





Article

Lithium-Containing Sorbents Based on Rice Waste for High-Temperature Carbon Dioxide Capture

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Abstract: This article studies the influence of the nature of the carrier from rice wastes on the sorption properties of lithium-containing sorbents, and also considers the impact of the modifying additive (K_2CO_3) and adsorption temperature on their characteristics. It has been shown that the sorption capacity of $11LiK/SiO_2$ at $500\text{ }^\circ\text{C}$ reached 36%, which is associated with the formation of lithium orthosilicate in the sorbent composition, as well as with an increase in the specific surface area of the sorbent. After 12 cycles of sorption–desorption, it was found that the sorption capacity of $11LiK/SiO_2$ for CO_2 decreased by only 8%. Rice waste-based sorbents have a high sorption capacity for CO_2 at high temperatures, which allows them to be used for carbon dioxide capture. The results of this study indicate the prospects of using agricultural residues to create effective adsorbents that contribute to reducing environmental pollution and combating global warming.

Keywords: capture; carbon dioxide; sorption; sorbent; rice waste



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1. Introduction

Mitigating the effects of global climate change is one of the most pressing challenges of our time [1–3]. At the Climate Change Summit held on 23 September 2019, it was announced that 77 countries, 10 regions, and more than 100 cities had committed to achieving net-zero carbon emissions by 2050 [4,5]. Achieving this ambitious goal requires the development of zero- and low-carbon energy technologies, which remains a top priority for these pioneering nations [6]. Among the key strategies to reduce carbon emissions is the advancement of carbon capture, utilization, and storage (CCUS) technologies, which are essential as fossil fuels will likely continue to play a major role in global energy consumption in the near future [7].

Carbon capture technologies can be categorized into three main approaches based on the point of carbon dioxide capture within fossil fuel power plants: pre-combustion, post-combustion, and oxy-combustion [8]. Historically, amine-based solvents have been widely used for capturing CO_2 from flue gases [9]. While effective, this method demands high energy for solvent regeneration and poses environmental concerns due to the release of hazardous by-products during the process. These drawbacks have shifted the focus of researchers towards solid adsorbents as a more sustainable alternative [10–12].

Solid adsorbents have gained renewed attention due to their lower energy requirements, environmental safety, faster adsorption kinetics, and greater stability under extreme conditions compared to liquid absorbents [13–15]. However, the capture and separation of CO_2 from large volumes of flue gas remain energy-intensive and costly. This has made the

development of efficient sorbents crucial, especially for concentrated gas flows, to reduce the overall cost of the adsorption process. Despite advancements, particularly in post-combustion CO₂ capture, no ideal sorbent has yet been identified. Current materials face significant challenges, including their low CO₂ capture capacity, poor selectivity under real pressure conditions, high costs, slow adsorption kinetics, and sensitivity to moisture [16]. Therefore, research efforts are increasingly focused on developing sorbents with lower regeneration energy, faster adsorption/desorption rates, and greater stability, aiming for more economically viable carbon capture technologies [17].

The scientific problem addressed by this study is the development of more efficient and cost-effective high-temperature CO₂ sorbents with improved stability over multiple cycles. Existing calcium-based sorbents suffer from significant degradation after 20–30 cycles of use, mainly due to abrasion and sintering, which reduce their overall effectiveness [18]. In contrast, lithium-based sorbents, particularly lithium orthosilicate (Li₄SiO₄), have demonstrated higher stability at elevated temperatures (550–700 °C) and are more effective for CO₂ capture in this temperature range [19]. However, lithium-based sorbents still face challenges related to adsorption kinetics and regeneration efficiency [20–22]. This research introduces rice waste as a sustainable source of silica and carbonized silica to enhance the sorption properties of lithium-containing materials. By investigating the comparative influence of silica and carbonized silica derived from rice waste on the high-temperature CO₂ sorption properties of lithium-based sorbents, this study aims to address these limitations and contribute to the development of more effective carbon capture technologies.

One effective solution to improve the performance of lithium-based sorbents involves doping with small amounts of alkali metal carbonates, such as K₂CO₃ or Na₂CO₃ [23]. Research has shown that doping Li₄SiO₄ with potassium or sodium carbonates enhances the CO₂ sorption capacity, although Na₂CO₃ doping can lead to sintering after multiple cycles [24,25]. The performance of Li₄SiO₄ is also strongly influenced by the synthesis method and the nature of the silicon precursor. Studies have demonstrated significant differences in the purity, crystallite size, crystallinity, and specific surface area of Li₄SiO₄ synthesized from different raw materials [26,27]. A cost-effective and abundant source of silicon oxide is rice waste, which is rich in silica.

This study investigates the comparative influence of carriers derived from rice waste, such as silicon oxide and carbonized silicon oxide, on the physicochemical properties and high-temperature CO₂ sorption performance of lithium-based sorbents. By utilizing rice waste, this research not only explores an eco-friendly and economically viable material for sorbent production but also seeks to improve the performance of lithium-containing sorbents for high-temperature CO₂ capture.

2. Materials and Methods

2.1. Synthesis of Silicon Oxide and Carbonized Silicon Oxide from Rice Wastes

Rice wastes (rice husks and stems) from the Kyzylorda region of the Republic of Kazakhstan were used as raw materials for obtaining silicon oxide (SiO₂) and carbonized silicon oxide. The process of obtaining SiO₂ from rice husks involved several steps of pretreatment and heat treatment. First, the rice husks were cleaned of dust and sand by washing them multiple times with distilled water, followed by drying at 120 °C for 4 h. After drying, the husks were mixed with concentrated hydrochloric acid (HCl) in a 1:10 ratio and heated at 90 °C for 24 h. The purpose of adding HCl at this stage is to remove metallic impurities (such as iron and calcium) and organic residues that can affect the purity of the SiO₂. The resulting mixture was filtered, washed several times with distilled water, dried again at 120 °C for 4 h, and calcined at 600 °C for 4 h. After calcination, a white powder (ash) was obtained, consisting mainly of SiO₂. To further increase the purity of the SiO₂, the ash was dissolved in a 2M NaOH solution at 90 °C for 2 h while being stirred on a magnetic stirrer. This step converts the SiO₂ into sodium metasilicate, a soluble form of silicon. Afterward, concentrated HCl was added to the solution. The second addition of HCl is necessary to neutralize the sodium metasilicate and precipitate the SiO₂ as a

solid. The resulting solution was filtered through a vacuum filter, and the solid SiO_2 was washed with hot distilled water and dried at $120\text{ }^\circ\text{C}$ for 12 h, resulting in highly purified SiO_2 . The elemental composition of the obtained sample consists of 99.4% SiO_2 , 0.4% K_2O , and 0.2% CaO . The specific surface area of the obtained sample is $150\text{ m}^2/\text{g}$. To obtain carbonized silicon oxide ($\text{SiO}_2 + \text{C}$), rice waste (rice husks, stems) were crushed to the size of 0.25 mm particles. The pellets were obtained by adding a binder to the milled rice waste. The resulting pellets were placed in a tubular furnace, hermetically sealed, and filled with gaseous nitrogen grade A. The carbonization process was carried out with a temperature rise rate of $10\text{ }^\circ\text{C}$ per minute up to $500\text{ }^\circ\text{C}$ and held at this temperature for 100 min. Activation was carried out with water vapour at a temperature of $850\text{ }^\circ\text{C}$ in a high temperature vacuum tube furnace of the BR-12 NFT series under the optimal conditions previously identified by us. The elemental composition of the obtained sample consists of 63% SiO_2 , 34% C, and 3% Na_2O . The specific surface area of the obtained sample is $273.5\text{ m}^2/\text{g}$.

