

Li₄SiO₄-based Adsorbents for CO₂ Capture at High Temperature: Performance Enhancement by Ball Milling Process

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Post-combustion capture technologies based on regenerable solid sorbents are attracting increasing attention as ways to reduce CO₂ emissions. The present study focused on the fabrication at industrial lab-scale of lithium orthosilicate (Li₄SiO₄) sorbents for CO₂ capture at high temperature and low concentration. The ball milling process was used during the reagents mixing phase to modify the microstructure of the obtained Li₄SiO₄ powders. The CO₂ sorption properties of the sorbents were studied in a controlled gas flow environment at low CO₂ concentration (4 vol%). The effect of different milling times (0-120 min) on the sorption performance of the sorbents was investigated together with the effect of the adsorption temperature (470-570 °C) by using the Response Surface Methodology, and predictive models for the Li₄SiO₄ conversion and the adsorption rate were developed. The results evidenced that the ball milling process increased the pure Li₄SiO₄ sorption performance, reaching a maximum sorption capacity of 156 mg CO₂/g sorbent for 80 min of milling and adsorption temperature of 515 °C.

1. Introduction

Currently, a lot of research efforts are focusing on carbon capture technologies as ways to reduce carbon dioxide (CO₂) emissions since they can be applied to power generation and industrial processes using fossil fuels to lower their carbon intensity and improve their environmental sustainability, representing one of the mitigation strategies of global energy transitions (Raganati et al., 2021). Post-combustion CO₂ capture based on regenerable solid sorbents can be a feasible technology for reducing CO₂ emissions of power plants, especially at low carbon content (Nedoma and Netušil, 2021). Among the emerging solid sorbents, metal-oxide-based ceramics allow the separation of CO₂ at temperatures typical of a power generation plant (450-750 °C) compared to zeolites, porous carbons, metal organic frameworks, and amine-functionalized adsorbents that operate only at low temperatures (from ambient to approximately 100 °C) (Ghani et al., 2022; Raganati et al., 2021; Zainol et al., 2021). Operating at high temperatures, they do not require further cooling processes, overcoming the main disadvantages related to the most commonly used wet-absorption methods. Moreover, the regeneration of the sorbent allows the process to be conducted continuously and to reduce the production of wastes (Chao et al., 2021). Lithium orthosilicate (Li₄SiO₄) is found as one of the most interesting materials for this application, showing potential use in integrated carbon capture and utilization (ICCU) processes for the in-situ CO₂ removal and conversion in value-added products (Tong et al., 2022). Li₄SiO₄ can capture reversibly CO₂ following the adsorption/desorption reaction:



Li₄SiO₄ combines a good sorption capacity (0.367 g CO₂/g sorbent) with lower costs and lower regeneration temperatures (< 700 °C) than other ceramic materials. Nevertheless, the application of pure Li₄SiO₄ under typical industrial operating conditions of low CO₂ concentration (e.g. 4 vol% CO₂ in the natural gas power plants) is still an open issue owed to its poor reactivity and conversion rate under these conditions (Hu et al., 2019; Tong et al., 2022; Yan et al., 2019). Kinetic limitations of the adsorption process at low CO₂ concentrations are

mainly due to the CO₂ diffusion resistance through the solid shell of reaction products, i.e. lithium carbonate (Li₂CO₃) and lithium metasilicate (Li₂SiO₃), that covers the Li₄SiO₄ particle. Therefore, several modification methods have been reported in literature for enhancing the performance of pure Li₄SiO₄ sorbents, such as microstructural modifications and doping of the sorbent with alkali carbonates, transition metals, or alkali-earth metals (Hu et al., 2019). Recent works have studied the effect of ball milling to reduce the particle size of pure Li₄SiO₄ on the final sorbent properties and the adsorption reaction kinetic (Romero-Ibarra et al., 2013; Yang et al., 2020), while other studies dealt with the use of hydration, organic acid treatment, or organic lithium precursors for increasing the sorbent surface area and thus enhancing the sorption performance of pure Li₄SiO₄ (Hu et al., 2019).

