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The Role of Alkaline/alkaline Earth Metal Oxides in CO_2 Capture: A Concise Review

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Authors' contributions

This work was carried out in collaboration among all authors. Author EV conceptualisation, data curation, investigation, methodology, writing -original draft, writing - review & editing, supervision, validation of the manuscript. Author BN writing - original draft of the manuscript. Author CUG, supervision, validation, visualisation, writing – original draft, review & editing, validation of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Reducing the concentration of CO_2 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 CO_2 from flue gas streams. In recent times metal oxides have received a lot of attention as potential adsorbents for solving this problem.They find 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 to form carbonates, which when heated liberates an almost pure stream of CO_2 which can be sequestered, thereby, 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.

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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 CO_2, SO_X, NO_X, Mercury, and Particulate matter that result from the combustion of these fuels. Recently, major attention has been focused on CO_2 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 CO_2 emissions both from the stationary sources with high CO_2 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 CO_2 concentration on the earth has been steadily increasing as seen in Fig. 1, as of December 2019, CO_2 concentration in the atmosphere had reached 412 ppm accounting for about 31% increase of that in 1958 with reports prognosticating that the CO_2 concentration in the air would surpass 550ppm by 2050 [4] if no further drastic actions are taken to curb these CO_2 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.

Recently carbon capture, utilization, and sequestration (CCUS) have been touted as a viable option to mitigate these CO_2 emissions within a short term. This technology involves using various sorbents to capture the CO_2 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 CO_2 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 CO_2 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 Fig. 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.

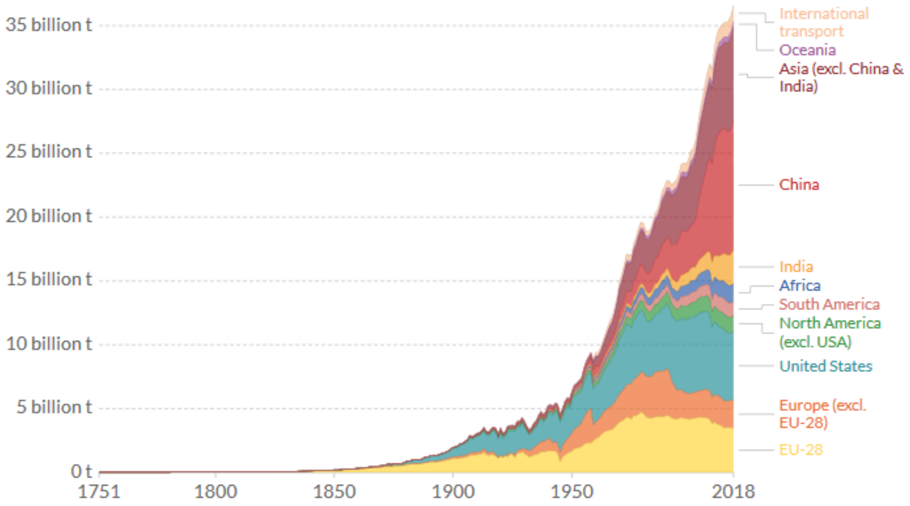

Fig. 1. Global carbon emission from 2006 – 2019, reproduced from [5]