2.2. Preparation of Sorbents

The sorbents used in this work were synthesized by the mixing method. Samples of $10\text{Li}/\text{SiO}_2$ and $10\text{Li}/\text{SiO}_2 + \text{C}$ were prepared by mixing Li_2CO_3 and amorphous SiO_2 and/or $\text{SiO}_2 + \text{C}$ in a ratio of 1:9. Samples of $11\text{LiK}/\text{SiO}_2$ and $11\text{LiK}/\text{SiO}_2 + \text{C}$ were prepared by mixing Li_2CO_3 and K_2CO_3 with amorphous SiO_2 and/or $\text{SiO}_2 + \text{C}$ in the ratio of 1:0.1:8.9.

After complete stirring, the mixture was dried at $200\text{ }^\circ\text{C}$ for 2 h and then subjected to heat treatment at $750\text{ }^\circ\text{C}$ for 3 h. The resulting sorbents were moulded into tablets with a diameter of 2–3 mm, then placed in a reactor and the CO_2 capture study was carried out.

2.3. Evaluation of CO_2 Sorption

The synthesized sorbents were tested in carbon dioxide capture at atmospheric pressure. To determine the sorption capacity, the composite sorbent (1 g) was placed in a fixed bed reactor, the reactor was placed in an electric furnace. Before starting the experiment, the samples were degassed at $200\text{ }^\circ\text{C}$ for 60 min. Then, 100% carbon dioxide was supplied to the sorbent at a rate of $15\text{ mL}/\text{min}$ for 30 min at a specific temperature, from 100 to $500\text{ }^\circ\text{C}$. After that, the gas composition was changed to pure helium to remove gaseous CO_2 from the reactor and the temperature of the reactor was raised to $750\text{ }^\circ\text{C}$.

The efficiency of cyclic sorption was tested using 12 sorption/desorption cycles. The CO_2 sorption/desorption process was carried out at $500\text{ }^\circ\text{C}$ in 100 vol.% CO_2 ($15\text{ mL}/\text{min}$) for 30 min and $750\text{ }^\circ\text{C}$ in 100 vol.% helium for 30 min.

The exhaust gasses were analyzed using a Chromos GC-1000 (Russia, Novosibirsk) gas chromatograph equipped with a thermal conductivity detector (TCD).

2.4. Investigation of the Physico-Chemical Characteristics of Samples

Physico-chemical characterization of the sorbents was carried out by XRD, Raman spectroscopy, SEM, etc. The spent sorbents were investigated in adsorption at $500\text{ }^\circ\text{C}$ and desorption at $750\text{ }^\circ\text{C}$.

X-ray diffractometric analysis was carried out on an automated diffractometer DRON-3 with $\text{CuK}\alpha$ -radiation, β -filter. Conditions of diffractograms shooting were the following: $U = 35\text{ kV}$; $I = 20\text{ mA}$; shooting θ -2 θ ; detector 2 deg/min. X-ray phase analysis on a semi-quantitative basis was performed on powder sample diffractograms using the method of equal suspensions and artificial mixtures. Quantitative ratios of crystalline phases were determined. The interpretation of diffractograms was carried out using the ICDD file data: PDF 2 (Powder Diffraction File) Release 2022 and the HighScorePlus programme. Content calculations were performed for the main phases.

A JEOL JSM-6390 LA model scanning electron microscope (JEOL, Tokyo, Japan) with a JED 2300 energy dispersive X-ray detector was used to investigate the morphology of the composite. The composites were imaged on carbon tape where micrographs were

taken at an accelerating voltage of 30 kV. The distribution of elements on the surface of the composites was performed with Analysis Station software version 3.62.07 (JEOL Engineering, Freising, Germany) using the standardless ZAF method.

To determine the structure of the formed carbon on the composites, measurements were performed on a Raman spectrometer Solver Spectrum (NT-MDT Company, Moscow, Russia) with excitation laser radiation of 473 nm. The laser was focused on the sample using a 100× objective to a spot with a diameter of 2 micrometres. A 600/600 diffraction grating with a spectral resolution of 4 cm⁻¹ was used to record the signal. The signal accumulation time was 60 s.

IR spectra were recorded and processed on a VERTEX 70 FT-IR spectrometer (Bruker VERTEX, Ettlingen, Germany) in the frequency range from 4000 to 500 cm⁻¹ and using a PIKE MIRacle ATR single impaired internal total reflection (SIRIR) attachment with a germanium crystal. The results were processed using the software OPUS 7.2.139.1294. Attenuated total internal reflection (ATR) is the most popular infrared spectroscopy technique because it is easy to use and provides high-quality spectra without prior sample preparation. ATR is used for the analysis of solids, liquids and gels. The sample is placed, pre-degreased with alcohol, on the ATR attachment of the IR spectrometer. The sample is placed horizontally on the surface of the optical material. To record the spectrum, it is enough to ensure contact between the sample under study and the crystal of the attachment. Observe the spectrum acquisition process. ATR spectra are practically no different from the absorption spectra obtained by the classical method and are easily identified from spectral libraries.

3. Results

Pre-Sorption Analysis

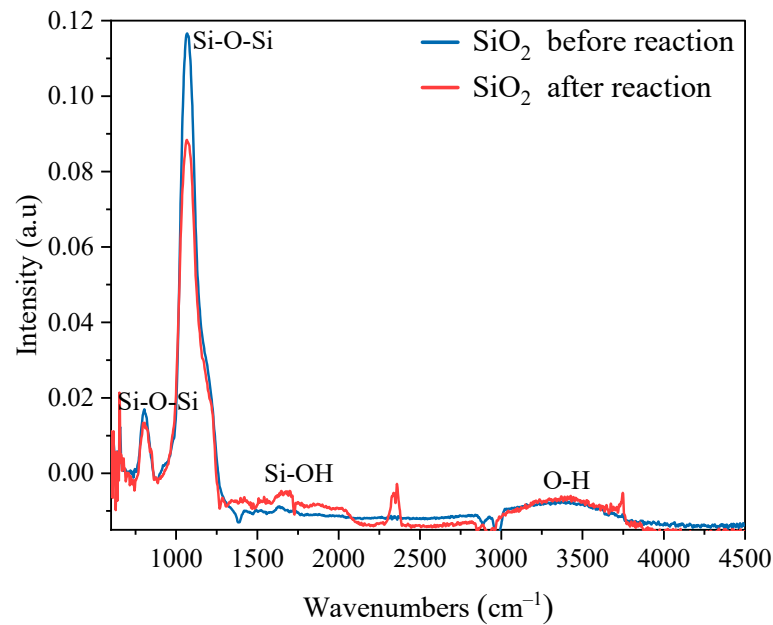
The FTIR spectra of fresh and spent silicon oxide and carbonized silicon oxide in the sorption and desorption of CO₂ are shown in Figure 1.

In the spectra of fresh carbonized silicon oxide, a wide absorption band is observed at 3500 cm⁻¹. According to the literature [28], absorption bands in the range of 3600–3100 cm⁻¹ are attributed to OH-stretching vibrations caused by surface hydroxyl groups and chemisorbed water. Low-intensity peaks are observed at ~1580 and ~2730 cm⁻¹, which are attributed to graphite-like carbon. In addition, there is a spectrum at 1050 cm⁻¹ related to the vibration of the Si-O bond in silicon oxide.

