The Journal of CPRI,
Vol. 10, No. 2, June 2014 pp. 395-408

Lithium Ceramics for High Temperature CO_2 Capture: A Review

Lakshminarayana Bhatta K G*, Seetharamu S** and Sharon Olivera***

Carbon dioxide capture and storage (CCS) technology is considered as promising option in the portfolio of mitigation actions for stabilization of atmospheric greenhouse gas concentration as fossil fuels continue to be the major source of energy in foreseeable future. Among the various options for CO_2 capture, the adsorption technology has been widely investigated as a means of an alternative to absorption technology that is having many formidable problems. Recently there is a growing interest in solid sorbents; those can efficiently capture CO_2 in the temperature range of 200-700 °C. Applications of high temperature adsorbents are envisioned mainly in sorption enhanced reformation processes (SERP) and CO_2 removal from hot flue gas/syngas. Lithium ceramics are important class of materials in this category. This paper aims at a review of lithium zirconates and lithium silicates as CO_2 adsorbents. The focus is on various aspects of sorbents such as sorption capacity, mechanism of adsorption, kinetic models, factors affecting the sorbent performance and methodologies developed for performance enhancement. However, CO_2 separating membranes made of lithium-based ceramics are not discussed.

Keywords: *CO_2 capture, Lithium zirconates, Lithium silicates, Doping, Adsorption, Synthesis*

1.0 INTRODUCTION

Carbon dioxide capture and storage (CCS) technology is considered as promising option in the portfolio of mitigation actions for stabilization of atmospheric greenhouse gas concentration as fossil fuels continue to be the major source of energy in foreseeable future [1-2]. It is best applied to large point sources such as fossil fuel power plants, fuel processing plants, and other industrial plants, particularly for the manufacture of iron, steel, cement, and bulk chemicals. CCS technology comprises three main steps; CO_2 capture, transportation, and utilization/storage. Today, the range of CCS technologies at various stages of research, development, demonstration, and deployment is wide and diverse [3]. However, there are many challenges for their complete commercialization including, the reduction of energy penalty on the host power plant, reasonable capital and operating expenditure, acceptable plant footprint, CO_2 production of high purity to meet the requirements, and legislation for subsequent transport and storage. Moreover, CO_2 capture from fossil fuel burning power plants presents several design challenges such as handling of large volume of gas and impurities, and capture process integration to original plants as well as new systems [4-5]. The CO_2 capture, being first step in CCS technology is very crucial since it accounts for ~70 % of the total operating costs. It is achieved through three technological pathways namely precombustion, postcombustion, and modified combustion (oxy fuel and chemical looping) with each one having its own inherent advantages as well as disadvantages [6-7]. For all the pathways, the four fundamental technological areas that are in either use or under development to separate CO_2 from other gases are absorption, adsorption, membranes, and cryogenic separation

*Centre for Emerging Technologies, Jain University, Ramanagarm-562112, India. Mobile: +91 9448282330, E-mail: kglbhat@gmail.com
**Central Power Research Institute, Bangalore-560080, India. E-mail: ssramu@cpri.in
***Centre for Emerging Technologies, Jain University, Ramanagarm-562112, India. E-mail:olivera333sharon@gmail.com

systems. Among these, the adsorption technology has been widely investigated as a means of an alternative to absorption technology that is having many formidable problems. Adsorbent materials possess many potential advantages including reduction in energy requirement for CO_2 capture, wide range of working temperature, greater capacity, selectivity, ease of handling, and lack of liquid waste streams [8-10].

The various classes of solid sorbents those are investigated so far include carbon based adsorbents, zeolites, alumina, silica, metal organic frameworks, regenerable alkali-metal carbonate-based sorbents, amine-functionalized solid sorbents,functionalized zeolite-based sorbents, functionalized polymer-based sorbents,functionalized silica-supported sorbents, impregnated alumina-supported sorbents, hydrotalcite-like compounds, alkali ceramic based sorbents, and metal based oxides. Generally, the solid adsorbents are classified into physisorbents and chemisorbents based on the type of adsorption. Besides, based on their adsorption/desorption temperatures, they are classified into low (below 200 °C), intermediate (between 200–400 °C), and high (above 400 °C) temperature adsorbents [11-12]. Solid sorbents are used in both post-combustion and pre-combustion capture processes. Selection of a suitable sorbent for a particular application is a major challenge. Some important criteria that a sorbent should satisfy include high adsorption capacity and good reversibility, high selectivity, fast kinetics, stability, easy of regeneration, and low cost [13-16]. The selection of sorbent is always a trade off as no single sorbent can meet all these criteria. Moreover, the desirable characteristics of sorbent depend upon the point in the capture process where it is applied, and a range of different physical conditions such as temperature, CO_2 volume concentration, presence of impurities, overall pressure, and CO_2 partial pressure.

Of late, there is a growing interest in solid sorbents; those can efficiently capture CO_2 in the temperature range of 200-700 °C. Applications of high temperature adsorbents are envisioned mainly in the following areas.

1.1 Sorption-Enhanced Water–Gas Shift (SEWGS)

In conventional steam methane reforming (SMR), typically 70–80 % of the methane feed is converted to hydrogen in a reactor at a temperature of 700–950 °C and a pressure of 1.5 – 4.0 MPa, yielding a product stream with about 57% H_2. The reversible water gas shift (WGS) reaction can be driven to completion by employing WGS catalyst and high-temperature CO_2 sorbent. The WGS reaction usually takes place between 200–500 °C. The sorption-enhanced WGS (SEWGS) reactor can remove 90 % of the carbon from product stream.

1.2 Sorption Enhanced Steam Reforming (SESR)

Both SMR and WGS reactions can also be achieved in a single process unit using a mixture of catalyst and selective adsorbent to remove CO_2, thus driving the reaction to completion. The presence of a catalyst allows the reaction to proceed without the need for a separate WGS stage, at significantly lower temperatures (400–600 °C) resulting in cost effectiveness by reducing heat exchange equipment size and avoiding expensive steel alloys.

1.3 CO_2 Removal from Hot Flue Gas/Syngas

The existing sorbents are effective in CO_2 removal only at low temperature (< 100 °C) and in absence/low concentration of the impurities in flue gas/product stream. This requires pre-treatment and cooling of flue gas/syngas in case of post-combustion/pre-combustion capture systems. The current research on high temperature sorbents aims at removal and recovery of CO_2 from flue gas/syngas without pre-cooling, pre-drying, or pre-compression in order to reduce energy penalty and enhance economic viability [17-18].

Thus far, materials proposed in the category of high temperature sorbents for CO_2 capture include hydrotalcite like compounds (HTlcs), CaO and MgO based sorbents, and Lithium ceramics.

