019). Thermokinetic evaluation of iron addition on lithium metazirconate (Fe-Li₂ZrO₃) for enhancing carbon dioxide capture at high temperatures. *Thermochimica Acta*. 673. <https://doi.org/10.1016/j.tca.2019.01.017>.
- [89] Pannocchia, G., Puccini, M., Seggiani, M., Vitolo, S. (2007): Experimental and modeling studies on high-temperature capture of CO₂ using lithium zirconate based sorbents. *Ind. Eng. Chem. Res.* 46, 6696–6706 <https://doi.org/10.1021/ie0616949>
- [90] Heriberto Pfeiffer, Enrique Lima, and Pedro Bosch (2006) Lithium–Sodium Metazirconate Solid Solutions, Li_{2-x}Na_xZrO₃ (0 ≤ x ≤ 2): A Hierarchical Architecture. *Chem. Mater.* 18, 2642-2647, Pages 1-3, <https://doi.org/10.1021/cm0600935>
- [91] Pfeiffer, H., Vázquez, C., Lara, V.H., Bosch, P. (2007): Thermal behavior and CO₂ absorption of Li_{2-x}Na_xZrO₃ solid solutions. *Chem. Mater.* 19, 922–926 <https://doi.org/10.1021/cm0623965>
- [92] Zhao, T., Rønning, M., Chen, D. (2007): Preparation and high-temperature CO₂ capture properties of nanocrystalline Na₂ZrO₃. *Chem. Mater.* 19, 3294–3301 <https://doi.org/10.1021/cm062732h>

- [93] Jimenez, D.B., Bretado, M.A.E., Gutierrez, D.L., Guitierrez, J.M.S., Ortiz, A.L., Martinez, V.C. (2013): Kinetic study and modelling of the high temperature CO₂ capture by Na₂ZrO₃ solid absorbent. *Int. J. Hydrogen Energy* 38, 2557–2564 <https://doi.org/10.1016/j.ijhydene.2012.11.063>
- [94] Zhao, T., Ochoa-Fernandez, E., Rønning, M., Chen, D., (2007). Preparation and High-Temperature CO₂ Capture Properties of Nanocrystalline Na₂ZrO₃. *Chem. Mater.* 19, 3294-3301.(DOI: 10.1021/cm062732h)
- [95] Yong Mok Kwon, Soo Chool Lee, Ho Jin Chae, Min Sun Cho, Yong Ki Park, Hwi Min Seo, Jae Chang Kim, (2019) Regenerable sodium-based lithium silicate sorbents with a new mechanism for CO₂ capture at high temperature, *Renewable Energy*, Volume 144, Pages 180-187, ISSN 0960-1481, <https://doi.org/10.1016/j.renene.2018.08.039>.
- [96] Yong Mok Kwon, Soo Chool Lee, Ho Jin Chae, Min Sun Cho, Yong Ki Park, Hwi Min Seo, Jae Chang Kim, Regenerable sodium-based lithium silicate sorbents with a new mechanism for CO₂ capture at high temperature, *Renewable Energy*, Volume 144, 2019, Pages 180-187, ISSN 0960-1481, <https://doi.org/10.1016/j.renene.2018.08.039>.
- [97] Rafael Rodríguez-Mosqueda and Heriberto Pfeiffer (2013) *The Journal of Physical Chemistry C* 2013 117 (26), 13452-13461 DOI: 10.1021/jp402850j
- [98] Abanades, J. C.; Grasa, G.; Alonso, M.; Rodriguez, N.; Anthony, E. J.; Romeo, L. M. (2007) Cost structure of a postcombustion CO₂ capture system using CaO. *Environ. Sci. Technol.*, 41, 5523-5527.
- [99] Abanades, J. C.; Rubin, E. S.; Anthony, E. J. (2004) Sorbent cost and performance in CO₂ capture systems. *Ind. Eng. Chem. Res.*, 43, 3462-3466.
- [100] Wu, S. F., Jiang, M. Z., 2010. Formation of a Ca₁₂Al₁₄O₃₃ Nanolayer and Its Effect on the Attrition Behavior of CO₂-Adsorbent Microspheres Composed of CaO Nanoparticles. *Ind. Eng. Chem. Res.* 49, 12269-12275.(DOI: 10.1021/ie901561e)
- [101] Manovic, V., Anthony, E. J., (2007). Steam Reactivation of Spent CaO-Based Sorbent for Multiple CO₂ Capture Cycles. *Environ. Sci. Technol.* 41, 1420-1425.(DOI: 10.1021/es0621344)
- [102] Li, Y., Zhao, C., Chen, H., Duan, L., & Chen, X. (2010). Cyclic CO₂ capture behavior of KMnO₄-doped CaO-based sorbent. *Fuel*, 89(3), 642-649.
- [103] Reddy, E. P., & Smirniotis, P. G. (2004). High-temperature sorbents for CO₂ made of alkali metals doped on CaO supports. *The journal of physical chemistry B*, 108(23), 7794-7800.