In this study, pure Li₄SiO₄ sorbents were fabricated at industrial lab-scale employing the ball milling process during the precursors mixing phase. The milling time and the adsorption temperature were varied, and the Li₄SiO₄ adsorption properties were tested in a thermal gravimetric analyzer for CO₂ capture at high temperature (470-570 °C) and low concentration (4 vol%). Scanning electron microscopy was used to characterize the prepared sorbents and to understand the relationship among milling time, sorbent microstructure, and CO₂ sorption properties. The Response Surface Methodology was applied for evaluating the optimal operating conditions to obtain high CO₂ adsorption performance.

2. Experimental

2.1 Sorbents production and characterization

Li₄SiO₄ sorbents were prepared according to the solid-state method, as reported in our previous works (Puccini et al., 2013; Seggiani et al., 2018). A scale-up of the production method at industrial lab-scale was carried out, and the wet milling process was employed both for obtaining the reagent mixture and to modify the microstructure of the final sorbents. Li₂CO₃ (technical grade, SQM Lithium) and crystalline silicon dioxide (SiO₂, Silica SA800 PO technical grade, 0.6-7.4 μm powder, Sibelco) were used as starting materials. First, the reagents (Li:Si molar ratio of 4:1) were ground and dispersed in water in a 300 mL ceramic jar equipped with zirconia spheres (ZrO₂, 5 mm of diameter) by using a planetary ball mill. The total solid content was 30 wt%, and the ball charge/solids weight ratio was 13/1. Different milling times were tested (0-60-120 min) at a speed rate of 520 rpm. After that, the obtained suspensions were collected and dried at 110 °C overnight. The reference suspension (milling time = 0 min) was prepared by mixing the reagents in the ceramic jar with water for only 60 seconds to ensure homogeneous mixing. Finally, the reagent powders were calcined in air at 900 °C for 4 h with temperature increase and decrease ramping rates of 60 °C/h. The resulting powders were dry milled for 60 seconds in the ceramic jar to break down any agglomeration due to the calcining step. The sorbents obtained by grinding the starting reagents for 0, 60, and 120 min were named LC, LC-60, and LC-120, respectively.

The particle size distributions of the reagent mixtures were monitored analyzing the suspensions after the wet milling process with a laser particle size analyzer (Mastersizer 300, Malvern). Powder X-ray diffraction (XRD) characterization of the prepared sorbents was performed using a Bruker D2 Phaser diffractometer with Cu-Kα radiation to determine the phase composition and verify the formation of crystalline Li₄SiO₄. The XRD patterns were recorded in a 2θ range of 10-65°. The sorbents particle size and morphology was examined by scanning electron microscopy (SEM) using a FEI Quanta FEG 450. The samples were previously coated with a homogeneous Pt layer of 5-6 nm thickness to induce electro conductivity.

2.2 CO₂ adsorption tests

The CO₂ adsorption performance of Li₄SiO₄ sorbents was studied by using a thermogravimetric analyzer (TA Instruments TGA Q500) operating at atmospheric pressure. Dynamic adsorption/desorption tests were first carried out to determine the adsorption temperature range for the subsequent isothermal adsorption tests. The samples were heat-treated from 40 to 800 °C (heating rate of 5 °C/min) under 4 vol% CO₂ gas flow (N₂ balance). Isothermal adsorption tests were then performed heating each sorbent (about 25 mg) to the selected adsorption temperature (varied between 470 and 570 °C) under a nitrogen flow of 100 mL/min at 20 °C/min. When the sample weight became stable, the total feed gas flow rate (100 mL/min) was changed to a CO₂/N₂ mixture containing 4 vol % of CO₂ and maintained for 120 min. The samples weight increase owed to CO₂ sorption was registered as a function of time, and the percentage conversion of Li₄SiO₄ was calculated as in Eq(2), where ΔW is the percentage weight change of the sorbent after 120 min of adsorption, and r_s is the stoichiometric CO₂ uptake by Li₄SiO₄ (0.367 g CO₂/g Li₄SiO₄). Besides, to assess the regeneration of the sorbents, the temperature was raised to 660 °C (at 20 °C/min), switching the feed gas to pure N₂, and maintained for 20 min.