Lithium ceramics are emerging materials considered as strong candidates for developing commercially competitive CO_2 adsorbent. Lithium zirconates and lithium silicates have been widely investigated for CO_2 sorption. Other ceramics such aslithium aluminate (Li_5AlO_4), lithium cuprate (Li_2CuO_2), lithium ferrite ($LiFeO_2$), lithium titanate (Li_4TiO_4), and lithium gallate (Li_5GaO_4) have been studied to a lesser extent [19-20]. This paper aims at a review of lithium zirconates and lithium silicates as CO_2 adsorbents. The focus is on various aspects of sorbents such as sorption capacity, mechanism of adsorption, kinetic models, factors affecting the sorbent performance, and methodologies developed for performance enhancement. However, CO_2 separating membranes made of lithium-based ceramics are not discussed.

2.0 LITHIUM ZIRCONATES

Li_2ZrO_3 reacts with CO_2 reversibly in the temperature range of 450–650 °C with 28.6 wt% theoretical uptake according to equation 1.

$$Li_2ZrO_3 + CO_2 \Leftrightarrow Li_2CO_3 + ZrO_2 \quad ....(1)$$

Nakagawa et al. of Toshiba Corporation first reported Li_2ZrO_3 as high temperature CO_2 sorbent in 1998. Subsequently, Li_2ZrO_3 attracted the attention of other researchers for its potential applications in integrated gasification combined cycle (IGCC), WGS, SMR, Sorption Enhanced Reaction Process (SERP), and CO_2 removal from hot flue gas. The advantages of this material include the large sorption capacity, suitable temperature window, small volume change during the CO_2 sorption/desorption cycles, selectivity over N_2 as well as H_2, low regeneration energy compared to CaO, cyclic stability, and thermal stability [21-25]. However, the major drawback of Li_2ZrO_3 is the low kinetic rate of CO_2 adsorption. $Li_6Zr_2O_7$ and Li_8ZrO_6 are other kinds of lithium zirconates reported in literature. The sorption characteristics of lithium zirconates depend upon many factors including crystal structure and lattice dynamics, size, composition, and preparation history. Hence, great efforts have been made to understand the reaction mechanism and develop strategies for performance enhancement. The performance enhancement methodologies include doping, development of various synthetic routes, and use of eutectic mixture.These aspects are summarized in the following sections.

2.1 Structure and Synthesis

Li_2ZrO_3 exists in two phases, namely tetragonal and monoclinic. It was found that t-Li_2ZrO_3 exhibits better performance as a CO_2 absorbent than its monoclinic counterpart with higher stability, faster uptake rate, and higher absorption capacity [26]. Nair et al. [27] carried out a systematic study on the properties of Li_2ZrO_3 with different crystal structures. They have compared the properties of powders prepared by the solid-state and sol-gel methods with commercial grade powder. It was found that Li_2ZrO_3 having tetragonal structure with smaller particle size captured CO_2 faster than their monoclinic with larger particle size counterparts. However, it was difficult to separate the relative effects of particle size and crystalline structure.

The synthesis route, calcination temperature, Li/Zr ratio in precursor mixture, type of precursor, and preparation history all will influence the parameters such as crystal structure, type of lithium zirconate formed, and size of particles and aggregates. These parameters in turn influence the adsorption amount, reaction rate, and stability of materials [26, 28].

The solid-state reaction is the conventional synthesis route of lithium zirconates. Investigating the optimum conditions for synthesis of Li_2ZrO_3 by the solid-state reaction Lin et al. [29] shown that m-Li_2ZrO_3 could be obtained from lithium carbonate and zirconia (1:1) in the temperature range of 850–1200 °C. The reaction was incomplete below this temperature range and sublimation of Li_2O would occur above the range. However, this method often needs high energy input, and it is difficult to control the sizes and phases of the final products [24, 30]. Therefore, many investigations have been focused on finding

other suitable routes. Some of them are sol-gel method, liquid phase co-precipitation method, precipitation combustion process (citrate route), and surfactant-template method.

Chen et al. [21, 31] prepared highly pure nanocrystals of tetragonal-Li_2ZrO_3 using novel soft-chemistry method. The complex solution obtained from mixing aqueous solution of zirconyl nitrate and lithium acetate was subjected to sequential spray drying, oxidation, and calcination. The sample showed high CO_2 uptake (27 wt %), improved kinetics (saturated in less than 5 min), and low regeneration temperature (650 °C). The enhanced properties were attributed to particle size and purity of Li_2ZrO_3 phase. The optimum calcination temperature was found to be 600 °C. Additionally, the soft-chemistry route was explored further to obtain Li_2ZrO_3 with high surface area. The prepared sample exhibited 29.87 wt% CO_2 uptake and 0.83 wt% min^{-1} reaction rate [23]. In another study, the highly crystalline, nanosized t-Li_2ZrO_3 containing m-$Li_6Zr_2O_7$ was obtained via a gelatin assisted biomimetic soft solution method. Compared with bulk Li_2ZrO_3, the prepared sample showed significantly improved CO_2 capture property. The results indicate that particle size and tetragonal phase are critical for enhancement of the CO_2 capture [30]. Similar observations were made for sorbents obtained from citrate based sol–gel method [24, 32]. Iliuta et al. [33] employed ultrasound assisted surfactant-template method to obtain porous nanoparticle Li_2ZrO_3 using precursors; $ZrO(NO_3)_2.xH_2O$, lithium acetate, and cetyltrimethylammonium bromide (CTAB). The prepared sample exhibited higher absorption rate, capacity, and cyclic stability than those obtained by the simple surfactant-template method (without sonication), and the conventional soft-chemistry route.

The aggregate size of Li_2ZrO_3 can also affect CO_2 sorption rate substantially. The rate increases with decreasing sorbent aggregate size. For example, the sorption rate of K- Li_2ZrO_3 with average aggregate size of 5 μm was four times higher (18 wt% in 30 min at 650 °C) than that of 15 μm [34].

2.2 Doped Li_2ZrO_3

Doping Li_2ZrO_3 with other alkali metals such as K and/or Na is another strategy to enhance sorbent performance in terms of sorption capacity and uptake rate. The doping will change the melting point of the system and produce a liquid eutectic mixed-salt molten shell on the outer surfaces of Li_2ZrO_3. This molten shell offers much lower resistance to CO_2 diffusion than hard Li_2CO_3 shell formed in case of pure Li_2ZrO_3. For instance, the CO_2 sorption rate of the K-doped Li_2ZrO_3 was about 40 times faster (20 wt% in 250 min) than the pure Li_2ZrO_3 at 500 °C even under 50% CO_2 flow [35]. The K-doped Li_2ZrO_3 synthesized using the starch-assisted sol–gel method combined with the freeze-drying technique showed excellent CO_2 capture properties and cyclic stability. At 550 °C and 0.25 bar, the uptake of CO_2 reached 22 wt% within 20 min (87% adsorption efficiency) [36]. The introduction of yttria to K-doped Li_2ZrO_3 was found to enhance the CO_2 sorption rate to a greater degree. Doping the +3 valent yttrium in zirconia will introduce a substantial amount of oxygen vacancy. This results in high diffusion flux of Li^+ and O^{2-} through the yttria doped zirconia shell [29]. However, Pannocchia et al. [22] showed that the sorbent having composition Li_2CO_3: ZrO_2: K_2CO_3 = 1.15:1.0:0.2 gives better CO_2 uptake rate without the necessity of adding such an expensive component as yttrium. These results clearly indicate the crucial role of carbonate salt content in CO_2 absorption. Investigating the rheological properties of pure Li_2ZrO_3 and K-doped Li_2ZrO_3 under CO_2 atmosphere, Olivares-Marín et al. [37] pointed out that the molten carbonate 'shell' not only allows the diffusion and sorption of CO_2 but also alters the viscoelastic properties of the sorbent mixture with high heating rates. Its nature will determine the effectiveness of the sorbent for CO_2 sorption uptake.

