



High and efficient Li_2CuO_2 - CO_2 chemisorption using different partial pressures and enhancement produced by the oxygen addition



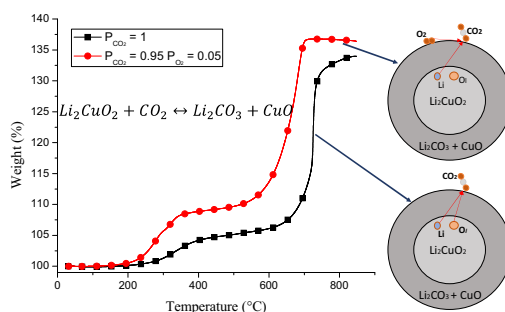
Hugo A. Lara-García, Heriberto Pfeiffer*

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito exterior s/n, Cd. Universitaria, Del. Coyoacán, CP 04510 Ciudad de México, Mexico

HIGHLIGHTS

- CO_2 partial pressure does not affect the CO_2 chemisorption.
- Oxygen addition highly improve the CO_2 chemisorption kinetics.
- Li_2CuO_2 can be used cyclically in the CO_2 carbonation-decarbonation process.

GRAPHICAL ABSTRACT



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ABSTRACT

CO_2 chemisorption in Li_2CuO_2 was studied under different CO_2 and O_2 partial pressures, through thermogravimetric analysis. Results showed that using low P_{CO_2} (0.05–0.2) did not impact in the final CO_2 chemisorption, in comparison to the $P_{\text{CO}_2} = 1$. When oxygen was added to the flow (P_{O_2} between 0.03 and 0.2) the CO_2 chemisorption presented different modifications: The CO_2 chemisorption is produced at lower temperatures; the CO_2 carbonation kinetics is improved and the material is able to perform CO_2 carbonation-decarbonation cycles. CO_2 chemisorption kinetic parameters were determined assuming a first order reaction between 450 and 750 °C, where k and ΔH^\ddagger values confirmed that CO_2 carbonation on Li_2CuO_2 is importantly enhanced with oxygen addition. If oxygen is not present in the flow gas, it has to be released from the Li_2CuO_2 crystalline structure to complete the carbonation process, while if oxygen is supplied in the flow gas the carbonation process is strongly facilitated, as the carbonation does not depend on the oxygen crystalline diffusion. Additionally, results evidenced that Li_2CuO_2 recrystallization, during the cyclic process, is performed by a different reaction mechanism. During the decarbonation process, partial lithium reincorporation, to the cuprate phase, produces $\text{Li}_3\text{Cu}_2\text{O}_4$. The formation of this secondary phase ($\text{Li}_3\text{Cu}_2\text{O}_4$) implies a partial copper oxidation, which must be induced by the P_{O_2} . When a total decarbonation is produced, Li_2CuO_2 is totally recovered.

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1. Introduction

Carbon capture and storage (CCS) technology is one of the most promising ways to reduce the emission of carbon dioxide (CO_2).

Nowadays, the global warming is one of the most threatening problems in the world, where CO_2 is the major emitted greenhouse gas (GHG). CO_2 is emitted into the atmosphere through numerous processes, but fossil-fuel-burning power plants are the largest anthropogenic emission sources globally. In this regard three main strategies are generally available for CO_2 capture and storage; post-combustion, pre-combustion and oxyfuel combustions, and their specific application depends on the concentrations of CO_2 gas

* Corresponding author.

E-mail address: pfeiffer@iim.unam.mx (H. Pfeiffer).

pressure [1–4]. Pre-combustion systems basically separate the CO₂ from the flue [5,6]. Post-combustion capture involves separating the CO₂ from other exhaust gases after combustion of the fossil fuel. Typical post-combustion flow gases contain approximately N₂ (65–75%), CO₂ (7–15%), O₂ (2–12%), H₂O (5–15%) and smaller concentrations of other polluting species [7]. Oxyfuel combustion technology involves the combustion of coal with the use of pure oxygen. Therefore, the major composition of the flue gases is CO₂, water, particulates and SO₂. The concentration of carbon dioxide is major in the oxyfuel process than the others [3,5,8].