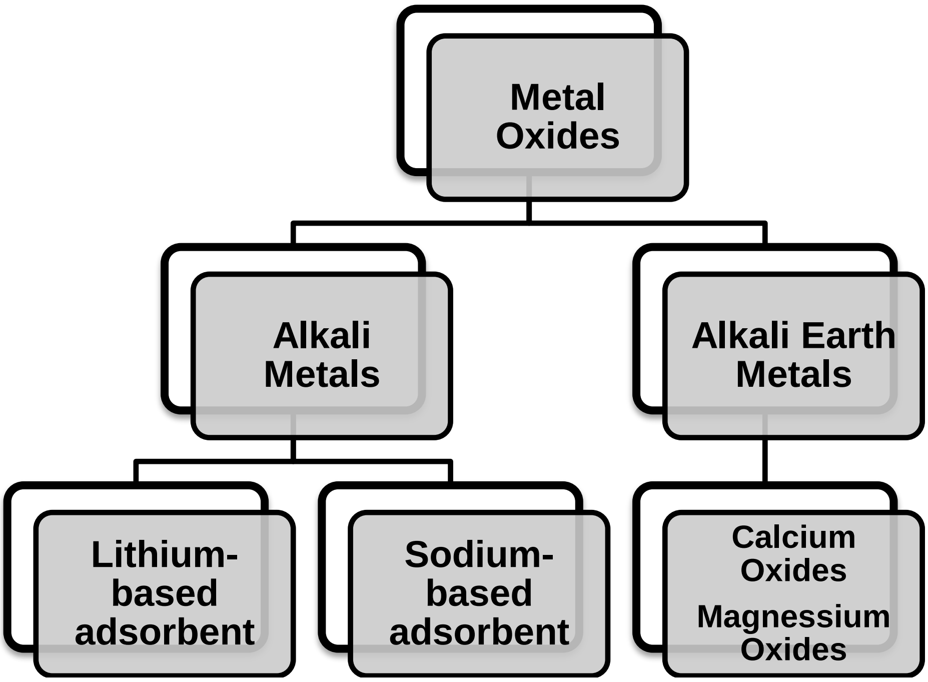

Fig. 2. Classification of metal oxide adsorbents as discussed in this review

2. METAL OXIDES

Metal oxides are regarded as promising chemisorbents for CO_2 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 CO_2 capture. In addition, with applicability within a wide range of temperatures from ambient conditions to temperatures of about 700^0C [18], research into the use of metal oxides for CO_2 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 Fig. 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 CO_2 gas which regenerates the oxides. Eventually, the generated pure CO_2 gas can either be sequestered underground or used for enhanced oil recovery [19].

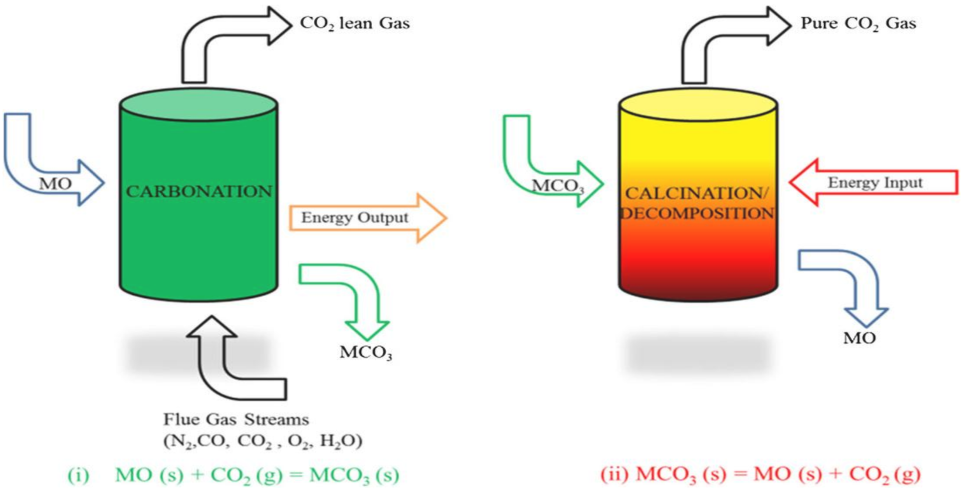

Fig. 3: Cyclic CO_2 capture process for metal oxides (MO) and metal carbonates (MCO_3) reproduced from [20]

However, the process efficiency of metal oxides for CO_2 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 CO_2 adsorption capacity of metal oxide adsorbents depends mainly on available active sites (basic sites) accessible to CO_2 molecules. The reaction rate is largely dependent on the rate of CO_2 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 CO_2 capture characteristics [22]. As a guiding rule, metal oxides that can qualify for CO_2 capture must be; bountiful, react with CO_2 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 CO_2 Capture:

2.1 Alkali Metal Based Oxides

Porous oxides such as alkali and alkaline-earth metals have been reported as promising candidates for CO_2 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 CO_2 absorption capacity at moderate working temperatures [23].