The sorbents performance can also be enhanced by Na doping. For instance, the Na-doped Li_2ZrO_3 nano squares exhibited 20 wt% CO_2 sorption at 650 °C in less than 20 min and found to be better sorbent than unmodified counterparts [32].

2.3 Eutectic Salt-Modification and Solid Solutions

The modification of Li_2ZrO_3 by eutectic salt also noticeably improves the CO_2 uptake rate and CO_2 sorption capacity. Formation of a eutectic molten carbonate layer on the outer surface of reactant Li_2ZrO_3 particles aids in facilitating the transfer of gaseous CO_2 during the sorption process. Fauth et al. [38] evaluated a number of Li_2ZrO_3 samples modified with different combinations of binary and ternary eutectic mixtures. The KF/Li_2CO_3-containing Li_2ZrO_3 sample gave the fastest rate (32.5 times faster) of CO_2 uptake, compared to the pure, unmodified sample.

Both zirconates, Li_2ZrO_3 and Na_2ZrO_3 are good absorbents. Further K doping enhances kinetics of Li_2ZrO_3. Hence, if solid solutions of lithium-potassium metazirconates and Lithium-sodium metazirconates present a synergetic effect, they should exhibit better sorption characteristics. This deduction motivated the investigation of these oxide solid solutions. Indeed, $Li_{2-x}Na_xZr_2O_7$ solid solutions presented a high CO_2 absorption, compared to pure Li_2ZrO_3 and Na_2ZrO_3. The sorption efficiency of 75.3% was achieved for $LiNaZrO_3$ sample at 600 °C [39]. Another study revealed that $Li_{2-x}K_xZrO_3$ solid solutions can absorbCO_2, five times faster than Li_2ZrO_3 in short time spans [40].

2.4 Reaction Mechanism and Kinetic Behaviors

Lithium oxide in the Li_2ZrO_3 structure reacts reversibly with CO_2 as demonstrated by equation 1. Many studies have been carried out to describe CO_2 sorption/desorption kinetic behaviors and reaction mechanism on Li_2ZrO_3. Lin and Ida [35] proposed a double shell model to describe the mechanism of the CO_2 absorption/desorption process on both Li_2ZrO_3 and K-doped Li_2ZrO_3. In the beginning, CO_2 diffuses to the surface of Li_2ZrO_3. Subsequently, it reacts with Li^+ and O^{2-} to form ZrO_2 and Li_2CO_3 nuclei. Gradually ZrO_2 nuclei grow to form a shell covering unreacted Li_2ZrO_3. Similarly, Li_2CO_3 nuclei would form another shell outside of ZrO_2 shell. Once these shells are formed, the absorption rate decreases because CO_2 molecules, Li^+, and O^{2-} ions have to diffuse through shells for carbonation reaction. The diagram of double shell model is shown in Figure 1.

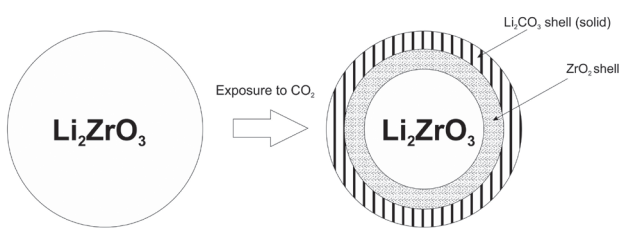

FIG. 1 DOUBLE SHELL MODEL FOR CO_2 SORPTION ON Li_2ZrO_3. REPRODUCED WITH PERMISSION FROM REF 22

In the case of K-modified Li_2ZrO_3 the Li/K carbonate layer covering Li_2ZrO_3 may melt and become a liquid layer (molten carbonate) because of its lower melting point. The diffusion of CO_2 in the molten carbonate is much faster than that in the solid carbonate. This explains the higher CO_2 sorption rate in the case of modified Li_2ZrO_3. Schematic illustration is shown in Figure 2.

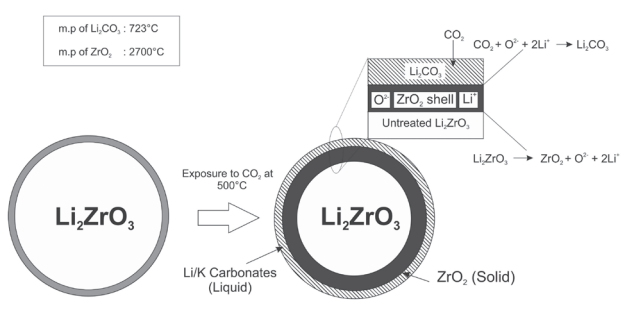

FIG. 2 CO_2 SORPTION ON Li_2CO_3/K_2CO_3–DOPED Li_2ZrO_3. REPRODUCED WITH PERMISSION FROM REF 35

During the desorption process Li_2CO_3 reacts with ZrO_2 on the interface to form Li_2ZrO_3 and CO_2. When the Li_2ZrO_3 forms a dense shell covering the unreacted ZrO_2, the desorption process continues with the diffusion of Li^+ and O^{2-} through the solid Li_2ZrO_3 shell, and CO_2 through the liquid Li_2CO_3 to the outside.The model was verified with experimental data of samples containing different microstructures. It was found that oxygen ion diffusion in ZrO_2 shell is the rate-limiting step of the sorption process.

However, double - shell model is based on quasi-steady-state assumption and could not account for the initial part of adsorption curve. Subsequently, the model was modified by Pannocchia et al. [22]. They considered the diffusion of O^{2-} in zirconia shell as rate limiting step and proposed two model parameters (ǎ and r) to explain transient dynamics of system. The developed model fits the experimental data very well for Li_2CO_3/K_2CO_3-doped Li_2ZrO_3. It can also be readily extended to different operating temperatures by adjusting these two model parameters. The model is illustrated schematically in Figure 3.

