The Role of Alkaline/alkaline Earth Metal Oxides in CO₂ Capture: A Concise Review

Emmanuel Victor a*, Umenweke Great C b,c and Ngozichukwu B d

a Chemical Engineering Department, Federal University of Technology, Owerri, Nigeria.
b University of Kentucky Center for Applied Energy Research, Lexington, KY 40511, USA.
c Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA.
d Chemical Engineering Department, Texas A&M University, College Station, USA.

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.

Article Information
DOI: 10.9734/JENRR/2021/v9i330235
Editor(s):
(1) Dr. Sreekanth. K. J., Kuwait Institute for Scientific Research, Kuwait.
Reviewers:
(1) Y. D. Dwivedi, Institute of Aeronautical Engineering, India.
(2) Meryeme Azaroual, Mohammed V University, Morocco.
Complete Peer review History, details of the editor(s), Reviewers and additional Reviewers are available here:
https://www.sdiarticle5.com/review-history/80871

Received 09 October 2021
Accepted 18 December 2021
Published 19 December 2021

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 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 CO₂ 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.
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, SOₓ, NOₓ, 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 Fig. 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.

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 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]
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 700°C [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 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 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. 2. Classification of metal oxide adsorbents as discussed in this review

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(Li₃SiO₄, Li₂SiO₃, and Li₂SiO₃), lithium-based zirconates (Li₂ZrO₃, Li₂ZrO₃, and Li₂ZrO₃), lithium-based aluminate (Li₃AlO₃), lithium cuprate (Li₃CuO₂), lithium ferrite (LiFeO₂), lithium titanate (Li₄TiO₃), 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, Li₂SiO₃ has shown great promise due to its higher CO₂ sorption capacity and cyclic stability. Additionally, the regeneration temperature of Li₂SiO₃ 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 this compounds, first beginning with chemical sorption of CO₂ 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 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 if 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.
A faster reaction rate has been reported for Na$_2$ZrO$_3$ when compared to synthetic adsorbents such as Li$_2$ZrO$_3$ and Li$_4$SiO$_4$ this has being attributed to the lamellar structure of Na$_2$ZrO$_3$ which enhances sodium mobility, unlike the more packed structure seen in Li$_2$ZrO$_3$ [30]. Alkaline ceramics have also being reported to show good selectivity in separation of CO$_2$ from flue gas with Li$_2$ZrO$_3$ 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$_2$ZrO$_3$ at low temperature range.

Similarly Ochoa et al [34] investigated the effect of steam addition on stability, capacity, and regeneration properties of Li$_2$ZrO$_3$, K-doped Li$_2$ZrO$_3$, Na$_2$ZrO$_3$, and Li$_4$SiO$_4$ 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$_2$ZrO$_3$ and Li$_4$SiO$_4$ 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$_2$ZrO$_3$ is the easiest to regenerate followed by Li$_4$SiO$_4$ [35] and Na$_2$ZrO$_3$ having a much lower regeneration rate than Li$_4$SiO$_4$ [36].

Li$_2$ZrO$_3$ and Li$_4$SiO$_4$ 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.
The chemisorption sorption process is limited by ultimately increasing capital and operational cost. It may require more heat and costly equipment. High temperature range of different concentrations of CO\textsubscript{2} present in the feed gas can affect the reaction rate. For instance, CO\textsubscript{2} absorbents with high theoretical CO\textsubscript{2} sorption capacity can absorb different concentrations of CO\textsubscript{2} within the temperature range of 450-700°C but suffers from high decomposition temperature (>800°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\textsubscript{2}CO\textsubscript{3} and Li\textsubscript{2}SiO\textsubscript{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\textsubscript{2} to form Li\textsubscript{2}CO\textsubscript{3}. The diffusion of CO\textsubscript{2} in the solid Li\textsubscript{2}CO\textsubscript{3} is recognised as the rate limiting step:

\[ \text{Li}_2\text{SiO}_4(s) + \text{CO}_2 \leftrightarrow \text{Li}_2\text{SiO}_3(s) + \text{Li}_2\text{CO}_3(s) \]

In a research done by Rodriguez et al [64], where they evaluated the CO\textsubscript{2} chemisorption capacity as a function of CO\textsubscript{2} flow rate, they revealed that the CO\textsubscript{2} capture rate is controlled by CO\textsubscript{2} diffusion through the Gas-film system, whereas at high CO\textsubscript{2} flows it is controlled by the CO\textsubscript{2} chemisorption reaction rate. After formation of the carbonate oxide external shell, the whole CO\textsubscript{2} capture process is controlled kinetically by lithium diffusion. Li\textsubscript{2}SiO\textsubscript{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,