Recently attention has being drawn to lithium-based silicates(Li_4SiO_4, Li_8SiO_6, and Li_2SiO_3) , lithium-based zirconates (Li_2ZrO_3, $Li_6Zr_2O_7$, and Li_8ZrO_6), lithium based- aluminate (Li_5AlO_4), lithium cuprate (Li_2CuO_2), lithium ferrite ($LiFeO_2$), lithium titanate (Li_4TiO_4), and sodium ceramics (Na_2ZrO_3, Na_2SiO_3, and Na_2TiO_3) due to their favourable characteristics . Also, the precursors of these compounds lithium oxide (Li_2O), lithium hydroxide (LiOH), and sodium hydroxide (NaOH) have also being studied for CO_2 adsorption but however have shown difficulty in regeneration, high reactivity, instability, and huge volume expansions during absorption[24]. Among these materials, Li_4SiO_4 has shown great promise given its higher CO_2 sorption capacity and cyclic stability. Additionally, the regeneration temperature of Li_4SiO_4 material is much lower when compared with the calcium-based CO_2 sorbents, indicating that lower energy consumption is required for its regeneration [25]. The efficacy of these sorbent materials is closely determined by temperature, pressure, CO_2 concentration, CO_2 flow rate, particle size, crystalline structure, and structural phase transitions during ceramic synthesis. A double sorption mechanism has being proposed for the sorption of this compounds, first beginning with chemical sorption of CO_2 over the surface of this 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 CO_2 [26-27]. This diffusion process is one of the rate determining steps of this mechanism [28].

It has being 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 if the composition of the external shell as depicted in Fig. 4 is composed of Li_2CO_3 and metal oxides or another lithium phase. According to their work, the presence of metal oxides reduces CO_2 chemisorption while the presence of Li_2CO_3 and another lithium phase, can either enhance or decrease the CO_2 chemisorption process depending on whether the secondary lithium phases have better lithium diffusion properties than Li_2CO_3 or not; although it should be noted that this only applies to cases where Li_2CO_3 is a solid.

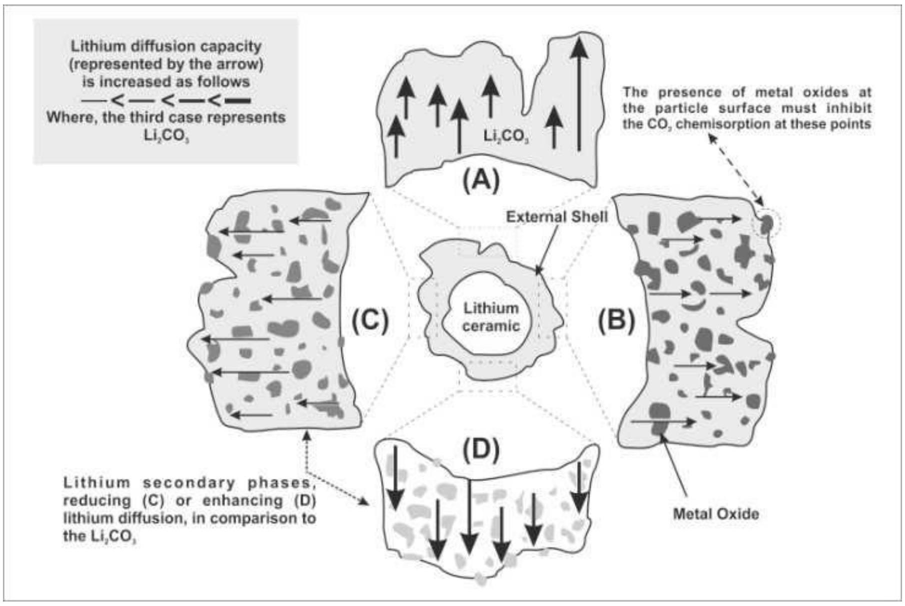

Fig. 4. Possible compositions of external shell reproduced from [23]

A faster reaction rate has being reported for Na_2ZrO_3 when compared to synthetic adsorbents such as Li_2ZrO_3 and Li_4SiO_4 this has being 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 being 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 being 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 this alkaline ceramics has also being studied although only Li_2ZrO_3 and Li_4SiO_4 have being 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 being proven to show good cyclic stability for a limited number of cycles (<100) with minimal loss of capacity, although not much studies has being 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 1.