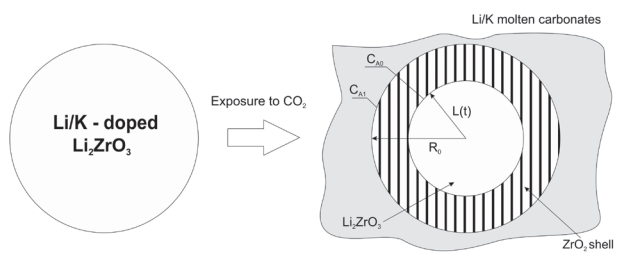

FIG 3. KINETIC MODEL FOR CO_2 SORPTION ON Li_2CO_3/K_2CO_3–DOPED Li_2ZrO_3. REPRODUCED WITH PERMISSION FROM REF 22

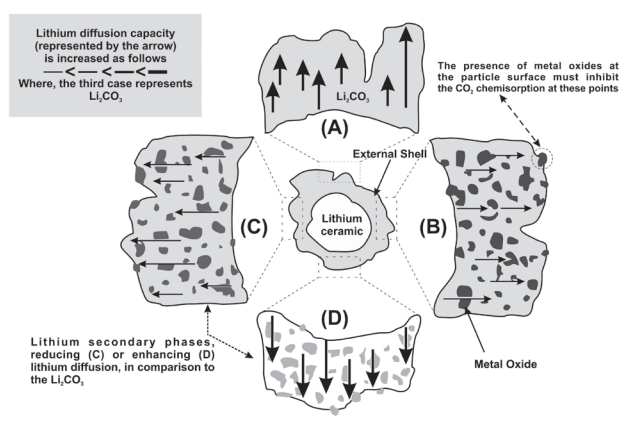

FIG 4. POSSIBLE EXTERNAL SHELL COMPOSITIONS. REPRODUCED WITH PERMISSION FROM REF 35

Pfeiffer et al. [19] further detailed the role and importance of lithium external shell. There are three possible compositions of external shell; pure Li_2CO_3, Li_2CO_3 mixed with a metal oxide such as ZrO_2, and Li_2CO_3 mixed with a secondary lithium phase. When the external shell is composed of Li_2CO_3 and metal oxides, the presence of metal oxides reduces CO_2 chemisorption. If the external lithium shell is composed of Li_2CO_3 and another lithium phase, the CO_2 chemisorption process can either be enhanced or decreased depending on the lithium diffusion coefficients of the secondary lithium phases. The scheme is shown in Figure 4. To elucidate this hypothesis, different solid solutions were prepared and tested. However, this model is applied only for the case where Li_2CO_3 is in a solid state.

3.0 LITHIUM SILICATE

Li_4SiO_4 reacts with CO_2 reversibly as shown in equation 2.

$$Li_4SiO_4 + CO_2 \Leftrightarrow Li_2CO_3 + Li_2SiO_3 \quad ....(2)$$

The sorption takes place in two stages; chemisorption and slow diffusion process. The theoretical CO_2 uptake is 36.5 wt%. In general, it absorbs CO_2 in the temperature range of 450 – 600 °C and desorbs above 700 °C. While the potential applications of Li_4SiO_4 remain same as that of Li_2ZrO_3, it has two major advantages over Li_2ZrO_3, namely faster kinetics and cost-effective precursors [41-43]. Kato et al. [41-42, 44-45] investigated sorption properties of Li_4SiO_4 and Li_2ZrO_3 pellets at different temperatures and CO_2 concentrations. Li_4SiO_4 absorbed CO_2 faster than Li_2ZrO_3 even in a lower CO_2 concentration (2% CO_2) and at lower temperatures (25 °C) due to the availability of more sites for Li^+ hopping. Li_4SiO_4 absorbed CO_2 about 30 times faster than Li_2ZrO_3 at 500 °C in 20% CO_2 gases (60 mg min^{-1} g^{-1}). The temperature and CO_2 concentrations strongly affect the sorbent performance. The absorption rate was highest in range of 550 – 600 °C for 10 vol% CO_2.

The different methodologies developed for performance enhancement, the reaction mechanism, and kinetic behaviors of Li_4SiO_4 are summarized in following sections.

3.1 Structure and Synthesis

The proposed modifications on Li_4SiO_4 for performance enhancement, reported in literature, include new synthesis routes and use of different

types of precursors. Sol-gel, impregnated suspension method, ball mill method, and impregnation precipitation method are main techniques employed to reduce primarily the particle size of Li_4SiO_4 [46-50]. The smaller particle size results in higher CO_2 adsorption efficiency and adsorption rate. The use of different types of precursors with different characteristics resulted in the smaller product grain size. The traditional high temperature solid-state methods lead to a number of problems including contamination, volatilization as well as lack of control on the microstructure and composition. Alternate methods offer low temperature synthesis, and control over morphology and microstructure of product. For instance, preparation of nanocrystalline Li_4SiO_4 by coupling sol–gel method with reverse microemulsion resulted in narrow and uniform size distribution of spherical particles (4–12 nm). The sample showed enhanced CO_2 sorption capacity and shorter retention times at higher temperature (~25.7 wt% at 610 °C). This was attributed to non-stoichiometric SiO_2 to SiO_x formation of the silicate molecule and strengthening of Li_2O-SiO_x bond [46]. Pfeiffer et al. [50] synthesized Li_4SiO_4 by three different techniques; solid-state reaction, precipitation, and sol-gel (using a microwave oven) methods to study particle size effect by fitting the experimental data to the double exponential model. Pure Li_4SiO_4 was obtained by solid-state and precipitation methods. The sol-gel method gave a mixture of lithium silicates and quartz due to earlier sublimation of lithium as Li_2O. The solid-state sample showed homogeneous polygonal particles with an average size equal to 36 μm where as the precipitation method yielded corrugated spherical particles of 3 μm average size. The CO_2 uptake by large particles was 33.7 wt % at 600 °C under a flux of 100% CO_2 which is very close the maximum theoretical capacity. On the contrary, the small particles absorbed up to 44.94 wt %, which is 8.24 wt % more than expected value. These results were explained in terms of reactivity for the chemisorption process. The small particles should have a higher reactivity due to the presence of more lithium atoms over the surface of the particles, and the generation of different steam pressures on the grain boundaries and triple points. Jia et al. [47] compared sorbent properties of sample obtained from impregnation precipitation method with those from solid-state method using two precursors; diatomite and analytical SiO_2. The sample obtained from impregnation precipitation using diatomite exhibited better adsorption efficiency, rate, and cyclic stability than other two samples (96 % in 15 min). This was ascribed to formation of smaller particle size grains and structural differences due to presence of Al as well as other elements in the diatomite. Ortiz et al. [49] demonstrated the superiority of impregnated suspension method over solid-state method. Using this technique, Li_4SiO_4 with better sorption efficiency (98.4 %) was synthesized at lower temperature (900 °C). Sinter-resisting precursor and product particle size were found to be the critical parameters. Another study revealed that the ball milling process is one more route for the preparation of sorbents with enhanced microstructural features resulting in improved CO_2 chemisorption properties [48].