Among these processes, several materials have been studied as CO₂ captors and some of them are used now in the industry. Nevertheless, all these materials may present several disadvantages such as saturation, corrosion, etc [1,4,9]. Numerous factors describe the quality or utility of CO₂ captors; fast sorption and desorption kinetics, large sorption capacities, infinite regenerability and stability, and a wide range of operating temperatures [9]. One of the most studied materials, for high temperature CO₂ capture, are the alkaline ceramics. It has been proved that this kind of materials exhibits some of the CO₂ capture properties described above [10–16]. However, most of the reports presented for these ceramics were performed under a saturated CO₂ atmosphere, which is far from the real industrial CO₂ concentrations. However, there are some reports using alkaline ceramics as CO₂ captors under non-saturated CO₂ atmospheres (P_{CO₂}), for example; sodium and lithium zirconates (Na₂ZrO₃ and Li₂ZrO₃) [10,17–20], lithium silicates (Li₂SiO₃, Li₄SiO₄ and Li₈SiO₆) [11,21,22] and lithium cuprate (Li₂CuO₂) [23]. Most of these reports mentioned that CO₂ chemisorption tends to importantly decrease when CO₂ partial pressure decreases. Nevertheless, the CO₂ chemisorption ability of Li₂CuO₂ does not seem to present any important variation on the CO₂ capture process, even using P_{CO₂} = 0.05 [23]. However this result was only analyzed dynamically. Thus, it is necessary to perform a deeper study. Additionally, lithium cuprate (Li₂CuO₂) has been reported as a material able to trap chemically CO₂ with saturated atmospheres according to the reaction (1), in a wide range of temperatures (40–750 °C) under different physicochemical conditions [23–29].



Among the alkaline ceramics studied as possible CO₂ captors it has been proposed different models to explain their reaction mechanism. Most of these reports assumed that the chemisorption process is composed of two main steps; i) the CO₂ superficial chemisorption and ii) the CO₂ bulk chemisorption controlled by ion-diffusion, meaning that once CO₂ reacts with the ceramic on the solid surface forming an external shell of Li₂CO₃ and CuO (for the Li₂CuO₂ case). Thus, Li¹⁺ and O²⁻ ions have to diffuse through the product layer in order to continue the carbonation process [30]. Most of these studies mention that ion diffusion seems limit the whole reaction process. However, there is only one reported including oxygen into the flow gas. The Li₂ZrO₃-CO₂-O₂ system described that the activation enthalpy (ΔH^\ddagger) of the CO₂ bulk chemisorption process is reduced when oxygen is added into the gas flow [31], indicating that oxygen addition somehow helps to the CO₂ chemisorption in that case. Therefore, the aim of this work was to study, dynamic and isothermally, the CO₂ chemisorption and cyclability in the Li₂CuO₂ under different partial pressure of carbon dioxide, in the absence or presence of oxygen. The present analysis should help to elucidate the use of this material into a more realistic combustion flow gas.

2. Experimental section

Lithium cuprate (Li₂CuO₂) was synthesized *via* solid-state method. Lithium oxide (Li₂O, Aldrich) and copper oxide (CuO,

Acros Organics) were mixed mechanically. The mixture was prepared using a lithium excess of 10 wt%, based on the stoichiometric lithium content on Li₂CuO₂. Then, the powders were calcined at 800 °C for 6 h in air. The Lithium cuprate structural and microstructural properties were analyzed as it was described in a previous paper (data not shown) [27].

To evaluate CO₂ chemisorption under different partial pressure of CO₂ and the effect of the oxygen addition in the flow a thermobalance (TA Instruments, model Q500SA) was used, where various dynamic and isothermal experiments were carried out. The experiments were performed using different gas mixtures of CO₂ (Praxair, grade 3), O₂ (Praxair, grade 2.6) and N₂ (Praxair, grade 4.8) as balance and carrier gas with a total flow rate of 60 mL/min. Mixtures were performed into a digital gas mixer (CHEM flow, Microtrac-Bel). Initially, the samples were dynamically heated from 30 to 850 °C at a heating rate of 5 °C/min using different CO₂:N₂ and CO₂:O₂:N₂ gas mixtures, where the P_{CO₂} varied between 0.05 and 1, while P_{O₂} was varied between 0.03 and 0.2. For the isothermal analysis samples were heated to the desired temperature (between 450 and 750 °C) under a N₂ flow. Then, when each sample reached the corresponding temperature, the gas flow was switched from N₂ to the corresponding gas mixture.