- [104] Skoufa, Z., Antzara, A., Heracleous, E., & Lemonidou, A. A. (2016). Evaluating the activity and stability of CaO-based sorbents for post-combustion CO₂ capture in fixed-bed reactor experiments. *Energy Procedia*, 86, 171-180.
- [105] Wang, M., Lee, C.G. (2009): Absorption of CO₂ on CaSiO₃ at high temperatures. *Energy Convers. Manag.* 50, 636–638
- [106] Huang, C. H., Chang, K. P., Yu, C. T., Chiang, P. C., Wang, C. F., 2010. Development of high-temperature CO₂ sorbents made of CaO-based mesoporous silica. *Chem. Eng. J.* 161, 129-135.(DOI: 10.1016/j.cej.2010.04.045)
- [107] Wu, Z., Hao, N., Xiao, G., Liu, L., Webley, P., Zhao, D., (2011). One-pot generation of mesoporous carbon supported nanocrystalline calcium oxides capable of efficient CO₂ capture over a wide range of temperatures. *Phys. Chem. Chem. Phys.* 13, 2495-2503
- [108] Li, L., King, D. L., Nie, Z., Howard, C., (2009). Magnesia-Stabilized Calcium Oxide Absorbents with Improved Durability for High Temperature CO₂ Capture. *Ind. Eng. Chem. Res.* 48, 10604-10613.(DOI: 10.1021/ie901166b)
- [109] Li, Z. S., Cai, N. S., Huang, Y. Y. (2006). Effect of Preparation Temperature on Cyclic CO₂ Capture and Multiple Carbonation - Calcination Cycles for a New Ca-Based CO₂ Sorbent. *Ind. Eng. Chem. Res.* 45, 1911 - 1917.(DOI: 10.1021/ie051211i)

- [110] Martavaltzi, C. S., Pampaka, E. P., Korkakaki, E. S., Lemonidou, A. A., (2010). Hydrogen Production via Steam Reforming of Methane with Simultaneous CO₂ Capture over CaOCa₁₂Al₁₄O₃₃. *Energy Fuels*. 24, 2589-2595.(DOI: 10.1016/j.ces.2010.04.038)
- [111] Hassanzadeh, A., Abbasian, J., (2010). Regenerable MgO-based sorbents for hightemperature CO₂ removal from syngas: 1. Sorbent development, evaluation, and reaction modeling. *Fuel*. 89, 1287-1297.(DOI: 10.1016/j.fuel.2009.11.017)
- [112] Zhang, K., Li, X. S., Duan, Y., King, D. L., Singh, P., Li, L., (2013). Roles of double salt formation and NaNO₃ in Na₂CO₃-promoted MgO absorbent for intermediate temperature CO₂ removal. *Int. J. Greenh.Gas control*.12,351358. (DOI:<http://dx.doi.org/10.1016/j.ijggc.2012.11.013>)
- [113] Mayorga, S. G., Weigel, S. J., Gaffney, T. R., & Brzozowski, J. R. (2001). Carbon dioxide adsorbents containing magnesium oxide suitable for use at high temperatures (No. US 6280503). Air Products and Chemicals, Inc.(Allentown, PA).
- [114] Bhagiyalakshmi, M., Lee, J. Y., & Jang, H. T. (2010). Synthesis of mesoporous magnesium oxide: its application to CO₂ chemisorption. *International Journal of Greenhouse Gas Control*, 4(1), 51-56.
- [115] Zukal, A., Pastva, J., Cejka, J., (2013). MgO-modified mesoporous silicas impregnated by potassium carbonatefor carbon dioxide adsorption. *Microporous Mesoporous Mater.* 167, 44-50.(DOI: <http://dx.doi.org/10.1016/j.micromeso.2012.05.026>)
- [116] Zhang, K., Li, X. S., Duan, Y., King, D. L., Singh, P., Li, L., (2013). Roles of double salt formation and NaNO₃ in Na₂CO₃-promoted MgO absorbent for intermediate temperature CO₂ removal. *Int. J. Greenh. Gas Control*. 12, 351-358. (DOI:<http://dx.doi.org/10.1016/j.ijggc.2012.11.013>)
- [117] Bian, S. W., Baltrusaitis, J., Galhotra, P., Grassian, V. H., (2010). A template-free, thermal decomposition method to synthesize mesoporous MgO with a nanocrystalline framework and its application in carbon dioxide adsorption. *J. Mater. Chem.* 20, 8705-8710
- [118] Jeon, H., Min, Y. J., Ahn, S. H., Hong, S. M., Shin, J. S., Kim, J. H., Lee, K. B., (2012). Graft copolymer templated synthesis of mesoporous MgO/TiO₂ mixed oxide nanoparticles and their CO₂ adsorption capacities. *Colloid Surface A*. 414, 75–81.(DOI: <http://dx.doi.org/10.1016/j.colsurfa.2012.08.009>)