The sorbents derived from cost-effective precursors showed promising results. Olivares-Marin et al. [51] synthesized K-doped Li_4SiO_4 sorbents using fly ash as source of SiO_2. The novel sorbents prepared exhibited good cyclic stability (tested for 10 cycles) and reach the plateau of maximum capture capacity in less than 15 min. The best one among the tested samples showed 10 wt% CO_2 uptake optimum conditions (at 600 °C with 40 mol% K_2CO_3). Diatomite was used as source of silica by other studies [52-53]. The sorbent exhibited better rate and sorption capacity (28.6 wt %) than the one from analytical pure SiO_2 (22 wt %). This is due to larger specific surface area and more uniform microstructure, produced by the presence of impurities like Al in diatomite. The optimum raw material ratio of diatomite to Li_2CO_3 was found to be 2.6:1. Highly efficient Li_4SiO_4-based sorbents were also developed using waste material, rice husk ash [54-55]. The sample showed better sorption capacity (32.4 wt %) than that of pure Li_4SiO_4 (22.1 wt %) under tested conditions. The metals like K and Na present in precursor were doped with Li_4SiO_4 resulting to inhibited growth of the particles, and increased pore volume and surface area.

Seggiani et al. [56] studied the sorbents obtained from three different types of silica (amorphous fumed silica, amorphous quartz wool and crystalline quartz) and two different doping methods (eutectic-doping and 10 mol % K_2CO_3 addition). Both doping methods improved sorption capacity to same degree for samples obtained from fumed silica and quartz wool (from 50 to 110 mg g^{-1}). However, the improvement in capacity for K added sorbent in case of sample from crystalline quartz is higher (from 50 to 270 mg g^{-1}) than that for eutectic doping (from 50 to 110 mg g^{-1}). This behavior was attributed to the higher surface area of the Li_4SiO_4 obtained from quartz which showed porous agglomerates of submicron particles in comparison with the Li_4SiO_4 samples obtained using amorphous silica that showed large dense particles. This can allow to a more efficient distribution of K_2CO_3 promoter on the smaller Li_4SiO_4 particles.

Xu et al. [57] studied the effect of precursor particle size on sorbent performance by comparing the sorbents obtained by using quartz powder of different particle sizes. The results indicated that when the particle size of the quartz powder decreased, the solid-state reaction performed more completely, the content of the Li_4SiO_4 phase increased, and the size of the grain agglomerates decreased gradually. The enhanced chemical reactivity of the quartz powder with Li_2CO_3, and the shortened diffusion distance as the quartz size decreases are helpful to the formation of the Li_4SiO_4 phase. The sorption analysis revealed that the samples synthesized using the quartz powder with smaller particle sizes experienced a more rapid absorption–desorption process with a higher absorption efficiency.

3.2 Doping and Eutectic Salt Modification

The sorbent performance can also be substantially enhanced/modified by addition of eutectic carbonate mixtures or by doping elements such as Na, K, Cs, Fe and Al. These promoters form eutectic mixture with product Li_2CO_3 lowering the melting point of Li_2CO_3 (> 500 °C). The resultant molten carbonate shell (liquid phase) greatly facilitates CO_2 diffusion throughout the product layer compared to the solid Li_2CO_3 shell in pure Li_4SiO_4 case [58-59]. Fe doping is thermodynamically preferred to Al doping. The vacancy doping is superior to interstitial doping as it facilitates O^{2-} diffusion by offering more sites for ion hopping. The absorption rate of Fe-doped Li_4SiO_4 was approximately one order of magnitude superior (0.15 wt% min^{-1} at 500 °C) to pure Li_4SiO_4 (0.01 wt% min^{-1} at 500 °C). Further, it exhibited better desorption characteristics (above 500 °C) than eutectic doped Li_4SiO_4 with K [43].

In another study [60] 16 samples of promoted Li_4SiO_4 with different amounts of alkali carbonates (K_2CO_3 and Na_2CO_3), binary (K_2CO_3/Li_2CO_3 and Na_2CO_3/Li_2CO_3), and ternary ($K_2CO_3/Na_2CO_3/Li_2CO_3$) eutectic mixtures were investigated at 580 °C under 4 vol % CO_2 flow. 30 wt % addition of promoter was found to be the optimal loading due to balance between distribution of promoter particles on sorbent surface and contribution of promoter to sorbent weight. The sorption rate and capacity values of K/Na doped sorbents were higher than sorbents promoted with eutectic mixtures as already existing Li-Na-K eutectic liquid phase offers additional diffusion resistance to CO_2 molecules. Among the tested samples, 30 % wt K_2CO_3 promoted Li_4SiO_4 showed the best sorption performance in terms of absorption rate, sorption capacity (23 wt%), and cyclic capacity (4 % wt loss during 25 cycles).

3.3 Reaction Mechanism and Kinetic Behaviors

Essaki et al. [42, 44] proposed a double-shell model to describe the CO_2 adsorption mechanism on Li_4SiO_4. According to this model, during the adsorption, CO_2 first diffuses to the surface of Li_4SiO_4. Later, it reacts with Li^+ and O^{2-} to form Li_2CO_3 and Li_2SiO_3. The Li_2SiO_3 forms a solid shell that covers unreacted Li_4SiO_4. Lithium carbonate forms another shell outside the Li_2SiO_3 shell. Consequently, once the external layer of alkaline carbonate is completely formed, Li^+ and O^{2-} have to diffuse throughout the Li_2SiO_3 shell to continue reacting with CO_2. Similarly, CO_2 also has to diffuse throughout the external Li_2CO_3

layer. Therefore, the successive build-up of the product layer limits the progress of adsorption, and the sorption rate begins to decrease. The scheme is represented in Figure 5.

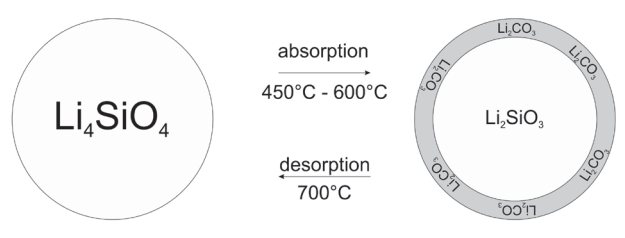

FIG 5. ABSORPTION AND EMISSION BY Li_4SIO_4. REPRODUCED WITH PERMISSION FROM REF 42

Several research groups [50, 58, 61-62] used double exponential model to describe the sorption mechanism and kinetic behavior. The reaction mechanism is explained by two processes. First, CO_2 reacts with the lithium present on the surface of the Li_4SiO_4 particles. This chemisorption involves the formation of an external shell composed of lithium carbonate. Later, once the external layer of lithium carbonate is totally produced, a diffusion process begins, where lithium has to diffuse throughout the carbonate layer in order to reach the surface, and react with the CO_2. Equation 3 is the expression for the model.

$$y = A\exp^{-k_1 t} + B\exp^{-k_2 t} + C \quad ....(3)$$

where, y represents the weight percentage of CO_2 chemisorbed; t is the time; k_1 is exponential constant for the CO_2 chemisorption produced directly over the Li_4SiO_4 particles, and k_2 is the exponential constant for CO_2 chemisorption kinetically controlled by lithium diffusion. A, B, and C are the pre-exponential factors. It was found that, experimental data from all these studies fitted well to model. k_1 values are, in general, one order of magnitude higher than those obtained for the k_2 constants. This indicates that the limiting step of the total process is the lithium diffusion.