$$X_{Li_4SiO_4} (\%) = \frac{\Delta W}{r_s} \quad (2)$$

2.3 Experimental design methodology

CO₂ adsorption properties of the produced Li₄SiO₄ sorbents were assessed applying the Design of Experiments (DoE) methodology. A Response Surface Method (RSM) DoE was developed in order to identify possible non-linear interactions between the sorbent synthesis conditions and the adsorption operating conditions. The experimental design was performed according to a 2² full-factorial randomized Central Composite Design (CCD) with 1 replicate, 4 axial points, and 4 replicates at the center point using the software Design Expert® 13 (Stat-Ease). The milling time (A) and the adsorption temperature (B) were selected as independent variables and were varied between a low (0 min; 470 °C) and a high level (120 min; 570 °C). A milling time greater than 120 min was not considered since preliminary tests have demonstrated that the sorbent morphology almost resulted unchanged, while the adsorption temperature range was chosen by the dynamic adsorption study results. The analyzed responses were Li₄SiO₄ conversion after 120 min of adsorption (Y₁) and the initial adsorption rate (Y₂, measured between 0.5 and 5 min). The experimental design matrix consisted of 2² + 4 + 4 = 12 runs.

3. Results and discussion

3.1 Sorbents characterization and CO₂ adsorption tests

For understanding the effect of the wet milling process on the sorbents fabrication method, the particle size both of the reagent powders before calcining and the final calcined sorbents was analyzed. All the reagent mixtures have shown a normal particle size distribution. The reference sample (milling time = 0 min) exhibits a median volume diameter (Dv50) of the particles of 2.50 μm whereas the samples grinded for 60 and 120 min present a Dv50 of 1.37 and 1.08 μm, respectively, showing a reduction in particle size with increasing the milling time, as expected. After the calcining step, SEM analysis was employed to observe the particle size and the surface morphology of sorbents, and the results are reported in Figure 1. The LC sorbent (Figure 1a) displays agglomerates with sizes of about 20-30 μm of dense particles with lesser dimensions (2-5 μm of diameter). For the wet milled sorbents LC-60 and LC-120, a reduction in the dense particles dimension can be observed with sizes even below 1 μm (Figures 1b,c), evidencing that the milling process could effectively reduce the particle size of the calcined sorbents. However, the particles result agglomerated in clusters approximately 20-30 μm diameter (as for the reference sorbent), which is probably owed to the severe synthesis conditions (900 °C for 4 h) that promote the sintering of the particles. The phase composition of obtained sorbents was investigated by XRD analysis, and the diffraction patterns are shown in Figure 2. All the sorbents exhibit the characteristic peaks of Li₄SiO₄ crystalline phase, indicating that the reagents have reacted completely. The wet milled sorbents present small peaks attributed to Li₂SiO₃ and lithium zirconate (Li₂ZrO₃), and their intensity slightly increase with increasing grinding time. The presence of Li₂ZrO₃ can be explained by considering the abrasion phenomena of the spheres in a planetary ball mill (Song et al., 2018): the ZrO₂ released during grinding could react with Li₂CO₃, leading to the formation of Li₂ZrO₃. Whereas, Li₂SiO₃ could be formed by sub-stoichiometric reaction between Li₂CO₃ and SiO₂. Lithium zirconate is capable of capturing CO₂ at high temperature (Hu et al., 2019), and its presence could improve the overall sorption capacity of the sorbent.

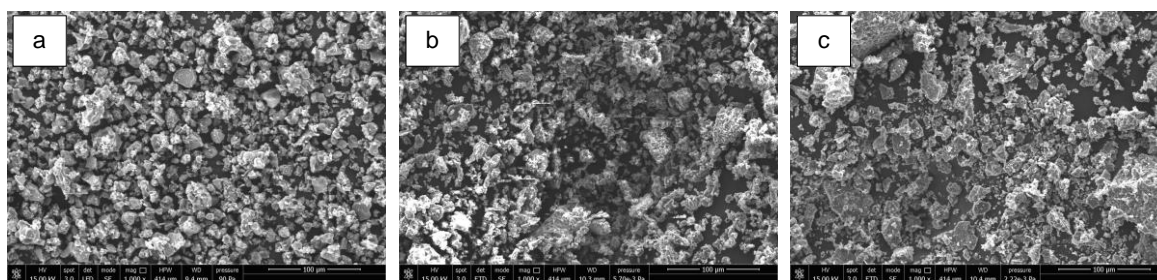


Figure 1: SEM images of Li₄SiO₄ sorbents: (a) LC, (b) LC-60, and (c) LC-120.