### Table 1. Absorption properties of alkaline ceramics

| S/N | Ceramic Adsorbent | Calcination temperature (°C) | CO\textsubscript{2} Uptake Ads. Cap. (wt\%) | Gas Composition | Ref. |
|-----|-------------------|------------------------------|-------------------------------------------|----------------|-----|
| 1   | Li\textsubscript{2}SiO\textsubscript{4} | 900                          | 27.0                                      | 4% CO\textsubscript{2} | 38  |
| 2   | Li\textsubscript{2}ZrO\textsubscript{3} | 600                          | 22.0                                      | 100% of CO\textsubscript{2} | 39  |
| 3   | Nano              | 600                          | 27.0                                      | 100% of CO\textsubscript{2} | 40  |
| 4   | K-Li\textsubscript{2}ZrO\textsubscript{3} | -                            | 22.0                                      | 100% of CO\textsubscript{2} | 41  |
| 5   | Y-Li\textsubscript{2}ZrO\textsubscript{3} | 700                          | 29.9                                      | 100% of CO\textsubscript{2} | 42  |
| 6   | Promoted          | 850                          | 23.0                                      | 100% of CO\textsubscript{2} | 43  |
| 7   | Li\textsubscript{2}SiO\textsubscript{4} from rice husk | 700                          | 30.5                                      | 100% of CO\textsubscript{2} | 44  |
| 8   | Li\textsubscript{2}SiO\textsubscript{4} from diatomite | -                            | 28.6                                      | 100% of CO\textsubscript{2} | 45  |
| 9   | Li\textsubscript{2}CuO\textsubscript{2} | -                            | 13.6                                      | 100% of CO\textsubscript{2} | 46  |
| 10  | Li\textsubscript{2}CuO\textsubscript{2} | 1000                         | 40.2                                      | 100% of CO\textsubscript{2} | 47  |
| 11  | Li\textsubscript{2}TiO\textsubscript{2} | -                            | 27.0                                      | CO\textsubscript{2}/Ar | 48  |
| 12  | Li\textsubscript{2}TiO\textsubscript{4} 600-1000 | 42.0                          | 900                                      | 100% of CO\textsubscript{2} | 49  |
| 13  | Li\textsubscript{2}SiO\textsubscript{4} | 800                          | 42.0                                      | 100% of CO\textsubscript{2} | 50  |
| 14  | Li\textsubscript{2}SiO\textsubscript{3} | 800                          | 52.1                                      | 100% of CO\textsubscript{2} | 51  |
| 15  | Na\textsubscript{2}ZrO\textsubscript{3} | 850                          | 47.5                                      | 100% of CO\textsubscript{2} | 52  |
| 16  | Na\textsubscript{2}ZrO\textsubscript{3} | 850                          | 23.8                                      | 100% of CO\textsubscript{2} | 53  |
| 17  | Na\textsubscript{2}SiO\textsubscript{3} | 700                          | 37.4                                      | 100% of CO\textsubscript{2} | 54  |
| 18  | Na\textsubscript{2}TiO\textsubscript{3} | 850                          | 12.0                                      | 100% of CO\textsubscript{2} | 55  |

#### 2.1.1 Lithium based adsorbents

Lithium based sorbents has been considered for use in CO\textsubscript{2} capture due to its ionic mobility and it's affinity for CO\textsubscript{2} [55]. These compounds are quite promising and have being thoroughly investigated for their CO\textsubscript{2} adsorption properties. Notably among them are LiFeO\textsubscript{3} [56], Li\textsubscript{2}CuO\textsubscript{2} [57], Li\textsubscript{2}ZrO\textsubscript{3} [58], Li\textsubscript{2}SiO\textsubscript{3} [59], and Li\textsubscript{2}SiO\textsubscript{4} [60-62].

#### A. Lithium Orthosilicates (Li\textsubscript{2}SiO\textsubscript{4})

Attention has been drawing to Lithium orthosilicates due to their high theoretical CO\textsubscript{2} sorption capacity (36.7 wt %, approximately 8.34 mmol CO\textsubscript{2}/Li\textsubscript{2}SiO\textsubscript{4} g) and good cyclic stability [17]. Research shows that Li\textsubscript{2}SiO\textsubscript{4} are high temperature CO\textsubscript{2} absorbents and can absorb different concentrations of CO\textsubscript{2} within the temperature range of 450-700°C but suffers from high decomposition temperature (>800°C) which may require more heat and costly equipment ultimately increasing capital and operational cost.
in-situ CO$_2$ removal with Li$_4$SiO$_4$ material as the CO$_2$ acceptor shifts the reaction equilibrium to hydrogen production, and exothermal absorption of CO$_2$ by the Li$_4$SiO$_4$ material provides heat for reforming, thus high hydrogen yield can be achieved [65]. Despite their excellent CO$_2$ sorption capabilities at high temperatures, Li$_4$SiO$_4$ 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$_4$SiO$_4$ sorbents. The solid-state reaction method is easy and the most commonly used technique to synthesize Li$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ 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$_4$SiO$_4$ 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-
Research also shows that the addition of dopants such as Al, Fe, Na, K and Cs increases the CO\textsubscript{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\textsubscript{2}CO\textsubscript{3}, he observed that the CO\textsubscript{2} capture efficiency improved with the addition of K\textsubscript{2}CO\textsubscript{3} because of the formation of a eutectic phase between K\textsubscript{2}CO\textsubscript{3} and Li\textsubscript{2}CO\textsubscript{3}, which facilitated CO\textsubscript{2} diffusion into the material bulk. The best capture capacity value (104mg CO\textsubscript{2}/g material) was obtained using the material produced from steel metallurgical slag with 20wt% K\textsubscript{2}CO\textsubscript{3}. Also Olivares-Marin et al. [83] reported that K-doped Li\textsubscript{2}SiO\textsubscript{4} obtained using fly ash as source of SiO\textsubscript{2} exhibited a capacity of 101 mg g\textsuperscript{-1} under optimum conditions (at 600°C with 40 mol % K\textsubscript{2}CO\textsubscript{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\textsubscript{2} capture capacity (35.3wt% CO\textsubscript{2} capture using 60% CO\textsubscript{2} Feed gas close to the theoretical value) with ultra-fast kinetics and enhanced stability at 650°C. Their work showed that the nanosheet morphology of the lithium silicon nanosheets allow for efficient CO\textsubscript{2} diffusion to ensure reaction with the entire sheet as well as providing extremely fast CO\textsubscript{2} capture kinetics (0.22 g g\textsuperscript{-1} min\textsuperscript{-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\textsubscript{2}SiO\textsubscript{4}-based absorbent using rice husk ash as silicon source, he reported that the adsorbent showed better CO\textsubscript{2} sorption capacity (32.4 wt%) and cyclic stability compared with pure Li\textsubscript{2}SiO\textsubscript{4} (22.1 wt%), due to high pore volume and high surface area.