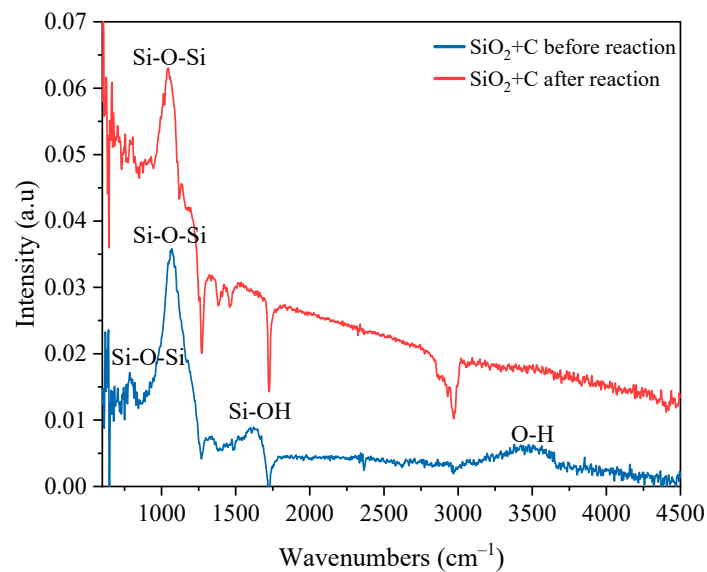
In the spectra of silicon oxide, an intense peak is observed at ~1050 cm⁻¹ related to silicon oxide. In samples of carbonized silicon oxide and silicon oxide after the adsorption and desorption of CO₂, the intensity of the peak related to SiO₂ decreases, which may be due to a change in the dispersity of the samples after the adsorption/desorption of CO₂ [29]. The phase analysis of composite sorbents based on silicon oxide is presented in Figure 2.

On the XRD profile of the 10Li/SiO₂ sorbent before and after adsorption at 500 °C, reflections are observed at 20°, 26.6° and 50°, which belong to SiO₂, and at 18.8°, 26.9° and 55.5°, which belong to the Li₂SiO₃ phase. On the sorbent, after CO₂ adsorption at 500 °C and desorption at 750 °C, the intensities of the peaks related to the Li₂SiO₃ and SiO₂ phases decrease and intense peaks appear at 23.8°, 24.7°, and 24.8°, which, according to [30], belong to the Li₂Si₂O₅ phase. The formation of the Li₂Si₂O₅ phase after CO₂ desorption may be associated with the phase transition of Li₂SiO₃ + SiO₂ = Li₂Si₂O₅, confirmed by a decrease in the intensity of the peaks related to Li₂SiO₃ and SiO₂.

Modification of the 10Li/SiO₂ sorbent with potassium carbonate leads to a decrease in the intensity of the peak related to SiO₂ and the formation of the Li₄SiO₄ phase, and the XRD spectrum (Figure 3) of the 11LiK/SiO₂ sorbent shows peaks at 22°, 28.4°, and 35.5°, which, according to [31], correspond to the Li₄SiO₄ phase.



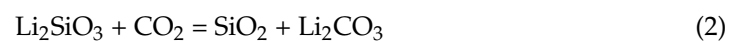
(a)



(b)

Figure 1. FTIR spectra of fresh and spent silicon oxide and carbonized silicon oxide in the sorption and desorption of CO₂: (a) carbonized silicon oxide before and after reaction; (b) silicon oxide before and after reaction.

On the 11LiK/SiO₂ sorbent after CO₂ adsorption at 500 °C and desorption at 750 °C, a decrease in the intensity of the Li₄SiO₄ peak and an increase in the intensity of the SiO₂ peak are observed, which may indicate phase transitions through the following reactions [32]:



The samples after CO₂ desorption do not show Li₂CO₃ reflections, which may indicate the complete desorption of CO₂ from the sorbent. On the XRD profile of the 10Li/SiO₂ + C

and 11LiK/SiO₂ + C sorbents, the peaks related to the SiO₂ and Li₂SiO₃ phases are shifted to a lower frequency region, which may be associated with an increase in the dispersion of the particle [33]. The XRD profile of samples of 10Li/SiO₂ + C and 11LiK/SiO₂ + C shows a reflection at 26.6°, which, according to [34], corresponds to the graphitic structure of carbon.

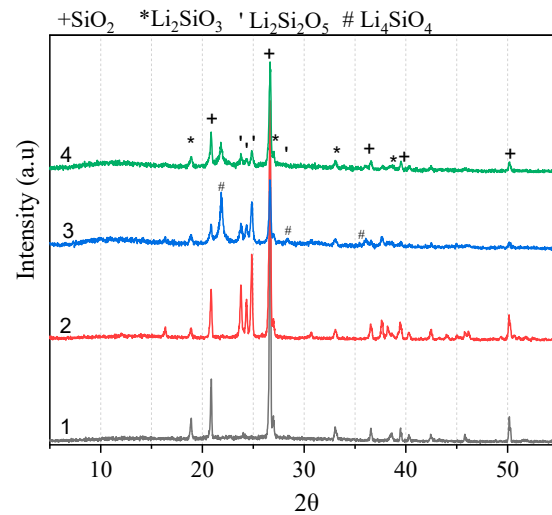


Figure 2. Diffractograms of sorbents: 1—10Li₂O/SiO₂ before adsorption of CO₂; 2—10Li₂O/SiO₂ after adsorption and desorption of CO₂; 3—10Li₂O + K/SiO₂ before adsorption of CO₂; 4—10Li₂O + K/SiO₂ after adsorption and desorption of CO₂.

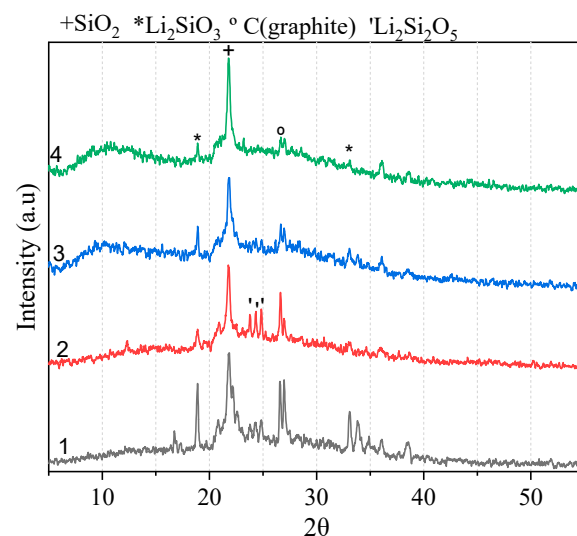


Figure 3. Diffractograms of sorbents: 1—10Li₂O/SiO₂ + C before adsorption of CO₂; 2—10Li₂O/SiO₂ + C after adsorption and desorption of CO₂; 3—10Li₂O + K/SiO₂ + C before adsorption of CO₂; 4—10Li₂O + K/SiO₂ + C after adsorption and desorption of CO₂.

Identification of phases was also carried out using Raman spectroscopy. The results of the samples are presented in Figures 4 and 5. The Raman spectrum of the sorbent 10Li/SiO₂ before the reaction shows bands at 604, 932 and 1094 cm⁻¹, which, according to [35], belong to the Li₂SiO₃ phase. After the sorption and desorption of CO₂ on the spectra of the 10Li/SiO₂ sorbent, in addition to the absorption bands of the Li₂SiO₃ phase, bands at 515 and 1100 cm⁻¹ are observed, which belong to the Li₂Si₂O₅ phase [36]. The spectra of the K₂CO₃-modified fresh sorbent show spectra at 973 and 1037 cm⁻¹, and according to [37], these absorption bands belong to the Li₄SiO₄ phase. All observed absorption bands

are mainly associated with the stretching or vibration of the Si–O bond. In the spectra of the 10Li/SiO₂ + C and 11LiK/SiO₂ + C sorbents, absorption bands related to graphite-like carbon and low-intensity absorption bands of the Si–O bond are observed [38].