The temperature range for the experimental design CO₂ adsorption tests in 4 vol% CO₂ stream was selected by carrying out dynamic adsorption/desorption experiments on the produced sorbents at different milling times, and the thermograms are shown in Figure 3a. The weight of the sorbents starts to increase at 420-450 °C, then increases with raising the temperature and reaches the highest value at a temperature of about 575 °C. With a further increase in temperature, the weight of the sorbents decreases indicating that the desorption process occurs. Therefore, the isothermal tests were investigated in the range 470-570 °C to ensure the adsorption process occurs. The CCD experimental design matrix for the CO₂ adsorption tests on Li₄SiO₄ sorbents along with the responses results (Li₄SiO₄ conversion after 120 min and initial adsorption rate) are reported in Table 1. The adsorption performance results were also displayed in Figure 3b. All the sorbents exhibit a typical gas-solid

reaction profile, with an initial fast reaction stage (high adsorption rates) followed by a slow reaction stage owed to an increase in the CO_2 diffusive resistance associated to the formation of the carbonation products solid layer, i.e. Li_2CO_3 and Li_2SiO_3 , on the Li_4SiO_4 surface, which makes the adsorption process diffusion-controlled. As shown, the Li_4SiO_4 conversion increases with increasing the milling time when the temperature is 570°C , while at lower temperatures $X_{\text{Li}_4\text{SiO}_4}$ presents a maximum for the sample LC-60. Moreover, the adsorption performance is enhanced when the adsorption temperature is 520°C , reaching a conversion of about 43 % (corresponding to a sorption capacity of $158\text{ mg CO}_2/\text{g sorbent}$). All sorbents evidence also good regenerability since the CO_2 is desorbed completely during the regeneration process.

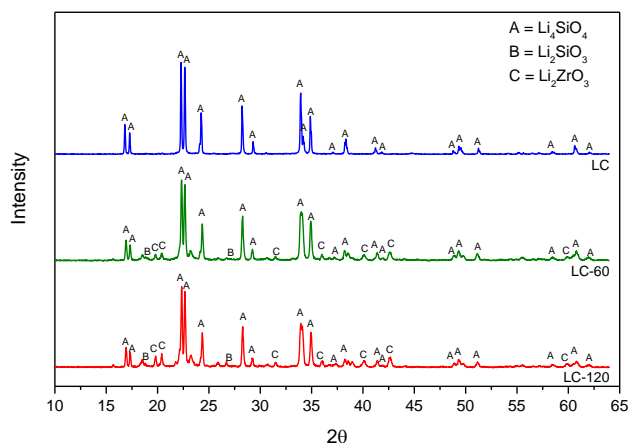


Figure 2: XRD patterns of Li_4SiO_4 sorbents: LC, LC-60, and LC-120.