Recently, with an aim todevelop a suitable model for the kinetic behaviors and reaction mechanism of the CO_2 sorption/desorption process on Li_4SiO_4, Qi et al. [63] carried out a comparative study of commonly reported models for solid sorbents; shrinking core, double exponential, and Avrami–Erofeev models. The CO_2 sorption/desorption temperature range and equilibrium conversion were calculated using FactSage 5.0 and confirmed with experiments carried out using TGA. The experimental data were used to analyze the models. The Avrami–Erofeev model was found to be most suitable for analyzing the kinetic behavior of both sorption/desorption process and effect of water.

Table 1 provides the sorption data of some lithium ceramics from literature.

TABLE 1

SORPTION DATA OF LITHIUM CERAMICS REPORTED IN LITERATURE

Material	T_{ads} (°C)	T_{des} (°C)	P_{CO_2} (bar)	P_{Total} (bar)	Sorption capacity (wt% CO_2)	Gas Composition	Ref
Nano t-Li_2ZrO_3	575	800	1	-	27.00	-	21
Li_2CO_3/K_2CO_3 -doped Li_2ZrO_3	550	800	-	-	23.00	60% CO_2 40% N_2	22
Yttria-doped Li_2ZrO_3	754	-	-	1	29.87	100% CO_2	23
Nano Li_2ZrO_3	550	650	0.5	1	26.00	CO_2+ N_2	24
Li_2ZrO_3	600	680	1	-	22.00	CO_2+ Ar	25
Li_2ZrO_3 Powder	450	-	-	-	26.28	-	27
Nano Li_2ZrO_3	575	650	1	-	27.00	100% CO_2	31
Na-doped Li_2ZrO_3	650	800	-	-	~20.00	100% CO_2	32

Porous Nano Li_2ZrO_3	575	690	1	-	22.00	100% CO_2	33
K-Li_2ZrO_3	550	650	0.25	1	22.00	CO_2+ N_2	36
Eutectic salt doped Li_2ZrO_3	700	850	-	-	12.00	-	38
$LiNaZrO_3$	600	-	-	-	19.60	100% CO_2	39
$Li_{3.7}Fe_{0.1}SiO_4$	650	800	1	-	28.8	100% CO_2	43
Li_4SiO_4	500	-	-	-	~26.00	20% CO_2 80% air	45
Nano Li_4SiO_4	610		-	1	25.8	100% CO_2	46
Li_4SiO_4 (diatomite)	700				34.2	50% CO_2 50% N_2	47
Li_4SiO_4 (3 µm)	600	-	-	-	37.4	100% CO_2	50
Li_4SiO_4 (diatomite)	700		-	-	28.62	-	53
Li_4SiO_4 (rice husk ash)	680	800	-	1	30.5	100% CO_2	55
Li_4SiO_4	580	750		1	27.0	4% CO_2 96% N_2	56
$Li_{3.85}Na_{0.15}SiO_4$	680	-	-	-	19.3	-	58
K- Li_4SiO_4	580	700	0.4	1	23.0	4% CO_2 96% N_2	60

4.0 CONCLUDING REMARKS AND PROSPECTS

Adsorption technology has been widely investigated as a means of an alternative to absorption technology that is having many formidable problems. Lithium ceramics such as Li_2ZrO_3 and Li_4SiO_4 are emerging materials, which are considered as strong candidates for developing commercially competitive CO_2 adsorbent. The advantages of these materials include large sorption capacity, attractive temperature window, small volume change during the CO_2 sorption / desorption cycles, selectivity, low regeneration energy compared to CaO, cyclic stability and thermal stability.

Li_2ZrO_3 and Li_4SiO_4 are extensively studied by few research groups. Few studies on other members of family indicate the opportunities for future research. Dependency of sorption property on structure and synthesis has driven the research towards development of nano particles and novel synthesis routes. However, nano particles may pose many challenges in industrial applications such as pressure drop due to particle agglomerations, rapid morphological changes, and susceptibility to tracer impurities. Hence, these challenges need to be addressed for practical applications of these materials. Novel materials and synthesis routes call for process optimization, scalability, and repeatability.

Most of the studies have been carried out in situ laboratory conditions. Little information is available about applicability of these materials in real flue gas conditions. There are only few studies under simulated SERP conditions, necessitating further study on stability of the material under large hydrothermal pressure and compatibility with SERP catalysts. The effects of CO_2 flow rate, concentration, temperature and pressure on sorbent performance were found to be complex. Optimization of these parameters is necessary for realistic CO_2 capture operations. The low kinetics of lithium ceramics materials remains as a major challenge in spite of great efforts to enhance the rate of sorption, providing future scope for fundamental as well as applied research.

REFERENCES

[1] B P Spigarelli and S K Kawatra, Opportunities and challenges in carbon dioxide capture, Journal of CO_2 Utilization, Vol. 1, Pp; 69, 2013.

[2] H Yang, Z Xu, M Fan, R Gupta, R B Slimane, A E Bland and I Wright, Progress in Carbon dioxide Separation and Capture: A review, J.Environ.Sci, Vol. 20, Pp; 14, 2008.

[3] S.A Rackley, Carbon Capture and Storage, Butterworth -Heinemann, Burlington, Pp; 67-75, 2010.

[4] T C Drage, C E Snape, L A Stevens, J Wood, J Wang, A I Cooper, R Dawson, X GuO, C Satterley and R Irons, Materials Challenges for the Development of Solid Sorbents for Post-Combustion Carbon Capture, J.Mater. Chem, Vol. 22, Pp; 2815, 2012.

[5] Y Lara, A Martínez, P Lisbona, I Bolea, A González and L M Romeo, Using the Second Law of Thermodynamic to Improve CO_2 Capture Systems, Energy. Procedia, Vol. 4, Pp; 1043, 2011.

[6] M Goel, Carbon Capture and Storage Technology for Sustainable Energy.

[7] J D Figueroa, T Fout, S Plasynski, H McIlvried and RD Srivastava, Advances in CO_2 Capture Technology—The U.S. Department of Energy's Carbon Sequestration Program, Int. J. Greenh. Gas Control, Vol. 2, Pp; 9, 2008.

[8] A Kargari and M T Ravanchi, Carbon Dioxide : Capturing and Utilization

[9] J Davison and K Thambimuthu, Technologies for Capture of Carbon Dioxide

[10] S Wong and R Bioletti, Carbon Dioxide Separation Technologies

[11] B J Maring and P A Webley, A New Simplified Pressure/Vacuum Swing Adsorption Model for Rapid Adsorbent Screening for CO_2 Capture Applications, Int. J. Greenh. Gas Control, Vol. 15, Pp; 16, 2013.