The Li₂CuO₂ cyclability experiments were performed at 700 °C using the following partial pressures; P_{CO₂}:P_{O₂}:P_{N₂} = 0.2:0.05:0.75 for the chemisorption and P_{O₂}:P_{N₂} = 0.05:0.95 for the desorption processes. As desorption process resulted to be slower than sorption one, the cyclability experiments were evaluated for 1 and 2 h for sorption and desorption processes, respectively. Finally, some cyclic products were analyzed by X-ray diffraction (XRD) using an equipment D8 Advance from Bruker.

3. Results and discussion

Dynamic TG curves of the Li₂CuO₂-CO₂ system, using different P_{CO₂} are shown in the Fig. 1. Initially, for the CO₂ saturated atmosphere case (P_{CO₂} = 1.0), the thermogram presented the typical behavior according to previous Li₂CuO₂ reports and other lithium ceramics [23–29]. First, between 250 and 500 °C the sample weight increased by 6 wt%. Here, a superficial reaction occurs, where an external lithium carbonate and CuO shell is formed over the surface of the Li₂CuO₂ ceramic particles. Then, the thermogram presented a slight weight increase up to 640 °C where a second CO₂

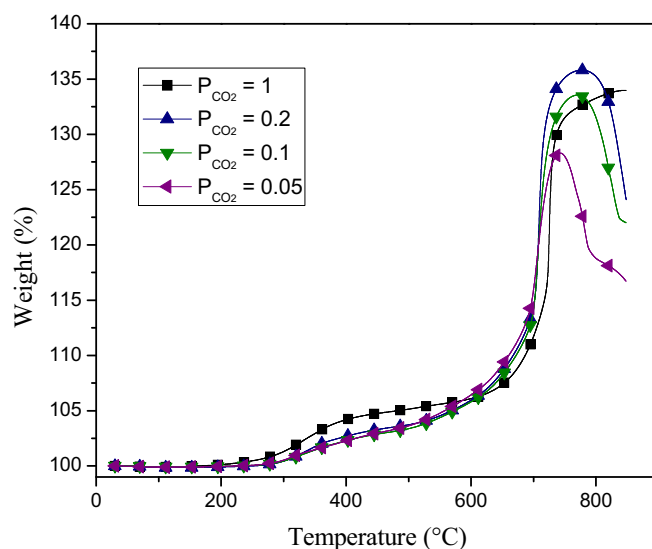


Fig. 1. Dynamic thermogravimetric analysis of the Li₂CuO₂ sample using different P_{CO₂} (0.05, 0.1, 0.2 and 1.0).

chemisorption process began. Between 650 and 840 °C the sample gained 28 wt%. Thus, the total weight increased by 34 wt%. In this temperature range, temperature increases sufficiently and the lithium and oxygen diffusion processes are activated (see [reaction 1](#)). Therefore, the reaction continues through the bulk of the material completing the CO₂ capture.

When the CO₂ capture was performed using different partial pressures (0.05, 0.1 and 0.2), thermograms presented similar trends than that observed at $P_{\text{CO}_2} = 1.0$. In fact, there were only small quantitative differences when the CO₂ concentration was reduced: 1) At moderate temperatures the superficial reaction seemed to be slightly reduced, from 6 wt% to ~4 wt% for the CO₂ saturated and partial pressures experiments, respectively; 2) The bulk CO₂ capture was shift to lower temperatures in around 30 °C, from 710 to 680 °C, for the CO₂ saturated and partial pressures experiments, respectively; and 3) The CO₂ desorption process was evidenced at lower temperatures for the partial pressure systems. All these changes can be attributed to variations in the CO₂ sorption-desorption equilibrium produced by the CO₂ partial pressure modifications. Nevertheless, something else must be pointed out, qualitatively, the CO₂ captured were not so different even at a $P_{\text{CO}_2} = 0.05$, from the saturated experiment ($P_{\text{CO}_2} = 1.0$).