**B. Lithium metazirconates (Li\textsubscript{2}ZrO\textsubscript{3})**

The pioneering work of Nakagawa and Ohasi in 1998 [85], where they investigated the capture of CO\textsubscript{2} using Li\textsubscript{2}ZrO\textsubscript{3} at high temperatures of (400-700°C) and reportedly captured about 4.5mol/kg (28wt%) was what sprung up massive interest in lithium zirconates as possible CO\textsubscript{2} capture adsorbents plus unlike other sorbents that had a limited CO\textsubscript{2}/N\textsubscript{2} selectivity, lithium zirconate does not absorb nitrogen at all and would result to infinitely large CO\textsubscript{2}/N\textsubscript{2} selectivity. Lithium zirconates also showed good stability over carbonation/calcination cycles. Furthermore, lithium zirconates have been used in the CO\textsubscript{2} oxidation, showing complete conversion to CO\textsubscript{2} between 450 and 600°C and subsequent capture of CO\textsubscript{2} that was produced [86]. Similarly to lithium silicates Li\textsubscript{2}ZrO\textsubscript{3} also suffers from a slow reaction rate due to the formation of Li\textsubscript{2}CO\textsubscript{3} shell which prevents the mobility or access of Li ions to CO\textsubscript{2}, hence Ultimately reducing the reaction rate almost making them impossible for industrial use [87], the mechanism for CO\textsubscript{2} adsorption on Li\textsubscript{2}ZrO\textsubscript{3} is as depicted in Fig.6.

Recent studies have shown that adding dopants such as Iron, Potassium, Sodium and Yttrium to Li\textsubscript{2}ZrO\textsubscript{3} increases the CO\textsubscript{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\textsubscript{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\textsubscript{2} chemical transformation to carbonate ions. Presence of Potassium as a dopant increases the CO\textsubscript{2} diffusion rate (which is usually the rate limiting step) towards the inner unreacted particles by forming a eutectic mixture with Li\textsubscript{2}ZrO\textsubscript{3} at 500°C. Presence of Yttrium as a Dopant on the other hand shifts the rate limiting step for CO\textsubscript{2} sorption to the diffusion of ions in the ZrO\textsubscript{2} formed during the adsorption process and did not increase the CO\textsubscript{2} sorption kinetics of Li\textsubscript{2}ZrO\textsubscript{3} [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\textsubscript{2} capture properties of certain sodium based compounds were first reported by Lopez-Ortiz et al. who stated that Na\textsubscript{2}ZrO\textsubscript{3}, Na\textsubscript{2}SbO\textsubscript{3}, and Na\textsubscript{2}TiO\textsubscript{3} could absorb CO\textsubscript{2} in the temperature range of 600-700°C. Observed that the reactivity followed the order Na\textsubscript{2}ZrO\textsubscript{3} > Na\textsubscript{2}SbO\textsubscript{3} > Na\textsubscript{2}TiO\textsubscript{3}, Na\textsubscript{2}ZrO\textsubscript{3} exhibited better absorption rate and inferior regeneration
The following sections that follow give an insight on this ceramics.

**A. Sodium Meta Zirconate (Na$_2$ZrO$_3$)**

With a CO$_2$ adsorption capacity of 23.75 wt% and a lower cost compared to lithium based oxides Na$_2$ZrO$_3$ 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$_2$ZrO$_3$ is able to absorb CO$_2$ even at room temperature the best temperature for CO$_2$ Absorption on Na$_2$ZrO$_3$ is said to be 600$^\circ$C [92].

Na$_2$ZrO$_3$ (s) + CO$_2$ (g) $\leftrightarrow$ Na$_2$CO$_3$ (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$_2$ZrO$_3$ particles in the temperature range of 150-700$^\circ$C, a fast kinetics was observed between 550 and 700$^\circ$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$_2$ZrO$_3$ at a similar temperature and partial pressure of 0.4-0.8 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 30-70$^\circ$C it was reported that Na$_2$ZrO$_3$ was able to absorb 5.8 mmol/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$_2$ZrO$_3$ with well-controlled crystal phase using a soft-chemical route. It was reported that monoclinic Na$_2$ZrO$_3$ showed much faster CO$_2$ capture rate than hexagonal Na$_2$ZrO$_3$ even at low CO$_2$ partial pressures (0.025 bar). Thus, a higher CO$_2$ capture rate is obtained for Nanosized Na$_2$ZrO$_3$ 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$_2$SiO$_3$)**

Na$_2$SiO$_3$ has been reported to show a low CO$_2$ adsorption rate 1-2 wt% at temperatures ranging from room temperature to 130$^\circ$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$_2$ adsorption rate has also been observed to increase with decreasing particle size of Na$_2$SiO$_3$ 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$_2$SiO$_3$ 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$_2$SiO$_3$ 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$_2$SiO$_3$ using solid-state reaction and combustion method. They reported that Na$_2$SiO$_3$ 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$_2$SiO$_3$ 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$_2$SiO$_3$. Thus, the recent results support the potential of Na$_2$SiO$_3$ 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$^\circ$C).

\[ \text{CaO(s)} + \text{CO}_2(g) \leftrightarrow \text{CaCO}_3(g) \]

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 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 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 postulated 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$^\circ$C with about 28.72% sorption efficiency using 15% CO$_2$ 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].

### 2.2.2 Magnesium Oxide (MgO)

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

\[
\text{MgO} + \text{CO}_2 \leftrightarrow \text{MgCO}_3 \quad \text{(magnesium carbonate)}
\]

It finds application in both pre and post combustion due to its low regeneration temperatures and has been 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 catalyzed 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. [114-118] 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 been 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 50-100°C and can be regenerated around 150-400°C.

From H₂O: According to the reaction

\[
\text{MgO + H}_2\text{O} \leftrightarrow \text{MgO} \cdot \text{H}_2\text{O} \\
\text{MgO \cdot H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{MgCO}_3 + \text{H}_2\text{O} \\
\text{MgO} + \text{CO}_2 \leftrightarrow \text{MgCO}_3
\]

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.

| S/N | Ceramic Adsorbent | Calcination temperature (°C) | CO₂ Uptake Ads. Cap. (wt%) | CO₂ Temp (Ads) | P (bar) | Gas Composition | Ref. |
|-----|------------------|------------------------------|-----------------------------|----------------|--------|----------------|------|
| 1   | CaO- based mesoporous silica | 950 | 80 | 580 | - | 100% of CO₂ | 106 |
| 2   | Mesoporous Nano crystalline CaO | 700 | 22 | 600 | 1 | 100% of CO₂ | 107 |
| 3   | CaO-MgO | 800 | 53 | 575 | - | 100% of CO₂ | 108 |
| 4   | CaO / Ca₁₂Al₁₄O₃₃ | 850 | 41 | 550 | 1 | 20% of CO₂ | 109 |
| 5   | NiO-CaO- Ca₁₂Al₁₄O₃₃ | 700 | 56 | 500 | 1 | 15% of CO₂ | 110 |
3. OUTLOOK AND CONCLUSION

The potential of metal oxides in ameliorating CO₂ emissions within the purview of sustainable chemical and energy production has been 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 a lot 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.