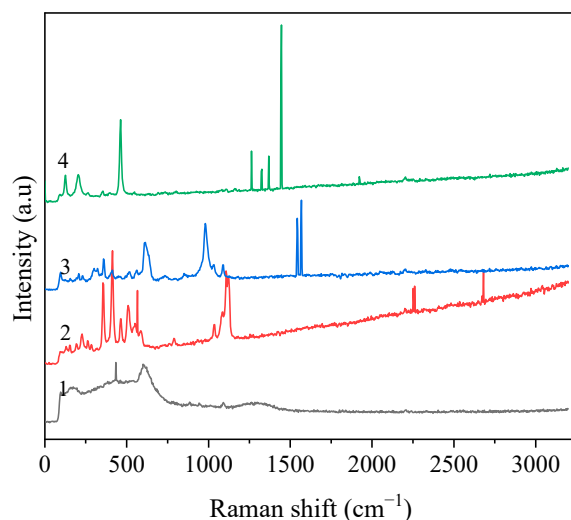


Figure 4. Raman spectra: 1—10Li/SiO₂ before sorption of CO₂; 2—10Li/SiO₂ after sorption and desorption of CO₂; 3—11LiK/SiO₂ before sorption of CO₂; 4—11LiK/SiO₂ after sorption and desorption of CO₂.

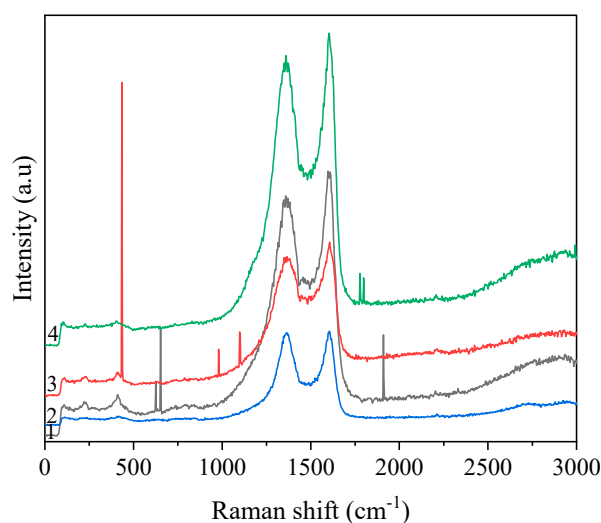


Figure 5. Raman spectra: 1—10Li/SiO₂ + C before sorption of CO₂; 2—10Li/SiO₂ + C after sorption and desorption of CO₂; 3—11LiK/SiO₂ + C before sorption of CO₂; 4—11LiK/SiO₂ + C after sorption and desorption of CO₂.

The synthesized sorbents were characterized by SEM and the surface morphologies of these sorbents are shown in Figures 6 and 7.

Micrographs of 10Li/SiO₂ are represented by aggregates of different sizes and shapes. After the sorption and desorption of CO₂ on the 10Li/SiO₂ sample, particles appear in the form of plates accumulated in a heap; perhaps these particles belong to the Li₂Si₂O₅ phase [39]. Modification of the 10Li/SiO₂ sorbent with K₂CO₃ leads to a change in the morphology of the sorbent, the porosity of the sorbent increases, which is also confirmed by BET results, and the specific surface area increases from 40 to 120 m²/g (Table 1). After the sorption and desorption of CO₂ on the 11LiK/SiO₂ sorbent, the dispersion of particle size increases, which is also confirmed by XRD results.

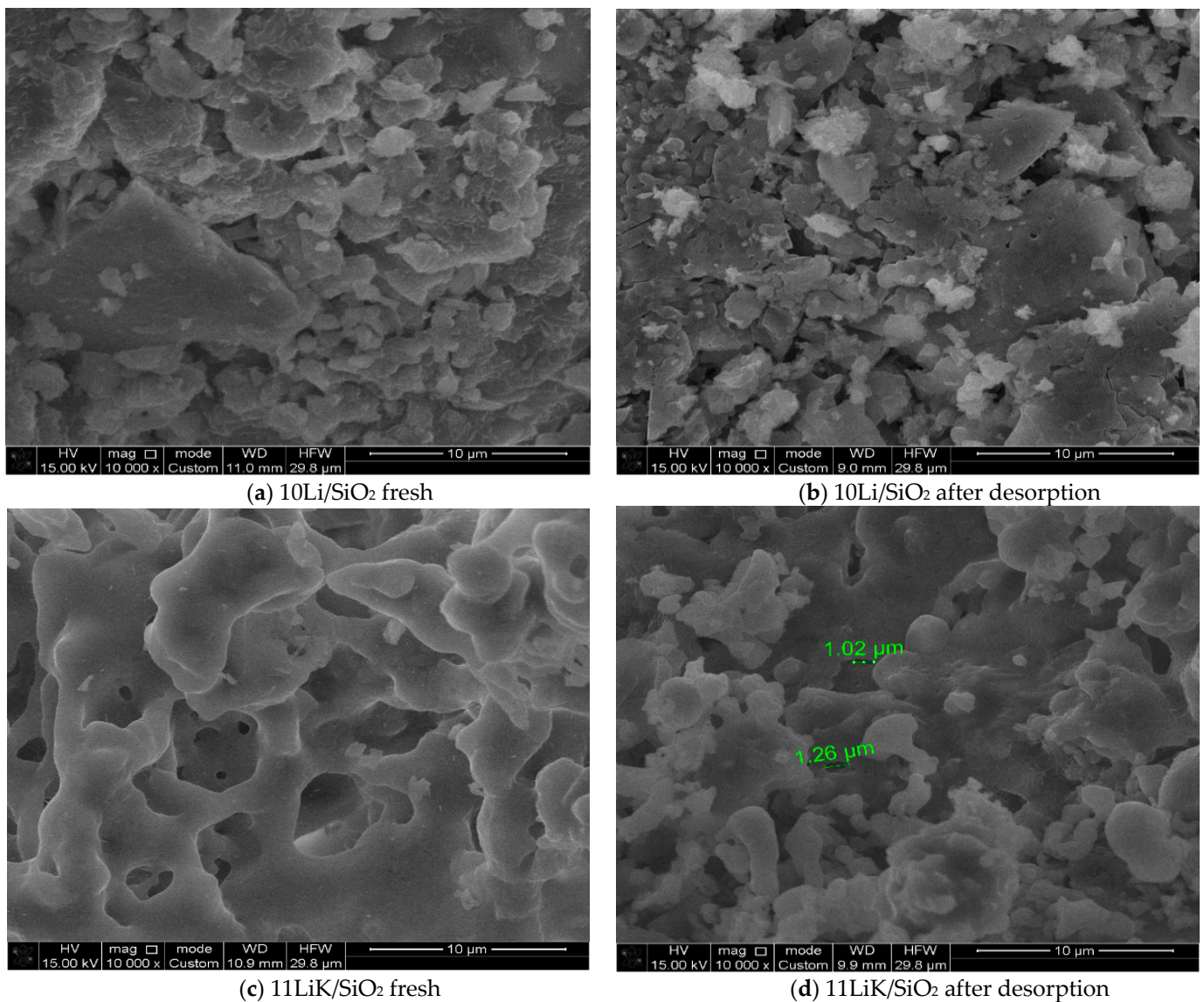


Figure 6. Microphotographs of sorbents before sorption (fresh) and after desorption: (a) 10Li/SiO₂ fresh; (b) 10Li/SiO₂ after desorption; (c) 11LiK/SiO₂ fresh; (d) 11LiK/SiO₂ after desorption.