As it was shown, the P_{CO_2} partial pressure does not seem to modify the CO₂ capture process on Li₂CuO₂, which is in good agreement with a previous report [23]. In addition, it has been already mentioned that Li₂CuO₂ carbonation process involves the lithium reaction and diffusion, but oxygen as well. Therefore, a second set of dynamic TG experiments were performed using different P_{O_2} (0.03, 0.05, 0.1 and 0.2, see [Fig. 2](#)). These experiments were performed using a P_{CO_2} of 0.2, which may resemble a CO₂ concentration in different combustion flow gases. As it could be expected, thermograms presented the same general trend. However, a very important difference was observed. In the oxygen presence, the CO₂ superficial chemisorption was highly enhanced and the CO₂ chemisorptions were shifted to lower temperatures. The CO₂ superficial process was observed at 180 °C, if oxygen was present in the gas mixture, in comparison to 280 °C (temperature where CO₂ superficial process began in absence of oxygen). Moreover, the maximum weight increment observed in the CO₂ superficial process, without oxygen was 5 wt%, while the experiments in the presence of oxygen double the weight increments (~10 wt%). It should be mentioned that this variation was observed indepen-

dently of the P_{O_2} used. Later, the CO₂ bulk chemisorption was shifted from 710 to 650 °C, in the oxygen presence. It means that in the oxygen presence the bulk CO₂ chemisorption is active at a lower temperature than in the oxygen absence. As a deeper analysis, [Fig. 3](#) shows two specific comparison cases, where the oxygen effect is more than evident. [Fig. 3-A](#) shows the dynamic thermograms when the P_{CO_2} was equal to 0.2, in the absence and presence of oxygen ($P_{\text{O}_2} = 0.05$). Under these physicochemical conditions CO₂ superficial process began at 280 and 180 °C, in the absence and presence of oxygen, respectively. It means that the oxygen reduces, in 100 °C, the CO₂ superficial chemisorption. Moreover, the amount of CO₂ captured was increased as well, from 5 to 10 wt% in the oxygen presence. In the second case ([Fig. 3-B](#)), dynamic TG of saturated CO₂ atmospheres are presented in absence and presence of oxygen ($P_{\text{CO}_2} = 0.95$ and $P_{\text{O}_2} = 0.05$). Although the gas flow was CO₂ saturated, oxygen enhanced, again, the Li₂CuO₂ carbonation. Here, the CO₂ superficial chemisorption process was very similar than in the previous case. However, the bulk CO₂ chemisorption was shifted, to lower temperatures, in more than 100 °C between 590 and 650 °C. All these results clearly show that oxygen enhances, at least qualitatively, the CO₂ chemisorption in Li₂CuO₂ at superficial and bulk levels. It must be pointed out that pure oxygen flows does not produce any weight change in the Li₂CuO₂ (data not shown). These initial qualitative results clearly show that oxygen addition importantly improves the CO₂ capture at different CO₂ chemisorption steps, at the surface and during the bulk processes. Therefore, in order to further understand the CO₂ chemisorption reaction and mechanism different analyses were performed in the Li₂CuO₂-CO₂ and Li₂CuO₂-CO₂-O₂ systems, varying the gas partial pressures.

[Figs. 4 and 5](#) show different isothermal experiments performed at specific P_{CO_2} and P_{O_2} . Initially, two different sets of isothermal experiments were performed under saturated CO₂ atmospheres; $P_{\text{CO}_2} = 1.0$ ([Fig. 4-A](#)) and P_{CO_2} - $P_{\text{O}_2} = 0.95$ -0.05 ([Fig. 4-B](#)). In both cases, isotherms presented growing exponential behaviors, chemisorbing more CO₂ as a function of temperature, as it could be expected. However, from these isotherms it is clearly evident that oxygen addition, into a saturated CO₂ atmosphere, improves the rate and final CO₂ chemisorptions. For example, at 450 °C the final weight increments in absence and presence of oxygen were 1 and 5 wt%. Similar effects were observed in the whole temperature range, where finally at 750 °C the weight increments were 38 and 35 wt%, with and without oxygen, respectively. Moreover, the initial reaction rate was clearly improved, as it is evidenced from the first couple of minutes of each isotherm; after 100 s of reaction the isotherm without oxygen gained 23.9 wt% while in presence of oxygen the weight increment was 35.6 wt%.