ACKNOWLEDGEMENT

The authors wish to acknowledge the pioneering efforts of the authors who have worked on metal oxides over the years as this is a motivation to the preparation of this paper.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Maroto-Valero MM, Song CS, Soong Y. Environmental challenges and greenhouse gas control for fossil fuel utilization in the 21st century. New York, NY: Kluwer Academic/Plenum Publishers; 2002.
2. Brovkin V, Sitch S, Von Bloh W, Claussen M, Bauer E, Cramer W. Role of land cover changes for atmospheric CO₂ increase and climate change during the last 150 years. Global Change Biol. 2004;10:1253–1266. DOI:10.1111/j.1365-2486.2004.00812.x
3. Song CS. Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing. Catal. Today. 2006;115:2–32. DOI:10.1016/j.cattod.2006.02.029
4. Smith MR, Myers SS. Impact of anthropogenic CO₂ emissions on global human nutrition. Nat. Clim. Change. 2018;8:834–839. DOI: 10.1038/s41558-018-0253-3
5. Hannah Ritchie, Max Roser. CO₂ and Greenhouse Gas Emissions, Our World Data. https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions (accessed October 8, 2020); 2020.

Table 3. Sorption properties of various MgO based sorbents

| S/N | Ceramic Adsorbent | Calcination temperature (°C) | CO₂ Uptake Ads. Cap. (wt% CO₂) | Gas Composition | Ref. |
|-----|--------------------|-----------------------------|--------------------------------|----------------|-----|
| 1   | Mg/K-SBA-15        | 300                         | 3.6                            | -              | 115 |
| 2   | Mg/K-SBA-16        | 300                         | 2.0                            | 20             | 115 |
| 3   | Mg/K-MCM-48        | 300                         | 2.5                            | 20             | 115 |
| 4   | Na₂CO₃-MgO         | 400                         | 15.0                           | 380            | 116 |
| 5   | Mesoporous MgO     | 800                         | 10.0                           | 100% of CO₂    | 117 |
| 6   | MgO/TiO₂           | 150                         | 2.1                            | 25             | 118 |
6. Markewitz P, Kuckshinrichs W, Leitner W, Linssen J, Zapp P, Bongartz R, et al. Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂. Energy Environ. Sci. 2012;5:7281–7305. DOI:10.1039/C2EE04303D

7. Little RJ, Versteeg GF, Van Swaaij WPM. Physical absorption into non-aqueous solutions in a stirred cell reactor. Chem. Eng. Sci. 1991;46:3308–3313.

8. Chiesa P, Consonni SP. Shift reactors and physical absorption for low-CO₂ emission IGCCs. J. Eng. Gas Turbines Power. 1999;121:295–305.

9. Bishnoi S, Rochelle GT. Absorption of carbon dioxide into aqueous piperazine: Reaction kinetics, mass transfer and solubility. Chem. Eng. Sci. 2000;55:5531–5543.

10. Rochelle GT. Amine scrubbing for CO₂ capture. Science. 2009;325:1652–1654.

11. Harlick PJE, Tezel FH. An experimental adsorbent screening study for CO₂ capture from N₂. Microporous Mesoporous Mater. 2004;76:71–77.

12. Powell CE, Qiao GG. Polymeric CO₂/N₂ gas separation membranes for the capture carbon dioxide from power plant flue gases. J. Membr. Sci. 2006;279:1–49.

13. Rochelle GT. Amine scrubbing for CO₂ capture. Science. 2009;325:1652–1654. DOI: 10.1126/science.1176731.

14. Rochelle GT. “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. 2016;3:35–67.

15. Tontiwachwuthikul P, Idem R. “Recent progress and new developments in post-combustion carbon-capture technology with reactive solvents,” in Recent progress and new developments in post-combustion capture technology with reactive solvents, Editors P, Tontiwachwuthikul and R. Idem, Future Science Book Series. 2013;2–8.

16. Pardakhti M, Jafari T, Tobin Z, Dutta B, Moharreri E, Shemshaki NS, Suib S, Srivastava R. Trends in solid adsorbent materials development for CO₂ Capture, ACS Appl. Mater. Interfaces. 2019;1134533–34559. DOI:10.1021/acsami.9b08487.

17. Yong Z, Mata V, Rodrigues AE. Adsorption of carbon dioxide at high temperature - A review. Sep. Purif. Technol. 2002;26:195–205. DOI:10.1016/S1383-5866(01)00165-4.

18. Wang S, Yan S, Ma X, Gong J. Recent advances in capture of carbon dioxide using alkali-metal-based oxides, Energy Environ. Sci. 2011;4:3805–3819. DOI: 10.1039/c1ee01116b.

19. Sally M. Benson, David R. Cole. CO₂ Sequestration in deep sedimentary formations. Elements. 2008;4(5):325–331. DOI: https://doi.org/10.2113/gselements.4.5.325.

20. Kumar S, Saxena SK. A comparative study of CO₂ sorption properties for different oxides. Mater Renew Sustain Energy. 2014;330. Available:https://doi.org/10.1007/s40243-014-0030-9.

21. Inamuddin, Abdullah M. Asiri, Erc Lichtfouse, Sustainable agriculture reviews 38: Carbon Sequestration Vol.2 Materials and chemical methods. 2019;77. Available:https://doi.org/10.1007/978-3-030-29337-6.

22. Hayder A. Alawand, Alaa H. Alminshid. CO₂ capturing methods: Chemical looping combustion (CLC) as a promising technique. 2021;1:5. Available:https://doi.org/10.1016/j.scitotenv.2021.147850.