Table 1. Absorption properties of alkaline ceramics

S/N	Ceramic Adsorbent	Calcination temperature (°C)	CO_2 Uptake			Gas Composition	Ref.
			Ads. Cap. (wt%)	Temp	P (bar)		
1	Li_4SiO_4	900	27.0	580	1	4% CO_2	38
2	Li_2ZrO_3	600	22.0	600	5	100% of CO_2	39
3	Nano Li_2ZrO_3	600	27.0	575	1	100% of CO_2	40
4	K-Li_2ZrO_3	-	22.0	550	1	100% of CO_2	41
5	Y-Li_2ZrO_3	700	29.9	500	1	100% of CO_2	42
6	Promoted Li_2ZrO_3	850	23.0	550	1	100% of CO_2	43
7	Li_4SiO_4 from rice husk	700	30.5	680	1	100% of CO_2	44
8	Li_4SiO_4 from diatomite	-	28.6	700	1	100% of CO_2	45
9	Li_2CuO_2	-	13.6	650	1	100% of CO_2	46
10	Li_2CuO_2	1000	40.2	875	1	100% of CO_2	47
11	Li_4TiO_4	-	27.0	900	1	CO_2/Ar	48
12	Li_4TiO_4	600-1000	42.0	856	1	100% of CO_2	49
13	Li_8SiO_6	800	42.0	550	1	100% of CO_2	50
14	Li_8SiO_6	800	52.1	650	1	100% of CO_2	51
15	Na_2ZrO_3	850	47.5	70	1	100% of CO_2	33
16	Na_2ZrO_3	850	23.8	550	1	100% of CO_2	52
17	Na_2SiO_3	700	37.4	50	1	100% of CO_2	53
18	Na_2TiO_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 CO_2 capture due to its ionic mobility and it's affinity for CO_2 [55]. These compounds are quite promising and have being thoroughly investigated for their CO_2 adsorption properties. Notably among them are $LiFeO_2$ [56], Li_2CuO_2 [57], Li_2ZrO_3 [58], Li_8SiO_6 [59], and Li_4SiO_4 [60-62].

A. Lithium Orthosilicates (Li_4SiO_4)

Attention has being drawn to Lithium orthosilicates due to their high theoretical CO_2 sorption capacity (36.7 wt %, approximately 8.34 mmol CO_2/ Li_4SiO_4 g) and good cyclic stability [17]. Research shows that Li_4SiO_4 are high temperature CO_2 absorbers and can absorb different concentrations of CO_2 within the temperature range of 450-700^{0}C but suffers from high decomposition temperature (>800^{0}C) 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 Li_2CO_3 and Li_2SiO_3 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 CO_2 to form Li_2CO_3. The diffusion of CO_2 in the solid Li_2CO_3 is recognised as the rate limiting step:

$$Li_4SiO_{4(s)} + CO_2 \leftrightarrow Li_2SiO_{3(s)} + Li_2CO_{3(s)}$$

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 CO_2 capture process is controlled kinetically by lithium diffusion. Li_4SiO_4 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,