In the micrograph of fresh 10Li/SiO₂ + C, aggregates are observed, with lamellar particles that are close to graphite [40]. In addition, rod-like particles are observed, which can be attributed to silicon oxide or to Li₂SiO₃ [41].

After the sorption and desorption of CO₂ on 10Li/SiO₂ + C, the morphology of the sample changes. Rod-shaped particles are observed in the microphotographs of the sample modified with potassium carbonate 11LiK/SiO₂ + C, which, according to [42], can be attributed to Li₂SiO₃. It is known [43] that the sorption temperature is a critical factor affecting the sorption capacity of sorbents for CO₂. Figure 8 shows the results of the influence of the potassium carbonate modifier and sorption temperature on the sorption properties of sorbents, which were studied by conducting CO₂ sorption experiments for 30 min in a fixed-bed reactor.

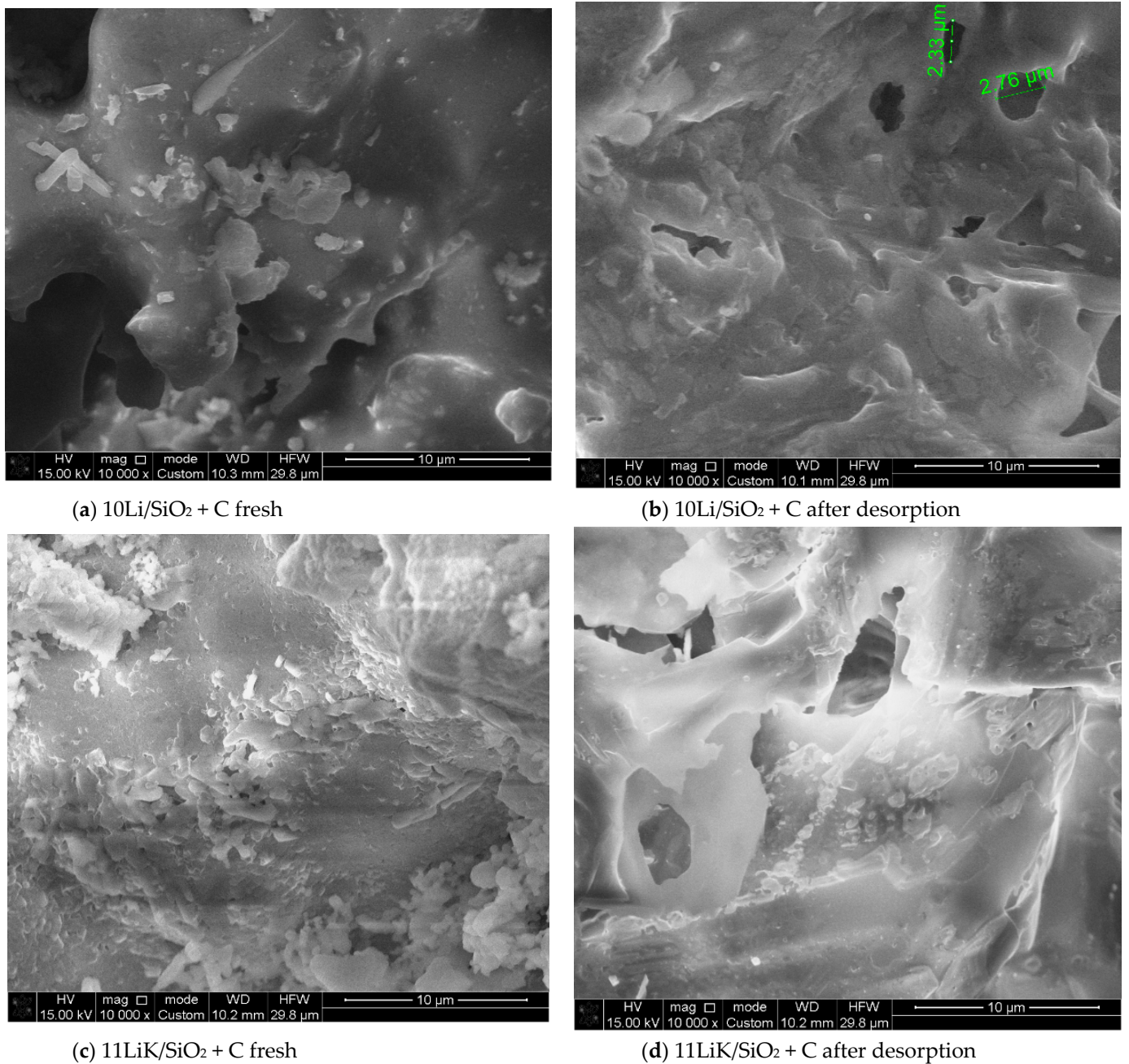


Figure 7. Microphotographs of sorbents before sorption (fresh) and after desorption: (a) 10Li/SiO₂ + C fresh; (b) 10Li/SiO₂ + C after desorption; (c) 11LiK/SiO₂ + C fresh; (d) 11LiK/SiO₂ + C after desorption.

Table 1. Designation of sorbents.

Composition	Designation	Specific Surface, m ² /g
10 wt. % Li ₂ CO ₃ /SiO ₂	10Li/SiO ₂	40
10 wt. % Li ₂ CO ₃ + 1 wt. % K ₂ CO ₃ /SiO ₂	11LiK/SiO ₂	120
10 wt. % Li ₂ CO ₃ /SiO ₂ + C	10Li/SiO ₂ + C	140
10 wt. % Li ₂ CO ₃ + 1 wt. % K ₂ CO ₃ /SiO ₂ + C	11LiK/SiO ₂ + C	191

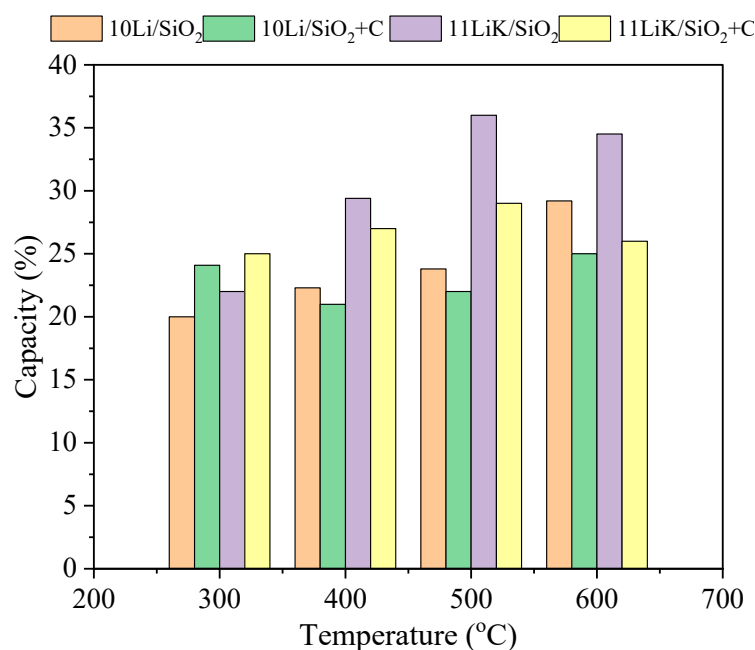


Figure 8. The influence of sorption temperature on the sorption capacity of sorbents for carbon dioxide.