23. Lakshminarayana Kudinali Gopalakrishna Bhatta, L. Kudinali Gopalakrishna Bhatta, Seetharamu Subramanyam, Subramanyam S, Madhusoodana D. Chengala, Chengala MD, Sharon Olivera, S. Olivera, & Krishna Venkatesh, K. Venkatesh. Progress in hydrotalcite like compounds and metal-based oxides for CO₂ capture: A review. Journal of Cleaner Production. 2015;103:171-196. DOI: 10.1016/j.jclepro.2014.12.059.

24. Mosqueda HA, Vazquez C, Bosch P, Pfeiffer H. Chemical sorption of Carbon Dioxide (CO₂) on Lithium Oxide (Li₂O) Chem. Mater. 2006;18. Available:https://doi.org/10.1021/cm060122b.

25. Xianyao Yan 1, Yingjie Li, Xiaotong Ma 1, Jianli Zhao 1, Zeyan Wang. Performance of Li₃SiO₄ Material for CO₂ Capture: A Review. 2019;1-2. DOI:10.3390/ijms20040928.

26. Dunstan MT, Donat F, Bork AH, Grey CP, Müller CR. CO₂ Capture at medium to high
temperature using solid oxide-based sorbents: Fundamental aspects, mechanistic insights, and recent advances. Chemical Reviews. 2021;121(20):12681-12745.

27. Ida JI, Xiong R, Lin YS. Synthesis and CO₂ sorption properties of pure and modified lithium zirconate. Sep. Purif. Technol. 2004;36. Available:https://doi.org/10.1016/S1383-5866(03)00151-5

28. Essaki K, Nakagawa K, Kato M, Uemoto H. CO₂ Absorption by lithium silicate at room temperature. J. Chem. Eng. Jpn. 2004;37. DOI: 10.1252/jcej.37.7772.

29. Romero-Ibarra I, Ortiz–Landeros J, Pfeiffer H. Microstructural and CO₂ chemisorption analyses of Li₅SiO₄: Effect of surface modification by the ball milling process. Thermochimica Acta. 2013;567:118:124. Available:https://doi.org/10.1016/j.tca.2012.11.018

30. Boon J, Cobden PD, van Dijk HAJ, van Sint MA. High-temperature pressure swing adsorption cycle design for sorption-enhanced water-gas shift. Chem. Eng. Sci. 2014;122:219-231. DOI: http://dx.doi.org/10.1016/j.ces.2014.09.034

31. Xiong R, Ida J, Lin YS. Kinetics of carbon dioxide sorption on Potassium doped lithium zirconate. Chem. Eng. Sci. 2003;58:4377-4385. DOI: 10.1016/S0009-2509(03)00319-1.

32. Pfeiffer Heriberto. 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: 2010. DOI: 10.1021/bk-2010-1056.ch015

33. Santillan-Reyes GG, Pfeiffer H. Analysis of the CO₂ capture in sodium zirconate (Na₂ZrO₃). Effect of the water vapor addition. Int. J. Greenhouse. Gas Control. 2011;5:1624-1629. DOI: 10.1016/j.ijggc.2011.09.009

34. Ochoa-Fernandez E, Zhao T, Rønning M, Chen D. 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. 2009;135:397-403.

35. Xiao Q, Liu Y, Zhong Y, Zhu W. A citrate sol-gel method to synthesize Li₂ZrO₃ nanocrystals with improved CO₂ capture properties. J. Mater. Chem. 2011;21:3838-3842. DOI: https://doi.org/10.1039/C0JM03243C.

36. López-Ortiz A, Rivera NGP, Rojas AR, Gutierrez DL. Novel carbon dioxide solid acceptors using sodium containing oxides. Separ Sci Technol. 2010;39:3559-3572. DOI: 10.1081/SS-200036766.

37. Yang W, Kim Y, Liu PKT, Sahimi M, Tsotsis TT. A study by in situ techniques of the thermal evolution of structure of a Mg-Al-CO₃ layered double hydroxide. Chem. Eng. Sci. 2002;57:2945-2953. DOI: 10.1021/ie900371r.

38. Seggiani M, Puccini M, Vitolo S. 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. 2011;5:741-748. DOI: 10.1016/j.ijggc.2011.03.003.

39. Ochoa-Fernandez E, Rusten HK, Jakobsen HA, Rønning M, Holmen A, Chen D. Sorption enhanced hydrogen production by steam methane reforming using Li₂ZrO₃ as sorbent: Sorption kinetics and reactor simulation. Catalyst Today. 2005;106:41-46. DOI: 10.1016/j.cattod.2005.07.146.

40. Ochoa-Fernandez E, Rønning M, Grande T, Chen D. Nanocrystalline lithium zirconate with improved kinetics for high-temperature CO₂ capture. Chem. Mater. 2006;18:1383-1385. DOI: 10.1021/cm052075d.

41. Xiao Q, Tang X, Zhong Y, Zhu W. A facile starch-assisted sol-gel method to synthesize k-doped Li₂ZrO₃ sorbents with excellent CO₂ capture properties. J. Am. Ceram. Soc. 2012;95:1544-1548. DOI: 10.1111/j.1551-2916.2012.05090.x.

42. Iwan A, Stephenson H, Ketchie WC, Lapkin AA. High temperature sequestration of CO₂ using lithium zirconates. Chem. Eng. J. 2009;146:249-258. DOI: 10.1016/jcej.2008.06.006.

43. Ochoa-Fernandez E, Rønning M, Grande T, Chen D. Synthesis and CO₂ capture properties of nanocrystalline lithium zirconate. Chem. Mater. 2006;18:6037-6046. DOI: 10.1021/cm061515d
44. Wang K, Zhao P, Guo X, Li Y, Han D, Chao Y. Enhancement of reactivity in Li$_3$SiO$_4$ based sorbents from the nano-sized rice husk ash for high-temperature CO$_2$ capture. Energ. Convers. Manage. 2014;81:447-454. DOI:http://dx.doi.org/10.1016/j.enconman.2014.02.054

45. Yun SS, Qing Ming J, LiHong J, Qinchao L, YaMing W, JinHui P. Preparation and kinetic analysis of Li$_3$SiO$_4$ sorbents with different silicon sources for high temperature CO$_2$ capture. Chinese Science Bulletin. 2012;57, 2475–2479.(DOI: 10.1007/s11434-012-5188-x)

46. Palacios-Romero, L. M., Pfeiffer H. Lithium Cuprate (Li$_2$CuO$_2$): A New Possible Ceramic Material for CO$_2$ Chemisorption. Chem. Lett. 2008;37:862-863. DOI: 10.1246/cl.2008.862.