[12] M Songolzadeh, M T Ravanchi and M Soleimani, Carbon Dioxide Capture and Storage: A General Review on Adsorbents, WASET, Vol. 70, Pp; 225, 2012.

[13] A Samanta, A Zhao, GKH Shimizu, P Sarkar and R Gupta, Post-Combustion CO_2 Capture Using Solid Sorbents: A Review, Ind. Eng. Chem. Res, Vol. 51, Pp; 1438, 2012.

[14] A Sayari, Y Belmabkhout and R Serna-Guerrero, Flue Gas Treatment via CO_2 Adsorption, Chem. Eng. J, Vol. 171, Pp; 760, 2011.

[15] R Singh, M K R Reddy, S Wilson, K Joshi, J C D d Costa and P Webley, High Temperature Materials for CO_2 Capture, Energy. Procedia, Vol. 1, Pp; 623, 2009.

[16] B Feng, H An and E Tan, Screening of CO_2 Adsorbing Materials for Zero Emission Power Generation Systems, Energ. Fuel, Vol. 21, Pp; 426, 2007.

[17] Q Wang, J Luo, Z Zhong and ABorgna, CO_2 Capture by Solid Adsorbents and their Applications: Current Status and New Trends, Energy. Environ. Sci, Vol. 4, Pp; 42, 2011.

[18] K B Lee, M G Beaver, H S Caram and S Sircar, Reversible Chemisorbents for Carbon Dioxide and their Potential Applications, Ind. Eng. Chem. Res, Vol. 47, Pp; 8048, 2008.

[19] J O Landeros, T L A-Rendon, C G Yanez and H Pfeiffer, Analysis and Perspectives Concerning CO_2 Chemisorption on Lithium Ceramics using Thermal Analysis, J Therm Anal Calorim, Vol. 108, Pp; 647, 2012.

[20] H Pfeiffer, Advances on Alkaline Ceramics as Possible CO_2 Captors, Vol. 1056, Pp; 233-253, 2010.

[21] E O Fernandez, M Ronning, T Grande and D Chen, Synthesis and CO_2 Capture Properties of Nanocrystalline Lithium Zirconate, Chem. Mater, Vol. 18, Pp; 6037, 2006.

[22] G Pannocchia, M Puccini, M Seggiani and S Vitolo, Experimental and Modeling Studies on High-Temperature Capture of CO_2 Using Lithium Zirconate Based Sorbents, Ind. Eng.Chem. Res, Vol. 46, Pp; 6696, 2007.

[23] A Iwan, H Stephenson, W C Ketchie and A A Lapkin, High Temperature Sequestration of CO_2 Using Lithium Zirconates, Chem. Eng. J, Vol. 146, Pp; 249, 2009.

[24] Q Xiao, Y Liu, Y Zhong and W Zhu, A Citrate Sol–Gel Method to Synthesize Li_2ZrO_3 Nanocrystals with Improved CO_2 Capture Properties, J. Mater. Chem, Vol. 21, Pp; 3838, 2011.

[25] E O-Fernandez, H K Rusten, H A Jakobsen, M Rønning, A Holmen and D Chen, Sorption Enhanced Hydrogen Production by Steam Methane Reforming using Li_2ZrO_3 as Sorbent: Sorption Kinetics and Reactor Simulation, Catalysis Today, Vol. 106, Pp; 41, 2005.

[26] S Wang, C An and Q H Zhang, Syntheses and Structures of Lithium Zirconates for High-Temperature CO_2 Absorption, J. Mater. Chem, Vol. 1, Pp; 3450, 2013.

[27] B N Nair, T Yamaguchi, H Kawamura and S-I Nakao, Processing of Lithium Zirconate for Applications in Carbon Dioxide Separation: Structure and Properties of the Powders, J. Am. Ceram. Sac, Vol. 87, Pp; 68, 2004.

[28] B N Nair, R P Burwood, V J Goh, K Nakagawa and T Yamaguchi, Lithium Based Ceramic Materials and Membranes for High Temperature CO_2 Separation, Prog. Mater Sci., Vol. 54, Pp; 511, 2009.

[29] J-I Ida, R Xiong and Y S Lin, Synthesis and CO_2 Sorption Properties of Pure and Modified Lithium Zirconate, Sep. Purif. Technol,Vol. 36, Pp; 41, 2004.

[30] S-Z Kang, T Wu , X Li and J Mu, Low Temperature Biomimetic Synthesis of the Li_2ZrO_3 Nanoparticles Containing $Li_6Zr_2O_7$ and High Temperature CO_2 Capture, Mater. Lett, Vol. 64, Pp; 1404, 2010.

[31] E O Fernandez, M Ronning, T Grande and D Chen, Nanocrystalline Lithium Zirconate with Improved Kinetics for High-Temperature CO_2 Capture, Chem. Mater, Vol. 18, Pp; 1383, 2006.

[32] M Khokhani, R B Khomane and B D Kulkarni, Sodium-Doped Lithium Zirconate Nano Squares: Synthesis, Characterization and Applications for CO_2 Sequestration, J Sol-Gel Sci Technol, Vol. 61, Pp; 316, 2012.

[33] H R Radfarnia and M C Iliuta, Surfactant-Template/Ultrasound-Assisted Method for the Preparation of Porous Nanoparticle Lithium Zirconate, Ind. Eng. Chem. Res, Vol. 50, Pp; 9295, 2011.

[34] R Xiong, J Ida and Y S Lin, Kinetics of Carbon Dioxide Sorption on Potassium-Doped Lithium Zirconate, Chem. Eng. Sci,Vol. 58, Pp; 4377, 2003.

[35] J Ida and Y S Lin, Mechanism of High-Temperature CO_2 Sorption on Lithium Zirconate, Environ. Sci. Technol,Vol. 37, Pp; 1999, 2003.

[36] Q Xiao, X Tang, Y Zhong and W Zhu, A Facile Starch-Assisted Sol–Gel Method to Synthesize K-Doped Li_2ZrO_3 Sorbents with Excellent CO_2 Capture Properties, J. Am. Ceram. Soc, Vol. 95, Pp; 1444, 2012.

[37] M O-Marin, M C-Diaz, T C Drage and M M Maroto-Valer, Use of Small-Amplitude Oscillatory Shear Rheometry to Study the Flow Properties of Pure and Potassium-Doped Li_2ZrO_3 Sorbents During the Sorption of CO_2 at High Temperatures, Sep.Purif. Technol, Vol. 73, Pp; 415, 2010.

[38] D J Fauth, E A Frommell, J S Hoffman, R P Reasbeck and H W Pennline, Eutectic Salt Promoted Lithium Zirconate: Novel High Temperature Sorbent for CO_2 capture, Fuel Process. Technol, Vol. 86, Pp; 1503, 2005.

[39] H Pfeiffer, C Vazquez, V H Lara and P Bosch, Thermal Behavior and CO_2 Absorption of $Li_{2-x}Na_xZrO_3$ Solid Solutions, Chem. Mater, Vol. 19, Pp; 922, 2007.