The choice of potassium as a modifier is justified by the fact that the best additives increasing the sorption capacity of lithium-containing sorbents for CO₂ are potassium and sodium carbonates, but in the work of Seggiani et al. [44], it was found that the addition of Na₂CO₃ leads to the severe sintering of the sorbent after multiple sorption–desorption cycles. It was shown in [45] that the decrease in the sorption capacity of Li₄SiO₄ was significantly improved after the addition of K₂CO₃. The addition of K₂CO₃ in the amount of 1 wt.% is due to the fact that the addition of a small amount of alkaline elements leads to an improvement in the sorption properties of Li₄SiO₄ [46].

It can be seen from the results that the sorption behaviour of sorbents promoted by potassium at all sorption temperatures differs significantly from the sorbents 10Li/SiO₂ and 10Li/SiO₂ + C. At an adsorption temperature of 300 °C, sorbents based on SiO₂ + C show a large sorption capacity.

It is possible that carbon micropores play a role at this sorption temperature, since it is known [47] that micropores with sizes less than 0.54 nm determine the ability to capture carbon sorbents. Starting from 400 °C, SiO₂-based sorbents exhibit a better sorption capacity compared to sorbents based on SiO₂ + C, most likely due to the high content of silicon oxide and the formation of silicates, which are sorption centres for CO₂ at high temperatures. Figure 9 shows the cyclic characteristics of 11LiK/SiO₂ and 11LiK/SiO₂ + C. After 12 cycles, the sorption efficiency of the 11LiK/SiO₂ sample was more than 92%, and the 11LiK/SiO₂ + C sample was 89%, which indicates the excellent characteristics of the regeneration cycle. Comparison of the sorption capacity of 11LiK/SiO₂ with other lithium-containing sorbents showed that it has good sorption capabilities compared to other sorbents [48–50] (Table 2).

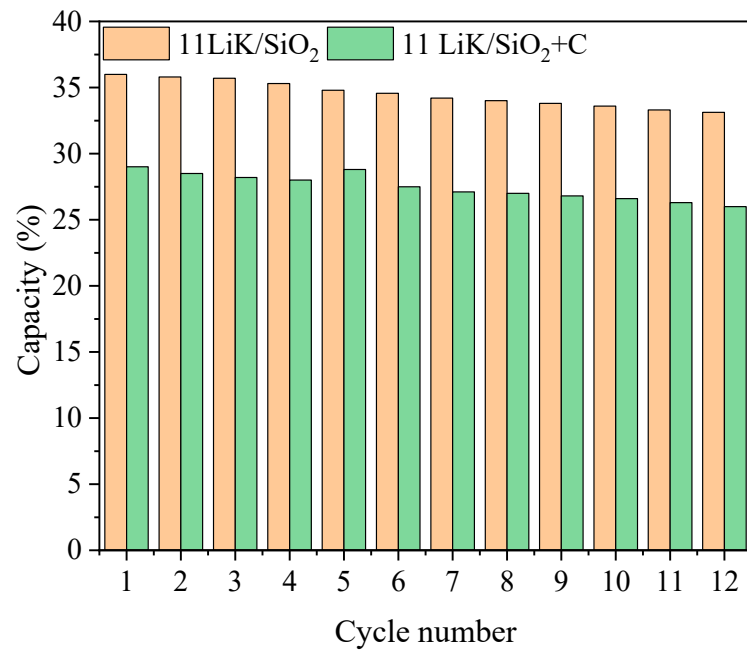


Figure 9. Cyclicality of CO₂ capture by sorbents at a temperature of 500 °C.

Table 2. Comparison of the CO₂ adsorption capacity of lithium-containing sorbents.

Composition of Sorbents	Preparation Methods	CO ₂ Sorption Temperature/°C	Sorption Time (min)	Sorption Capacity	Ref./This Work
Li ₂ /Na ₂ /K ₂ CO ₃	-	580	120	0.179 gCO ₂ /g sorbent	[44]
NaF-doped Li ₄ SiO ₄	Sacrificial carbon template method	575	30	0.30 gCO ₂ /g sorbent	[46]
Li ₄ SiO ₄	Solid state reaction process	400	-	31%	[48]
LS-LO10Na	Solid-state reaction method	550	-	0.308 gCO ₂ /g sorbent	[49]
Li ₄ SiO ₄ with 10 wt% Na ₂ CO ₃ and 5 wt% K ₂ CO ₃	Impregnated suspension method	550	30	0.296 gCO ₂ /g sorbent	[50]
11LiK/SiO ₂	Mixing method	500	30	36%	[This work]

4. Conclusions

In this paper, a comparative study of the influence of the nature of the carrier synthesized from rice waste on the sorption and physicochemical characteristics of lithium-containing sorbents was carried out. The influence of the potassium carbonate-modifying additive and adsorption temperature on the sorption properties of the sorbents was investigated. Firstly, the sorbents show excellent CO₂ sorption properties at high adsorption temperatures. The sorption capacity of 11LiK/SiO₂ at 500 °C reached 36% at atmospheric pressure, which is due to the formation of lithium orthosilicate in the sorbent composition, as well as to the increase in the specific surface area of the sorbent. After 12 cycles of sorption–desorption, it was found that the CO₂ sorption capacity of 11LiK/SiO₂ decreased by only 8%. This shows that the sorbent has good thermal stability. The results showed that rice waste-based sorbents can be used as high temperature sorbents for carbon dioxide capture. Therefore, using agricultural waste to create CO₂ sorbents not only helps reduce pollution from crop waste, but also effectively combats global warming. This is of great significance to the ongoing environmental remediation efforts and promotes the development

of the solid waste industry to reduce pollution and carbon emissions. However, additional research is needed to gain a deeper understanding of the processes occurring during the sorption/desorption of CO₂ on sorbents obtained from rice waste.