47. Matsukura Y, Okumura T, Kobayashi R, Oh-ishi K. Synthesis and CO$_2$ absorption properties of single-phase Li$_2$CuO$_2$ as a CO$_2$ Absorbent. Chem. Lett. 2010;39:966-967.

48. Ueda S, Inoue R, Sasaki K, Wakuha K, Ariyama T. CO$_2$ absorption and desorption abilities of Li$_2$O-TiO$_2$ Compounds. ISIJ International. 2011;51:530-537.

49. Togashi N, Okumura T, Oh-Ishi K. Synthesis and absorption property of Li$_3$TiO$_4$ as a novel CO$_2$ absorbent. J. Ceram. Soc. Jpn. 2007;115:324-328.

50. Romero-Ibarra IC, Duran-Munoz F, Pfeiffer H. Influence of the K$_2$O- Na$_2$O- KNa$_2$CO$_3$ additions during the CO$_2$ chemisorption on lithium oxosilicate (Li$_3$SiO$_4$). Greenhouse Gas Sci Technol. 2014;4(4):145-154. DOI: 10.1002/ghg.

51. Duran-Munoz F, Romero-Ibarra IC, Pfeiffer H. Analysis of the CO$_2$ chemisorption reaction mechanism in lithium oxosilicate (Li$_3$SiO$_4$): A new option for high temperature CO$_2$ capture. J. Mater. Chem. A. 2013;1:3919-3925. DOI: 10.1039/c3ta00421j.

52. Martinez-deCruz L, Pfeiffer H. Microstructural thermal evolution of the Na$_2$CO$_3$ phase produced during a Na$_2$ZrO$_2$-CO$_2$ chemisorption process. J. Phys. Chem. C. 2012;116:9675-9680. DOI: dx.doi.org/10.1021/jp301917a.

53. Rodríguez-Mosqueda R, Pfeiffer H. High CO$_2$ Capture in Sodium Metasilicate (Na$_2$SiO$_3$) at Low Temperatures (30-60 °C) through the CO$_2$-H$_2$O Chemisorption Process. J. Phys. Chem. C. 2013;117:13452-13461. DOI: dx.doi.org/10.1021/jp302850j

54. Sanchez-Camacho P, Romero-Ibarra IC, Duan Y, Pfeiffer H. Thermodynamic and kinetic analyses of the CO$_2$ chemisorption mechanism on Na$_2$TiO$_3$: Experimental and theoretical evidences. J. Phys. Chem. 2014;C:118:19822-19832. DOI: dx.doi.org/10.1021/jp504922e

55. Gómez-Garduño N, Pfeiffer H. Thermokinetic evaluation of iron addition on lithium metazirconate (Fe-Li$_2$ZrO$_3$) for enhancing carbon dioxide capture at high temperatures. Thermochimica Acta. 2019;673:129-137. Available:https://doi.org/10.1016/j.tca.2019.01.017

56. Drage TC, Snape CE, Stevens LA, Wood J, Wang J, Cooper AI, Dawson R, Guo X, Satterley C, Irons R. Materials challenges for the development of solid sorbents for post-combustion carbon capture. J. Mater. Chem. 2012;22:2815-2823.

57. Spigarelli BP, Kawatra SK. Opportunities and challenges in carbon dioxide capture. Journal of CO$_2$ Utilization. 2013;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. Recent developments in solvent absorption technologies at the CO$_2$CRC in Australia. Energy Procedia. 2009;1:1549-1555.

59. Songolzadeh M, Ravanchi MT, Soleimani M. Carbon dioxide capture and storage: A general review on adsorbents. World Academy of Science, Engineering and Technology. 2012;70:225-232.

60. Figueroa JD, Fout T, Plasynski S, McIlvried H, Srivastava RD. Advances in CO$_2$ capture technology-The U.S. department of energy’s carbon sequestration program. Int. J. Greenh. Gas Control. 2008;2:9-20. DOI: 10.1016/S1750-586X(07)00094-1

61. Rusten HK, Ochoa-Fernández E, Lindborg H, Chen D, Jakobsen, H.A. Hydrogen production by sorption-enhanced steam methane reforming using lithium oxides as CO$_2$-acceptor. Ind. Eng. Chem. Res. 2017;46:8729–8737. Available:https://doi.org/10.1021/ie0707770 k
62. Yu Zhang, Yanshan Gao, Heriberto Pfeiffer, benoit Louis, Luyi Sun, Dermot O’Hare, Qiang Wang. Recent advances in lithium containing ceramic based sorbents for high-temperature CO\textsubscript{2} capture. Journal of Materials Chemistry A. 2019;7(14):1-3. DOI: 10.1039/C8TA08932A

63. Zhang Q, Han D, Liu Y, Qian Y, Zhu Z. Analysis of CO\textsubscript{2} sorption/desorption kinetic behaviors and reaction mechanisms on Li\textsubscript{2}SiO\textsubscript{4}. AIChE J. 2013;59:901–911.