[40] M Y V-Enriquez, G Gonzalez and H Pfeiffer, Synthesis and CO_2 Capture Evaluation of $Li_{2_x}K_xZrO_3$ Solid Solutions and Crystal Structure of a New Lithium–Potassium Zirconate Phase, J. Solid State Chem,Vol. 180, Pp; 2485, 2007.

[41] K Essaki and M Kato, Influence of Temperature and CO_2 Concentration on the CO_2 Absorption Properties of Lithium Silicate Pellets, J. Mater. Sci. Lett, Vol. 40, Pp; 5017, 2005.

[42] M Kato, K Nakagawa, K Essaki, Y Maezawa, S Takeda, R Kogo and Y Hagiwara, Novel CO_2 Absorbents Using Lithium-Containing Oxide, Int. J. Appl. Ceram. Technol, Vol. 2, Pp; 467, 2005.

[43] C Gauer and W Heschel, Doped Lithium Orthosilicate for Absorption of Carbon Dioxide, J. Mater. Sci,Vol. 41, Pp; 2405, 2006.

[44] K Essaki, M Kato and K Nakagawa, CO_2 Removal at High Temperature Using Packed Bed of Lithium Silicate Pellets, J. Ceram. Soc. Jpn, Vol. 114, Pp; 739, 2006.

[45] M Kato, K Nakagawa and S Yoshikawa, Carbon Dioxide Absorption by Lithium Ortho silicate in a Wide Range of Temperature and Carbon Dioxide Concentrations, J. Mater. Sci. Lett, Vol. 21, Pp; 485, 2002.

[46] R B Khomane, B K Sharma, S Saha and B. D Kulkarni, Reverse Microemulsion Mediated Sol–Gel Synthesis of Lithium Silicate Nanoparticles Under Ambient Conditions: Scope for CO_2 Sequestration, Chem. Eng. Sci, Vol. 61, Pp; 3415, 2006.

[47] S Y Shan, S M Li, Q M Jia, L H Jiang, Y M Wangand J H Peng, Impregnation Precipitation Preparation and Kinetic Analysis of Li_4SiO_4 Based Sorbents with Fast CO_2 Adsorption Rate, Ind. Eng. Chem. Res,Vol. 52, Pp; 6941, 2013.

[48] IC R-Ibarra, J O-Landeros and H Pfeiffer, Microstructural and CO_2 Chemisorption Analyses of Li_4SiO_4: Effect of Surface Modification by the Ball Milling Process, Thermochim Acta, Vol. 567, Pp; 118, 2013.

[49] M E Bretado, V G Velderrain, D L Gutierrez, V C Martinez and A L Ortiz, A New Synthesis Route to Li_4SiO_4 as CO_2 Catalytic/Sorbent, Catal. Today, Vol. 107, Pp; 863, 2005.

[50] M J Venegas, E F-Israel, R Escamilla and H Pfeiffer, Kinetic and Reaction Mechanism of CO_2 Sorption on Li_4SiO_4: Study of the Particle Size Effect, Ind. Eng. Chem. Res, Vol. 46, Pp; 2407, 2007.

[51] M O-Marin, T C Drage and M MM-Valer, Novel Lithium-Based Sorbents from Fly Ashes for CO_2 Capture at High Temperatures,Int. J. Greenh. Gas Control, Vol. 4, Pp; 623, 2010.

[52] S Y Shan, Q M Jia, L H Jiang, Q C Li, Y M Wang and J H Peng, Novel Li_4SiO_4-Based Sorbentsfrom Diatomitefor High Temperature CO_2 Capture, Ceram. Int, Vol. 39, Pp; 5437, 2013.

[53] S Y Shan, S M Li, Q M Jia, L H Jiang, Y M Wangand J H Peng, Preparation and Kinetic Analysis of Li_4SiO_4 Sorbents with Different Silicon Sources for High Temperature CO_2 Capture, Mater. Sci, Vol. 57, Pp; 2475, 2012.

[54] K Wang, X Guo, P Zhao, F Wang and C Zheng, High Temperature Capture of CO_2 on Lithium-Based Sorbents from Rice Husk Ash, J. Hazard. Mater, Vol. 189, Pp; 5301, 2011.

[55] K Wang, P Zhao, X Guo, Y Li, D Han and Y Chao, Enhancement of Reactivity in Li_4SiO_4-based Sorbents from the Nano-Sized Rice Husk Ash for High-Temperature CO_2 Capture, Energ. Convers. Manage,Vol. 81, Pp; 447, 2014.

[56] M Seggiani, M Puccini and S Vitolo, High-Temperature and Low Concentration CO_2 Sorption on Li_4SiO_4 Based Sorbents: Study of the Used Silica and Doping Method Effects, Int. J. Greenh. Gas Control,Vol. 5, Pp; 741, 2011.

[57] H Xu, W Cheng, X Jin, G Wang, H Lu, H Wang, D Chen, B Fan, T Hou and R Zhang, Effect of the Particle Size of Quartz Powder on the Synthesis and CO_2 Absorption Properties of Li_4SiO_4 at High Temperature, Ind. Eng. Chem. Res,Vol. 52, Pp; 1886, 2013.

[58] V L M-Trejo, E F-Israel and H Pfeiffer, Textural, Structural and CO_2 Chemisorption Effects Produced on the Lithium Orthosilicate by Its Doping with Sodium ($Li_{4-x}Na_xSiO_4$), Chem. Mater, Vol. 20, Pp; 7171, 2008.

[59] P V Korake and A G Gaikwad, Capture of Carbon Dioxide Over Porous Solid Adsorbents Lithium Silicate, Lithium Aluminate and Magnesium Aluminate at Pre-Combustion Temperatures, Front Chem. Sci. Eng,Vol. 5, Pp; 215, 2011.

[60] M Seggiani, M Puccini and S Vitolo, Alkali Promoted Lithium Orthosilicate for CO_2 Capture at High Temperature and Low Concentration, Int. J. Greenh. Gas Control, Vol. 17, Pp; 25, 2013.

[61] Y Duan, H Pfeiffer, B Li, I.C R-Ibarra, D C Sorescu, D R Luebkea and J. W Halleyd, CO_2 Capture Properties of Lithium Silicates with Different Ratios of Li_2O/SiO_2: an Ab Initio Thermodynamic and Experimental Approach, Phys. Chem. Chem. Phys, Vol. 15, Pp; 13538, 2013.

[62] R R-Mosqueda and H Pfeiffer, Thermo-kinetic Analysis of the CO_2 Chemisorption on Li_4SiO_4 by Using Different Gas Flow Rates and Particle Sizes, J. Phys. Chem. A,Vol. 114, Pp; 4535, 2010.

[63] Z Qi, H Daying, L Yang, Y Qian and ZZibin, Analysis of CO_2 Sorption/ Desorption Kinetic Behaviors and Reaction Mechanisms on Li_4SiO_4, AIChE Journal, Vol. 59, Pp; 901, 2013.