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References

1. Dossunov, K.; Yergazieva, G.Y.; Churina, D.H.; Tayrabekova, S.Z.; Tulebayev, E.M. Effect of the Method of Preparation of a Supported Cerium Oxide Catalyst on Its Activity in the Conversion of Ethanol to Ethylene. *Theor. Exp. Chem.* **2016**, *52*, 123–126. [[CrossRef](#)]
2. Gao, X.; Li, J.; Zheng, M.; Cai, S.; Zhang, J.; Askari, S.; Dewangan, N.; Ashok, J.; Kawi, S. Recent Progress in Anti-Coking Ni Catalysts for Thermo-Catalytic Conversion of Greenhouse Gases. *Process Saf. Environ. Prot.* **2021**, *156*, 598–616. [[CrossRef](#)]
3. Mehryar, M.; Hafezalkotob, A.; Azizi, A.; Sobhani, F.M. Cooperative Reliability Allocation in Network Flow Problems Considering Greenhouse Gas Emissions: Optical Fiber Networks Structure. *J. Clean. Prod.* **2021**, *326*, 129315. [[CrossRef](#)]
4. Hincks, S.; Carter, J.; Connelly, A. A New Typology of Climate Change Risk for European Cities and Regions: Principles and Applications. *Glob. Environ. Chang.* **2023**, *83*, 102767. [[CrossRef](#)]
5. Voldsund, M.; Jordal, K.; Anantharaman, R. Hydrogen Production with CO₂ Capture. *Int. J. Hydrogen Energy* **2016**, *41*, 4969–4992. [[CrossRef](#)]
6. Li, C.; Ahmad, S.F.; Ahmad Ayassrah, A.Y.A.B.; Irshad, M.; Telba, A.A.; Mahrous Awwad, E.; Imran Majid, M. Green Production and Green Technology for Sustainability: The Mediating Role of Waste Reduction and Energy Use. *Heliyon* **2023**, *9*, e22496. [[CrossRef](#)]
7. Okorie, D.I.; Wesseh, P.K., Jr. Fossil Fuel Subsidy Removal, Economic Welfare, and Environmental Quality under Alternative Policy Schemes. *J. Clean. Prod.* **2024**, *450*, 141991. [[CrossRef](#)]
8. Soeptyan, F.B.; Habib, M.; Zhang, Z.; Nemetz, L.R.; Haque, M.E.; Esquino, A.M.; Rivero, J.R.; Bhattacharyya, D.; Lipscomb, G.G.; Matuszewski, M.S.; et al. Optimization of a Natural Gas Power Plant with Membrane and Solid Sorbent Carbon Capture Systems. *Carbon Capture Sci. Technol.* **2024**, *10*, 100165. [[CrossRef](#)]
9. Sheng, L.; Wang, K.; Deng, J.; Chen, G.; Luo, G. Gas–Liquid Microdispersion and Microflow for Carbon Dioxide Absorption and Utilization: A Review. *Curr. Opin. Chem. Eng.* **2023**, *40*, 100917. [[CrossRef](#)]
10. Li, Y.; Dai, Y.; Dai, W.; He, F.; Li, Z.; Zhong, X.; Tao, Q. Bifunctional Solid-State Ionic Liquid Supported Amidoxime Chitosan Adsorbents for Th(IV) and U(VI): Enhanced Adsorption Capacity from the Synergistic Effect. *Int. J. Biol. Macromol.* **2024**, *257*, 128708. [[CrossRef](#)]
11. Lin, L.; Meng, Y.; Ju, T.; Han, S.; Meng, F.; Li, J.; Du, Y.; Song, M.; Lan, T.; Jiang, J. Characteristics, Application and Modeling of Solid Amine Adsorbents for CO₂ Capture: A Review. *J. Environ. Manag.* **2023**, *325*, 116438. [[CrossRef](#)] [[PubMed](#)]
12. Zhang, D.; Zhang, Y.; Lei, P.; Yang, Z.; Liu, L.; Zhang, Z. CaO-Based Adsorbents Derived from Municipal Solid Waste Incineration Bottom Ash for CO₂ Capture. *Sustain. Mater. Technol.* **2024**, *39*, e00856. [[CrossRef](#)]
13. Jiao, J.; Cao, J.; Xia, Y.; Zhao, L. Improvement of Adsorbent Materials for CO₂ Capture by Amine Functionalized Mesoporous Silica with Worm-Hole Framework Structure. *Chem. Eng. J.* **2016**, *306*, 9–16. [[CrossRef](#)]
14. Liu, Z.; Teng, Y.; Zhang, K.; Chen, H.; Yang, Y. CO₂ Adsorption Performance of Different Amine-Based Siliceous MCM-41 Materials. *J. Energy Chem.* **2015**, *24*, 322–330. [[CrossRef](#)]
15. Zhao, P.; Zhang, G.; Yan, H.; Zhao, Y. The Latest Development on Amine Functionalized Solid Adsorbents for Post-Combustion CO₂ Capture: Analysis Review. *Chin. J. Chem. Eng.* **2021**, *35*, 17–43. [[CrossRef](#)]
16. Liu, X.; Saren, S.; Chen, H.; Jeong, J.H.; Li, M.; Dang, C.; Miyazaki, T.; Thu, K. Open Adsorption System for Atmospheric CO₂ Capture: Scaling and Sensitivity Analysis. *Energy* **2024**, *294*, 130805. [[CrossRef](#)]
17. Xu, C.; Zhang, Y.; Peng, Y.-L.; Zou, J.-S.; Yang, T.; Liu, Z.; Qiu, F.; Liu, C.; Jiang, S. Probing the Differences in CO₂ Adsorption/Desorption Behaviors of Solid Amine Sorbents in Fixed and Fluidized Beds. *Sep. Purif. Technol.* **2024**, *343*, 127171. [[CrossRef](#)]
18. Li, X.; Zhao, K.; Li, Z.; Li, X.; Peng, K. All-solid-waste-derived CaO-based sorbents for simultaneously enhanced calcium looping CO₂ capture and thermochemical energy storage. *J. Clean. Prod.* **2024**, *470*, 143270. [[CrossRef](#)]