64. Rafael Rodriguez-Mosqueda, Heriberto Pfeiffer. Thermokinetic Analysis of the CO\textsubscript{2} Chemisorption on Li\textsubscript{2}SiO\textsubscript{4} by using different gas flow rates and particle sizes. The Journal of Physical Chemistry A. 2010;114(13):4535-4541. DOI: 10.1021/jp911491t

65. Qi Zhang, Chen Shen, Sai Zhang, Yongqiang Wu. Steam methane reforming reaction enhanced by a novel K\textsubscript{2}CO\textsubscript{3}-Doped Li\textsubscript{2}SiO\textsubscript{4} sorbent: Investigations on the sorbent and catalyst coupling behaviors and sorbent regeneration strategy February 2016 International Journal of Hydrogen Energy. 2016;41(8). DOI: 10.1016/j.ijhydene.2015.12.116

66. Pfeiffer H, Bosch P, Bulbulian S. Synthesis of lithium silicates. J Nucl Mater. 1998;257:309-17.

67. Kato M, Yoshikawa S, Nakagawa K. Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations. J Mater Sci Lett. 2002;21:485–7. Available: http://dx.doi.org/10.1023/A:1015338808533

68. Subha PV, Nair BN, Hareesh P, Mohamed AP, Yamaguchi T, Warrier KGK, Hareesh US. Enhanced CO\textsubscript{2} absorption kinetics in lithium silicate platelets synthesized by a sol–gel approach. J Mater Chem A. 2014;2:12792–8. Available:https://doi.org/10.1039/C4TA01976H

69. Izquierdo MT, Turan A, Garcia S, Maroto-Valer MM. Optimization of Li\textsubscript{2}SiO\textsubscript{4} synthesis conditions by a solid state method for maximum CO\textsubscript{2} capture at high temperature. J Mater Chem A. 2018;6:3249–57. Available:https://doi.org/10.1039/C7TA08738A

70. Wang K, Wang X, Zhao P, Guo X. High-temperature capture of CO\textsubscript{2} on lithium based sorbents prepared by a water-based sol–gel technique. Chem Eng Technol. 2014;37:1552–8.

71. Cruz D, Bulbulian S, Lima E, Pfeiffer H. Kinetic analysis of the thermal stability of lithium silicates (Li\textsubscript{2}SiO\textsubscript{4} and Li\textsubscript{2}SiO\textsubscript{3}). Journal of Solid State Chemistry. 2006;179(3):909–916. Available:https://doi.org/10.1016/j.jssc.2005.07.098

72. Wu X, Wen Z, Xu X, Wang X, Lin J. Synthesis and characterization of Li\textsubscript{2}SiO\textsubscript{4} 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 ME, Guzmán Velderrain V, Lardizábal Gutiérrez D, Collins-Martínez V, Ortiz AL. A new synthesis route to Li\textsubscript{2}SiO\textsubscript{4} as CO\textsubscript{2} catalytic/sorbent. Catalysis Today. 2005;107–108, 863–867. Available:https://doi.org/10.1016/j.cattod.2005.07.098

74. Ortiz AL, Bretado MAE, Velderrain VG, Zaragoza MM, Gutierrez JS, Gutierrez DL, Collins-Martínez V. Experimental and modeling kinetic study of the CO\textsubscript{2} absorption by Li\textsubscript{2}SiO\textsubscript{4} Int J Hydrog Energy. 2014;39:16656–66.

75. Choudhary A, Sahu BS, Mazumder R, Bhattacharyya S, Chaudhuri P. Synthesis and sintering of Li\textsubscript{2}SiO\textsubscript{4} powder from rice husk ash by solution combustion method and its comparison with solid state method. J Alloys Compd. 2014;590:440–5.

76. Rao GJ, Mazumder R, Bhattacharyya S, Chaudhuri P. Synthesis, CO\textsubscript{2} absorption property and densification of Li\textsubscript{2}SiO\textsubscript{4} powder by glycine-nitrate solution combustion method and its comparison with solid state method. J Alloys Compd. 2017;725:461–71.

77. Niu M, Li X, Ouyang J, Yang H. Lithium orthosilicate with halloysite as silicon source for high temperature CO\textsubscript{2} capture. RSC Adv. 2016;6:44106–12. Available:https://doi.org/10.1039/C6RA0504B

78. Wang K, Zhao P, Guo X, Han D, Chao Y. High temperature capture of CO\textsubscript{2} on Li\textsubscript{2}SiO\textsubscript{4} based sorbents from biomass ashes. Environ Prog Sustain Energy. 2015;34:526–32. Available:https://doi.org/10.1002/ep.11986

79. Olivares-Marín M, Drage T, Maroto-Valer MM. Novel lithium based sorbents from fly ashes for CO\textsubscript{2} capture at high temperatures. Int J Greenh Gas Control. 2010;4:623–9.
89. Pannocchia G, Buccini M, Seggiani M, Vitolo S. Experimental and modeling studies on high-temperature capture of CO$_2$ using lithium zirconate based sorbents. Ind. Eng. Chem. Res. 2007; 46:6696–6706. Available: https://doi.org/10.1021/ie0619649

90. Heriberto Pfeiffer, Enrique Lima, Pedro Bosch. Lithium–Sodium Metazirconate Solid Solutions, Li$_2$Na$_x$ZrO$_3$ (0 ≤ x ≤ 2): A Hierarchical Architecture. Chem. Mater. 2006;18:2642-2647, 1-3. Available: https://doi.org/10.1021/cm0600935

91. Pfeiffer H, Vazquez C, Lara VH, Bosch P. Thermal behavior and CO$_2$ absorption of Li$_2$Na$_x$ZrO$_3$ solid solutions. Chem. Mater. 2007;19:922–926. Available: https://doi.org/10.1021/cm0623965

92. Zhao T, Rønning M, Chen D. Preparation and high-temperature CO$_2$ capture properties of nanocrystalline Na$_2$ZrO$_3$. Chem. Mater. 2007;19:3294–3301. Available: https://doi.org/10.1021/cm062732h

93. Jimenez DB, Bretado MAE, Gutierrez DL, Gutierrez JMS, Ortiz AL, Martinez VC. Kinetic study and modelling of the high temperature CO$_2$ capture by Na$_2$ZrO$_3$ solid absorbent. Int. J. Hydrogen Energy. 2013;38:2557–2564. Available: https://doi.org/10.1016/j.ijhydene.2012.11.063

94. Zhao T, Ochoa-Fernandez E, Rønning M, Chen D. Preparation and high-temperature CO$_2$ capture properties of nanocrystalline Na$_2$ZrO$_3$. Chem. Mater. 2007;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. Regenerable sodium-based lithium silicate sorbents with a new mechanism for CO$_2$ capture at high temperature. Renewable Energy. 2019;144:180–187. ISSN 0960-1481.
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. 2019;144:180-187. ISSN 0960-1481. Available:https://doi.org/10.1016/j.renene.2018.08.039.