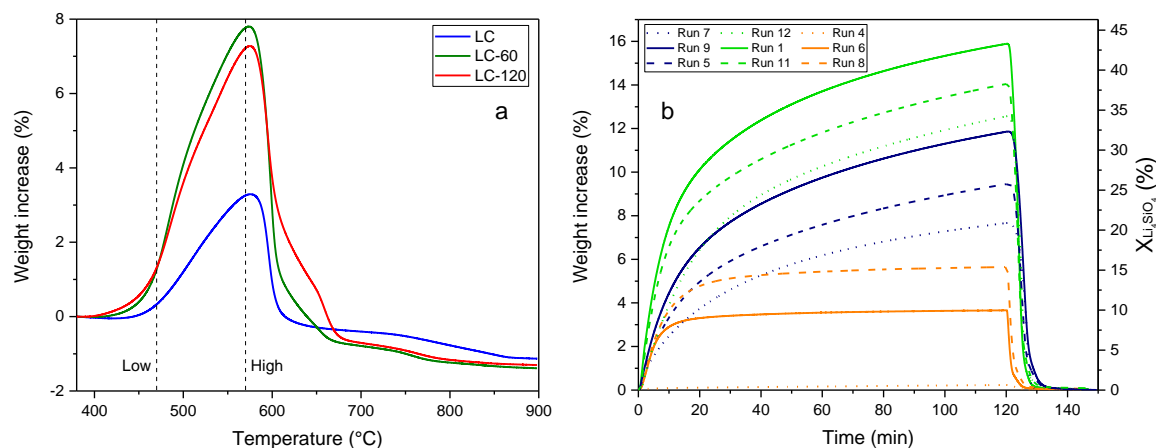


Figure 3: CO_2 adsorption performance of Li_4SiO_4 sorbents in 4 vol% CO_2 stream: (a) dynamic tests and (b) DoE isothermal experiments at different milling times (0-120 min) and adsorption temperatures (470 - 570°C).

Table 1: Experimental design matrix and responses results.

Run	A-factor Milling time (min)	B-factor Adsorption temperature ($^\circ\text{C}$)	Response 1 $X_{\text{Li}_4\text{SiO}_4}$ (%)	Response 2 Adsorption rate (1/min)
1	60	520	43.26	0.0279
2	60	520	41.34	0.0265
3	60	520	43.23	0.0274
4	0	570	0.6377	0.000262
5	120	470	25.73	0.0118
6	60	570	9.968	0.0117
7	0	470	20.87	0.00901
8	120	570	15.38	0.0131
9	60	470	32.28	0.0154
10	60	520	36.81	0.0249
11	120	520	38.25	0.0243
12	0	520	34.20	0.0122

3.2 Parametric models and statistical analysis

To investigate the combined effect of the sorbent synthesis conditions and the adsorption operating conditions, the CCD responses results of Table 1 were implemented into the Design Expert® 13 software. Regression calculations were performed to obtain polynomial models that best fit the experimental results. Main and interaction effects were calculated for each model term, and statistic values were determined. The statistical significance of the selected models was verified by applying the analysis of variance (ANOVA), and the results for both responses are reported in Table 2. The obtained models result both statistically significant (p -value < 0.05), with an insignificant lack of fit (p -value > 0.05) and high values of adjusted R^2 (> 0.95). The final parametric models in terms of coded factors for Li_4SiO_4 conversion and adsorption rate are given by Eq(3) and Eq(4), respectively. For both responses, a quadratic model was found to best fit the experimental data. The relationship between factors and responses can be visualized through three-dimensional (3D) response surface plots (Figure 4). According to ANOVA results (Table 2) and the model equations, the adsorption temperature is the variable that most affects both the Li_4SiO_4 conversion and the adsorption rate, and it demonstrates a quadratic effect on the responses (due to B^2 term) visible by a curvature in the model graphs of Figure 4.

Table 2: ANOVA results of Li_4SiO_4 conversion and adsorption rate responses for RSM DoE.

	Y ₁ - Li_4SiO_4 conversion				Y ₂ - Adsorption rate			
	Sum of Squares	df	F-value	p-value	Sum of Squares	df	F-value	p-value
Model	2088.71	4	45.82	< 0.0001	$8.511 \cdot 10^{-4}$	5	54.22	< 0.0001
A	93.21	1	8.18	0.0243	$1.286 \cdot 10^{-4}$	1	40.96	0.0007
B	466.20	1	40.91	0.0004	$2.074 \cdot 10^{-5}$	1	6.61	0.0423
AB	-*	-*	-*	-*	$2.497 \cdot 10^{-5}$	1	7.95	0.0304
A ²	72.22	1	6.34	0.0400	$1.196 \cdot 10^{-4}$	1	38.09	0.0008
B ²	1099.31	1	96.46	< 0.0001	$3.464 \cdot 10^{-4}$	1	110.33	< 0.0001
Residual	79.77	7			$1.884 \cdot 10^{-5}$	6		
Lack of Fit	52.06	4	1.41	0.4052	$1.362 \cdot 10^{-5}$	3	2.61	0.2258
Pure Error	27.72	3			$5.217 \cdot 10^{-6}$	3		
R ²	0.9632				0.9783			
Adjusted R ²	0.9422				0.9603			