19. Cai, L.; Xue, H.; Yang, X.; Lin, Y.; Hu, X.; Zhang, Y. Facile synthesis of polymer-derived K, Ti co-doped Li₄SiO₄-based sorbent for efficient and stable post-combustion CO₂ capture. *Chem. Eng. J.* **2024**, *493*, 152399. [[CrossRef](#)]
20. Afandi, N.; Satgunam, M.; Mahalingam, S.; Manap, A.; Nagi, F.; Liu, W.; Johan, R.B.; Turan, A.; Wei-Yee Tan, A.; Yunus, S. Review on the Modifications of Natural and Industrial Waste CaO Based Sorbent of Calcium Looping with Enhanced CO₂ Capture Capacity. *Heliyon* **2024**, *10*, e27119. [[CrossRef](#)]
21. Li, P.; Jiang, Z.; Guo, H.; Zhao, W.; Zheng, F.; Chen, Y.; Yan, B.; Chen, D. Lithium Based High Temperature Sorbent from Copper Slag: Synthesis and CO₂ Capture Performance. *Ceram. Int.* **2023**, *49*, 37435–37444. [[CrossRef](#)]
22. Teixeira, P.; Correia, P.; Pinheiro, C.I.C. CO₂ Capture by CaCO₃-MgO and CeO₂-MgO Sorbents Promoted by Ternary Alkali Metal Salts in a Fixed Bed Reactor. *Chem. Eng. Sci.* **2024**, *289*, 119856. [[CrossRef](#)]
23. Liang, S.; Aihemaiti, A.; Cai, Y.; Su, Y.; Li, R.; Quan, Z.; Zhang, Z. New Insights into Stabilizing Mechanism of Ca₉Al₆O₁₈ Stabilizing Ca-Based Sorbents for CO₂ Cyclic Capture under Mild Conditions. *Chem. Eng. J.* **2023**, *474*, 145908. [[CrossRef](#)]
24. Cai, L.; Tan, G.; Yang, X.; Xue, H.; Lin, Y.; Hu, X.; Song, Z.; Zhang, Y. Efficient Carbon Dioxide Adsorption Properties of Cellular Structure Li₄SiO₄ Sorbents Prepared by Additive Manufacturing Based on Polymer-Derived Ceramics Strategy. *Chem. Eng. J.* **2024**, *483*, 149125. [[CrossRef](#)]
25. Wang, J.; Chen, K.; Wang, Y.; Lei, J.; Alsubaie, A.; Ning, P.; Wen, S.; Zhang, T.; Almalki, A.S.A.; Alhadhrami, A.; et al. Effect of K₂CO₃ Doping on CO₂ Sorption Performance of Silicate Lithium-Based Sorbent Prepared from Citric Acid Treated Sediment. *Chin. J. Chem. Eng.* **2022**, *51*, 10–20. [[CrossRef](#)]
26. Cui, H.; Li, X.; Chen, H.; Gu, X.; Cheng, Z.; Zhou, Z. Sol-Gel Derived, Na/K-Doped Li₄SiO₄-Based CO₂ Sorbents with Fast Kinetics at High Temperature. *Chem. Eng. J.* **2020**, *382*, 122807. [[CrossRef](#)]
27. Rossi, D.; Anguillesi, I.; Desideri, U.; Seggiani, M. Easy Fabrication Method of Li₄SiO₄-K₂CO₃ Based Pellets for CO₂ Capture at High Temperature. *Chem. Eng. J.* **2024**, *481*, 148615. [[CrossRef](#)]
28. Seggiani, M.; Stefanelli, E.; Puccini, M.; Vitolo, S. CO₂ Sorption/Desorption Performance Study on K₂CO₃-Doped Li₄SiO₄-Based Pellets. *Chem. Eng. J.* **2018**, *339*, 51–60. [[CrossRef](#)]
29. Stefanelli, E.; Puccini, M.; Vitolo, S.; Seggiani, M. CO₂ Sorption Kinetic Study and Modeling on Doped-Li₄SiO₄ under Different Temperatures and CO₂ Partial Pressures. *Chem. Eng. J.* **2020**, *379*, 122307. [[CrossRef](#)]
30. Dantas, T.L.; Rodrigues, A.E.; Moreira, R.F.P.M. Separation of Carbon Dioxide from Flue Gas Using Adsorption on Porous Solids. *Greenh. Gases-Capturing Util. Reduct.* **2012**, *3*, 57–80. [[CrossRef](#)]
31. Rahmatmand, B.; Keshavarz, P.; Ayatollahi, S. Study of Absorption Enhancement of CO₂ by SiO₂, Al₂O₃, CNT, and Fe₃O₄ Nanoparticles in Water and Amine Solutions. *J. Chem. Eng. Data* **2016**, *61*, 1378–1387. [[CrossRef](#)]
32. Zhang, H.; Wang, J.; Yang, J. Hydrothermal Synthesis and Methylene Blue Adsorption Performance of Novel 3D Hierarchical Li₂Si₂O₅ Hydrate Particles. *Sci. Rep.* **2020**, *10*, 5545. [[CrossRef](#)] [[PubMed](#)]
33. Sanna, A.; Ramli, I.; Maroto-Valer, M.M. Novel Na-Silicates CO₂ Sorbents from Fly Ash. *Energy Procedia* **2014**, *63*, 739–744. [[CrossRef](#)]
34. Wang, K.; Zhao, P.; Guo, X.; Han, D.; Chao, Y. High Temperature Capture of CO₂ on Li₄SiO₄-Based Sorbents from Biomass Ashes. *Environ. Prog. Sustain. Energy* **2015**, *34*, 526–532. [[CrossRef](#)]
35. Zhao, M.; Fan, H.; Yan, F.; Song, Y.; He, X.; Memon, M.Z.; Bhatia, S.K.; Ji, G. Kinetic Analysis for Cyclic CO₂ Capture Using Lithium Orthosilicate Sorbents Derived from Different Silicon Precursors. *Dalton Trans.* **2018**, *47*, 9038–9050. [[CrossRef](#)]
36. Tsubouchi, N.; Nishio, M.; Shinohara, Y.; Bud, J.; Mochizuki, Y. Production of Activated Carbon from Peat by with Natural Soda Ash and Effect of Nitrogen Addition on the Development of Surface Area. *Fuel Process. Technol.* **2018**, *176*, 76–84. [[CrossRef](#)]
37. Buchner, S.; Balzaretto, N.M. Pressure and Temperature Stability Range of Crystalline Lithium Metasilicate in a Binary Li₂O-2SiO₂ Glass. *J. Phys. Chem. Solids* **2013**, *74*, 1179–1183. [[CrossRef](#)]
38. Osman, A.I.; Hefny, M.; Abdel Maksoud, M.I.A.; Elgarahy, A.M.; Rooney, D.W. Recent Advances in Carbon Capture Storage and Utilisation Technologies: A Review. *Environ. Chem. Lett.* **2021**, *19*, 797–849. [[CrossRef](#)]
39. Subha, P.V.; Nair, B.N.; Visakh, V.; Sreeranjini, C.R.; Mohamed, A.P.; Warriar, K.G.K.; Yamaguchi, T.; Hareesh, U.S. Germanium-Incorporated Lithium Silicate Composites as Highly Efficient Low-Temperature Sorbents for CO₂ Capture. *J. Mater. Chem. A* **2018**, *6*, 7913–7921. [[CrossRef](#)]
40. Li, J.; Michalkiewicz, B.; Min, J.; Ma, C.; Chen, X.; Gong, J.; Mijowska, E.; Tang, T. Selective Preparation of Biomass-Derived Porous Carbon with Controllable Pore Sizes toward Highly Efficient CO₂ Capture. *Chem. Eng. J.* **2019**, *360*, 250–259. [[CrossRef](#)]
41. Xue, L.; Haseeb, M.; Mahmood, H.; Alkhateeb, T.T.Y.; Murshed, M. Renewable Energy Use and Ecological Footprints Mitigation: Evidence from Selected South Asian Economies. *Sustainability* **2021**, *13*, 1613. [[CrossRef](#)]
42. Mahmud, N.A.; Osman, N.; Jani, A.M.M. Characterization of Acid Treated Activated Carbon From Oil Palm Empty Fruit Bunches (EFB). *J. Phys. Conf. Ser.* **2018**, *1083*, 012049. [[CrossRef](#)]
43. Xu, H.; Cheng, W.; Jin, X.; Wang, G.; Lu, H.; Wang, H.; Chen, D.; Fan, B.; Hou, T.; Zhang, R. Effect of the Particle Size of Quartz Powder on the Synthesis and CO₂ Absorption Properties of Li₄SiO₄ at High Temperature. *Ind. Eng. Chem. Res.* **2013**, *52*, 1886–1891. [[CrossRef](#)]
44. Alemi, A.; Khademinia, S. Part I: Lithium Metasilicate (Li₂SiO₃)—Mild Condition Hydrothermal Synthesis, Characterization, and Optical Properties. *Int. Nano Lett.* **2015**, *5*, 15–20. [[CrossRef](#)]
45. Zhang, T.; Li, M.; Ning, P.; Jia, Q.; Wang, Q.; Wang, J. K₂CO₃ Promoted Novel Li₄SiO₄-Based Sorbents from Sepiolite with High CO₂ Capture Capacity under Different CO₂ Partial Pressures. *Chem. Eng. J.* **2020**, *380*, 122515. [[CrossRef](#)]

46. Seggiani, M.; Puccini, M.; Vitolo, S. Alkali Promoted Lithium Orthosilicate for CO₂ Capture at High Temperature and Low Concentration. *Int. J. Greenh. Gas Control* **2013**, *17*, 25–31. [[CrossRef](#)]
47. Zhang, Q.; Shen, C.; Zhang, S.; Wu, Y. Steam Methane Reforming Reaction Enhanced by a Novel K₂CO₃-Doped Li₄SiO₄ Sorbent: Investigations on the Sorbent and Catalyst Coupling Behaviors and Sorbent Regeneration Strategy. *Int. J. Hydrogen Energy* **2016**, *41*, 4831–4842. [[CrossRef](#)]
48. Zhou, Z.; Wang, K.; Yin, Z.; Zhao, P.; Su, Z.; Sun, J. Molten K₂CO₃-Promoted High-Performance Li₄SiO₄ Sorbents at Low CO₂ Concentrations. *Thermochim. Acta* **2017**, *655*, 284–291. [[CrossRef](#)]
49. Zhang, Z.; Zhou, J.; Xing, W.; Xue, Q.; Yan, Z.; Zhuo, S.; Qiao, S.Z. Critical Role of Small Micropores in High CO₂ Uptake. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2523. [[CrossRef](#)]
50. Ghuge, N.S.; Debashis Mandal, M.C.; Jadeja, B. Chougule. Carbon dioxide absorption in packed bed of lithium orthosilicate pebbles. *Sep. Sci. Technol.* **2022**, *58*, 849–861. [[CrossRef](#)]

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