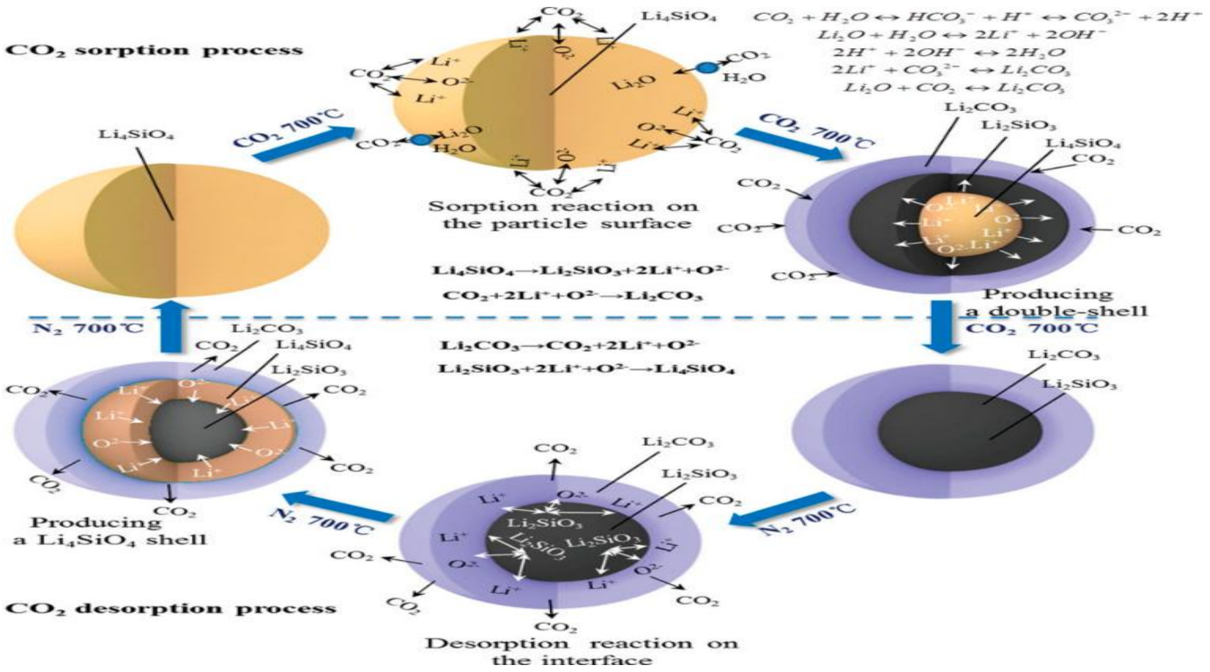

Fig. 5. Double-shell mechanism of Li_4SiO_4 material for CO_2 absorption and regeneration [63]

in-situ CO_2 removal with Li_4SiO_4 material as the CO_2 acceptor shifts the reaction equilibrium to hydrogen production, and exothermal absorption of CO_2 by the Li_4SiO_4 material provides heat for reforming, thus high hydrogen yield can be achieved [65]. Despite their excellent CO_2 sorption capabilities at high temperatures, Li_4SiO_4 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 CO_2 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 Li_4SiO_4 sorbents. The solid-state reaction method is easy and the most commonly used technique to synthesize Li_4SiO_4 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 Li_4SiO_4 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 Li_4SiO_4 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 Li_4SiO_4 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 CO_2 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 600^0C 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 650^0C. 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 absorbent 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 (400-700^0C) 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°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 CO_2 chemical transformation to carbonate ions. Presence of Potassium as a dopant increases the CO_2 diffusion rate (which is usually the rate limiting step) towards the inner unreacted particles by forming a eutectic mixture with Li_2ZrO_3 at 500^0C. Presence of Yttrium as a Dopant on the other hand shifts the rate limiting step for CO_2 sorption to the diffusion of ions in the ZrO_2 formed during the adsorption process and did not increase the CO_2 sorption kinetics of Li_2ZrO_2 [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].

2.1.2 Sodium based sorbents

The CO_2 capture properties of certain sodium based compounds were first reported by Lopez-Ortiz et al. who stated that Na_2ZrO_3, Na_2SbO_3, and Na_2TiO_3 could absorb CO_2 in the temperature range of 600-700^0C. Observed that the reactivity followed the order Na_2ZrO_3 > Na_2SbO_3 > Na_2TiO_3, Na_2ZrO_3 exhibited better absorption rate and inferior regeneration