* AB is not reported for the response Y₁ since it was evaluated as not significant by the ANOVA (p -value = 0.1551 > 0.05).

$$Y_1 = 41.25 + 3.942 \cdot A - 8.815 \cdot B - 5.204 \cdot A^2 - 20.30 \cdot B^2 \quad (3)$$

$$Y_2 = 2.609 \cdot 10^{-2} + 4.629 \cdot 10^{-3} \cdot A - 1.859 \cdot 10^{-3} \cdot B + 2.498 \cdot 10^{-3} \cdot AB - 6.696 \cdot 10^{-3} \cdot A^2 - 1.140 \cdot 10^{-2} \cdot B^2 \quad (4)$$

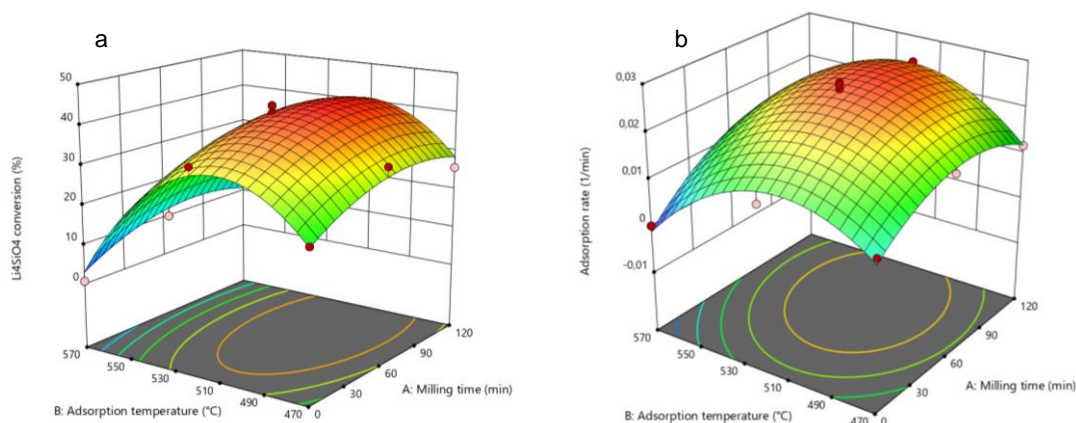


Figure 4: 3D response surface graphs obtained by RSM analysis for (a) Li_4SiO_4 conversion and (b) adsorption rate as function of milling time and adsorption temperature.

As shown, both responses increase with increasing the adsorption temperature, reaching a maximum at about 520 °C. Then, they decrease as the temperature increases from 520 to 570 °C. This result could be associated with the reaction thermodynamic, for which the proximity to the equilibrium temperature (about 575 °C) leads to the not negligible presence of the desorption process, thus reducing the performance of the sorbents. The milling time influences less markedly the Li_4SiO_4 conversion and the adsorption rate, however exhibiting a quadratic effect on both responses (owed to A^2 term). Either conversion and rate display a maximum for milling times between 60 and 120 min at 520 °C. This result could be attributed to the particle size reduction obtained by

employing the wet milling process, as observed by SEM analysis (Figure 1). As shown, milling times of 60 and 120 min leads to sorbents with smaller particle size and thus to higher contact areas (surface area) between the sorbent particles and the CO₂ molecules. The larger surface area obtained with the milling process could produce a higher CO₂ direct chemisorption, hence the adsorption rate is enhanced and the fast reaction stage extended leading to higher sorbent conversion (Hu et al., 2019; Romero-Ibarra et al., 2013). Nevertheless, the calcining step leads to the presence of clusters in the sorbents final structure that could limit the modification effect of wet milling the reagents, hence resulting in a not gradual enhancement of the sorption performance with increasing milling duration. Finally, the obtained parametric models from the CCD experimental design were used for multi-objective optimization in the Design Expert® 13 software. The optimum conditions for maximizing together the Li₄SiO₄ conversion and the adsorption rate are 80 min of milling time for the reagent suspension, operating the CO₂ adsorption (in 4 vol% CO₂ stream) of the resulting sorbent at 515 °C. The sorption capacity in these conditions reaches 156 mg CO₂/g sorbent (Li₄SiO₄ conversion of about 42.7 %).