97. Rafael Rodríguez-Mosqueda, Heriberto Pfeiffer. The Journal of Physical Chemistry C. 2013;117(26):13452-13461. DOI: 10.1021/jp307560j.

98. Abanades JC, Grasa G, Alonso M, Rodríguez N, Anthony EJ, Romeo LM. Cost structure of a postcombustion CO₂ capture system using CaO. Environ. Sci. Technol. 2007;41:5523-5527.

99. Abanades JC, Rubin ES, Anthony EJ. Sorbent cost and performance in CO₂ capture systems. Ind. Eng. Chem. Res. 2004;43:3462-3466.

100. Wu SF, Jiang MZ. Formation of a Ca₃Al₂O₅ nanolayer and its effect on the attrition behavior of CO₂-adsorbent microspheres composed of CaO nanoparticles. Ind. Eng. Chem. Res. 2010;49:12269-12275. DOI: 10.1021/ie901561e.

101. Frascioli D, Anthony EJ. Steam reactivation of spent CaO-based sorbent for multiple CO₂ Capture Cycles. Environ. Sci. Technol. 2007;41:1420-1425. DOI: 10.1021/es0602144.

102. Li Y, Zhao C, Chen H, Duan L, Chen X. Cyclic CO₂ capture behavior of KMnO₄-doped CaO-based sorbent. Fuel. 2010;89(3):642-649.

103. Reddy EP, Smirniotis PG. High-temperature sorbents for CO₂ made of alkali metals doped on CaO supports. The Journal of Physical Chemistry B. 2004;108(23):7794-7800.

104. Skoufa Z, Antzara A, Heracleous E, Lemonidou AA. Evaluating the activity and stability of CaO-based sorbents for postcombustion CO₂ capture in fixed-bed reactor experiments. Energy Procedia. 2016;86:171-180.

105. Wang M, Lee CG. Absorption of CO₂ on CaSiO₃ at high temperatures. Energy Convers. Manag. 2009;50:636-638.

106. Huang CH, Chang KP, Yu CT, Chiang PC, Wang CF. Development of high-temperature CO₂ sorbents made of CaO-based mesoporous silica. Chem. Eng. J. 2010;161:129-135. DOI: 10.1016/j.cej.2010.04.045.

107. Wu Z, Hao N, Xiao G, Liu L, Webley P, Zhao D. 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. 2011;13:2495-2503.

108. Li L, King DL, Nie Z, Howard C. Magnesia-stabilized calcium oxide absorbents with improved durability for high temperature CO₂ capture. Ind. Eng. Chem. Res. 2009;48:10604-10613. DOI: 10.1021/ie901166b.

109. Li ZS, Cai NS, Huang YY. Effect of preparation temperature on cyclic CO₂ capture and multiple carbonation-Calcination Cycles for a New Ca-Based CO₂ Sorbent. Ind. Eng. Chem. Res. 2006;45:1911-1917. DOI: 10.1021/ie051211L.

110. Martavaltzi CS, Pampaka EP, Korkakaki ES, Lemonidou AA. Hydrogen production via steam reforming of methane with simultaneous CO₂ capture over CaOCa₂Al₂O₅. Energy Fuels. 2010;24:2589-2595. DOI: 10.1016/j.ijgf.2010.04.038.

111. Hassanzadeh A, Abbassin J. Regenerable MgO-based sorbents for hightemperature CO₂ removal from syngas: 1. Sorbent development, evaluation, and reaction modeling. Fuel. 2010;89:1287-1297. DOI: 10.1016/j.fuel.2009.11.017.

112. Zhang K, Li XS, Duan Y, King DL, Singh P, Li L. Roles of double salt formation and NaNNO₃ in Na₂CO₃-promoted MgO absorbent for intermediate temperature CO₂ removal. Int. J. Greenh.Gas control. 2013;12:351358. DOI: http://dx.doi.org/10.1016/j.ijggc.2012.11.013.

113. Mayorga SG, Weigel SJ, Gaffney TR, Brzozowski JR. Carbon dioxide adsorbents containing magnesium oxide suitable for use at high temperatures (No. US 6280503). Air Products and Chemicals, Inc.(Allentown, PA); 2001.

114. Bhagiyalakshmi M, Lee JY, Jang HT. Synthesis of mesoporous magnesium oxide: Its application to CO₂ chemisorption. International Journal of Greenhouse Gas Control. 2010;4(1):51-56.
115. Zukal A, Pastva J, Cejka J. MgO-modified mesoporous silicas impregnated by potassium carbonate for carbon dioxide adsorption. Microporous Mesoporous Mater. 2013;167:44-50. DOI: http://dx.doi.org/10.1016/j.micromeso.2012.05.026.

116. Zhang K, Li XS, Duan Y, King DL, Singh P, Li L. Roles of double salt formation and NaNO$_3$ in Na$_2$CO$_3$-promoted MgO absorbent for intermediate temperature CO$_2$ removal. Int. J. Greenh. Gas Control. 2013;12:351-358. DOI: http://dx.doi.org/10.1016/j.ijggc.2012.11.013.

117. Bian SW, Baltrusaitis J, Galhotra P, Grassian VH. A template-free, thermal decomposition method to synthesize mesoporous MgO with a nanocrystalline framework and its application in carbon dioxide adsorption. J. Mater. Chem. 2010;20:8705-8710.

118. Jeon H, Min YJ, Ahn SH, Hong SM, Shin JS, Kim JH, Lee KB. Graft copolymer templated synthesis of mesoporous MgO/TiO$_2$ mixed oxide nanoparticles and their CO$_2$ adsorption capacities. Colloid Surface A. 2012;414:75–81. DOI: http://dx.doi.org/10.1016/j.colsurfa.2012.08.009.