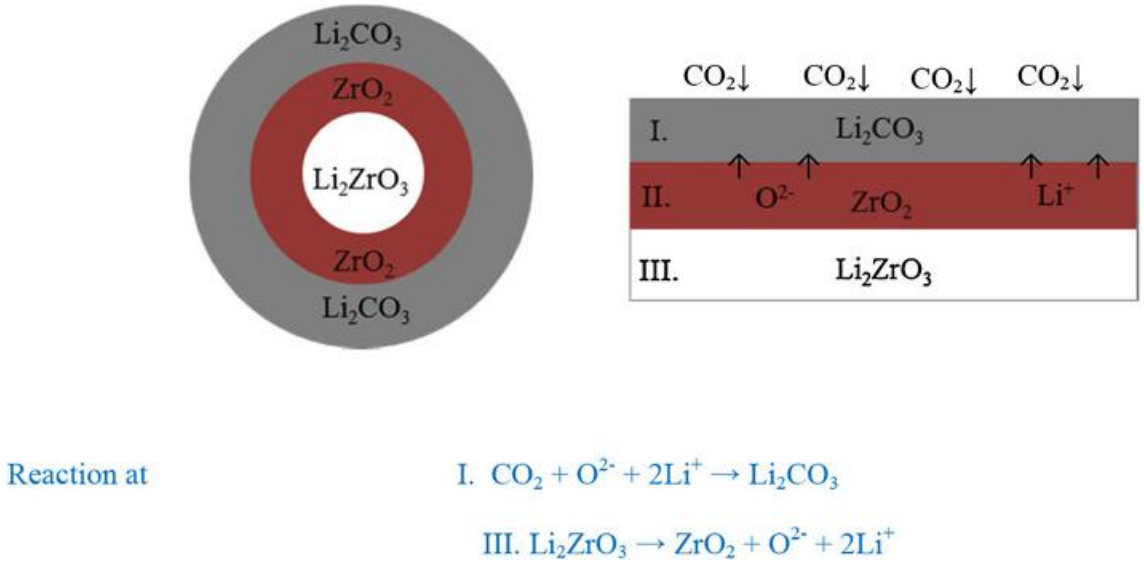

Fig. 6. Proposed mechanisms for CO_2 sorption on Li_2ZrO_3 reproduced from [20]

performance compared to Li_4SiO_4 and Li_2ZrO_3. The following sections that follow give an insight on this ceramics.

A. Sodium Meta Zirconate (Na_2ZrO_3)

With a CO_2 adsorption capacity of 23.75wt% and a lower cost compared to lithium based oxides Na_2ZrO_3 has gained attention as a good CO_2 adsorbent. They can operate at higher temperature plus a higher reaction rate has also being 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 600^0C [92].

$$Na_2ZrO_{3(s)} + CO_{2\,(g)} \leftrightarrow Na_2CO_{3(s)} + ZrO_{2(s)}$$

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 150-700^0C, a fast kinetics was observed between 550 and 700^0C, 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 0.4-0.8atm 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 30-70^0C it was reported that Na_2ZrO_3 was able to absorb 5.8mmol/g of CO_2 in the presence of water, therefore enabling it's 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 1-2wt% at temperatures ranging from room temperature to 130^0C, 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 being 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 being 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 (>600^0C).

$$Cao_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(g)}$$

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 being 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 Li < Na < K < Rb < 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 CO_2 At 400^0C with about 28.72% sorption efficiency using 15% CO_2 and the rest Nitrogen. However the CO_2 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].

2.2.2 Magnesium Oxide (MgO)

MgO has being considered for CO_2 capture given its high abundance, cost effectiveness, low toxicity, and thermodynamic stability of the products of the reaction.

$MgO + CO_2 \leftrightarrow MgCO_3$ (magnesium carbonate)

It finds application in both pre and post combustion due to its low regeneration temperatures and has being reported to have good selectivity for CO_2 over N_2 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 CO_2 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. [114-118] on carbon templated mesoporous MgO, who showed that the mesoporosity enhanced CO_2 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 CO_2 adsorption capacity using K_2CO_3 modified MgO, as both MgO and K_2CO_3 can adsorb CO_2 in the presence of water vapour at low temperatures. The modified materials absorbs CO_2 effectively over a temperature range of 50-100^{0}C and can be regenerated around 150-400^{0}C.

From H_2O:- According to the reaction

$MgO + H_2O \leftrightarrow MgO . H_2O$
$MgO . H_2O + CO_2 \leftrightarrow MgCO_3 + H_2O$
$MgO + CO_2 \leftrightarrow MgCO_3$

Although water catalyzes the reaction but the formation of $MgCO_3$ layer resists the mobility of CO_2 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 2. Sorption properties of CaO based sorbents

S/N	Ceramic Adsorbent	Calcination temperature (^oC)	CO_2 Uptake			Gas Composition	Ref.
			Ads. Cap. (wt%)	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

Table 3. Sorption properties of various MgO based sorbents

S/N	Ceramic Adsorbent	Calcination temperature (°C)	CO_2 Uptake			Gas Composition	Ref.
			Ads. Cap. (wt% CO_2)	Temp (Ads)	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_2CO_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 CO_2 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 CO_2 and subsequently capturing the CO_2 produced in the process, Also there application as Dual functional materials in reactive capture of CO_2 in which these metal oxides are combined with a hydrogenation catalyst for CO_2 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.

DISCLAIMER

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.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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