4. Conclusions

The present work proposed a method for the fabrication of pure Li₄SiO₄ sorbents for CO₂ capture at high temperature, which employed the ball milling process in the reagents mixing phase for enhancing the CO₂ adsorption properties of the produced sorbents. The effect of the reagents milling time on the sorbents microstructure was studied, and the combined effect of milling time and adsorption temperature was investigated by means of Response Surface Methodology. The results showed that Li₄SiO₄ conversion and adsorption rate were enhanced by the ball milling process, owing to a reduction of sorbents particle size that leads to higher surface area. The optimum operating conditions to maximize both conversion and sorption rate (80 min of milling, 515 °C adsorption temperature) allowed to obtain a pure sorbent that was able to adsorb 156 mg CO₂/g.

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References

- Chao, C., Deng, Y., Dewil, R., Baeyens, J., Fan, X., 2021, Post-combustion carbon capture, *Renewable and Sustainable Energy Reviews*, 138, 110490.
- Ghani, S.M.M., Chow, X.E., Kumeressan, R., Rabat, N.E., 2022, Improved Hydrogel as Potential Carbon Dioxide Adsorbent, *Chemical Engineering Transactions*, 97, 457–462.
- Hu, Y., Liu, W., Yang, Y., Qu, M., Li, H., 2019, CO₂ capture by Li₄SiO₄ sorbents and their applications: Current developments and new trends, *Chemical Engineering Journal*, 359, 604–625.
- Nedoma, M., Netušil, M., 2021, CO₂ Separation from Flue Gases by Adsorption, *Chemical Engineering Transactions*, 88, 421–426.
- Puccini, M., Seggiani, M., Vitolo, S., 2013, CO₂ Capture at High Temperature and Low Concentration on Li₄SiO₄ Based Sorbents, *Chemical Engineering Transactions*, 32, 1279–1284.
- Raganati, F., Miccio, F., Ammendola, P., 2021, Adsorption of Carbon Dioxide for Post-combustion Capture: A Review, *Energy and Fuels*, 35, 12845–12868.
- Romero-Ibarra, I.C., Ortiz-Landeros, J., Pfeiffer, H., 2013, Microstructural and CO₂ chemisorption analyses of Li₄SiO₄: Effect of surface modification by the ball milling process, *Thermochimica Acta*, 567, 118–124.
- Seggiani, M., Stefanelli, E., Puccini, M., Vitolo, S., 2018, CO₂ sorption/desorption performance study on K₂CO₃-doped Li₄SiO₄-based pellets, *Chemical Engineering Journal*, 339, 51–60.
- Song, D.H., Kim, J.Y., Kahng, Y.H., Cho, H., Kim, E.S., 2018, Long-Term Effects on Graphene Supercapacitors of Using a Zirconia Bowl and Zirconia Balls for Ball-Mill mixing of Active Materials, *Journal of the Korean Physical Society*, 72, 900–905.
- Tong, Y., Chen, S., Huang, X., He, Y., Chen, J., Qin, C., 2022, CO₂ capture by Li₄SiO₄ Sorbents: From fundamentals to applications, *Separation and Purification Technology*, 301, 121977.
- Yan, X., Li, Y., Ma, X., Zhao, J., Wang, Z., Yan, X., Li, Y., Ma, X., Zhao, J., Wang, Z., 2019, Performance of Li₄SiO₄ material for CO₂ capture: a review, *International Journal of Molecular Sciences*, 20, 928.
- Yang, Y., Yao, S., Hu, Y., Sun, J., Cao, J., Li, Q., Liu, W., 2020, Mechanochemically activated Li₄SiO₄-based adsorbent with enhanced CO₂ capture performance and its modification mechanisms, *Fuel*, 273, 117749.
- Zainol, M.M., Hoe, T.T., Yussuf, M.A.M., Amin, N.A.S., 2021, Carbon Cryogel Preparation via Urea-furfural Gel Synthesis as an Adsorbent for CO₂ Capture Application, *Chemical Engineering Transactions*, 89, 187–192.