Based on the previous isothermal results, two new set of experiments were performed using a P_{CO_2} of 0.2 in the presence and absence of the same P_{O_2} ([Fig. 5](#)). As in the CO₂ saturated atmosphere, isotherms presented growing exponential behaviors, chemisorbing more CO₂ as a function of temperature, but in these cases the chemisorption-desorption equilibrium seem to be modified. Isotherms performed with P_{CO_2} of 0.2 and without oxygen, presented a growing trend as a function of temperature between 450 and 700 °C, capturing approximately 5 and 35 wt%, respectively. However, the isotherm performed at 750 °C only chemisorbed 25 wt%. This isotherm did presented the fastest CO₂ carbonation rate at short time (between 0 and 400 s), but after that time a partial CO₂ desorption process was evidenced. As it could be expected, CO₂ chemisorption-desorption equilibrium was shifted to lower temperatures due to the P_{CO_2} , in comparison to the CO₂ saturated isotherms previously described. Then, when oxygen was added ($P_{\text{O}_2} = 0.05$) the CO₂ isotherms ($P_{\text{CO}_2} = 0.2$) presented higher weight increments and the CO₂ chemisorption-desorption equilibrium shift to lower temperatures was not present. Here,

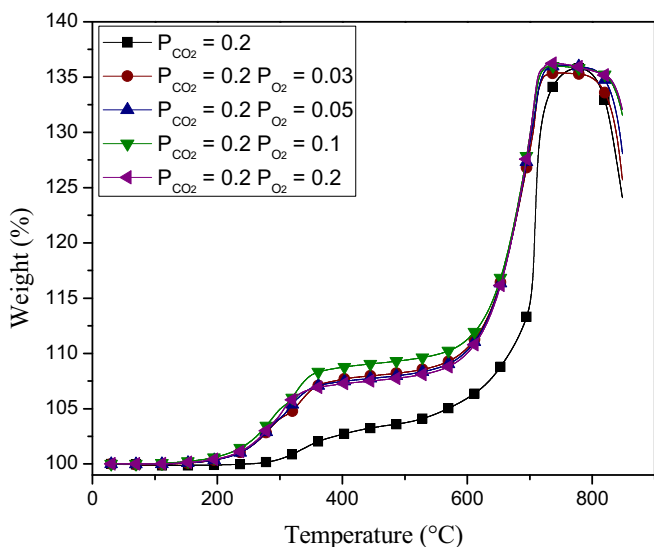


Fig. 2. Dynamic thermogravimetric analysis of the Li₂CuO₂ sample into a $P_{\text{CO}_2} = 0.2$ and different P_{O_2} (0.03, 0.1 and 0.2).

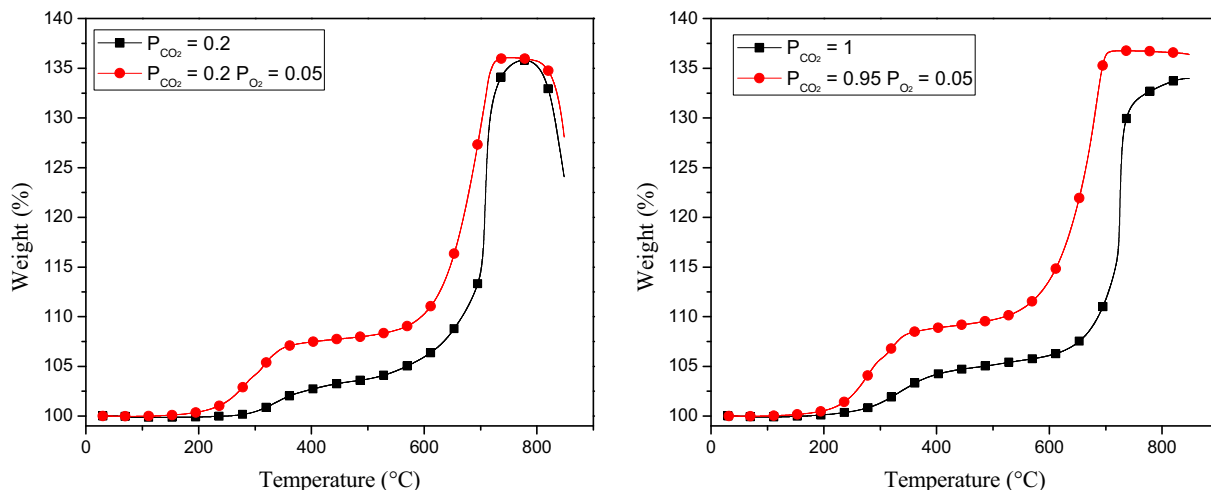


Fig. 3. Comparison of two specific cases of dynamic TG analysis: A) $P_{CO_2} = 0.2$ with and without oxygen; B) CO_2 saturated atmosphere with and without oxygen.

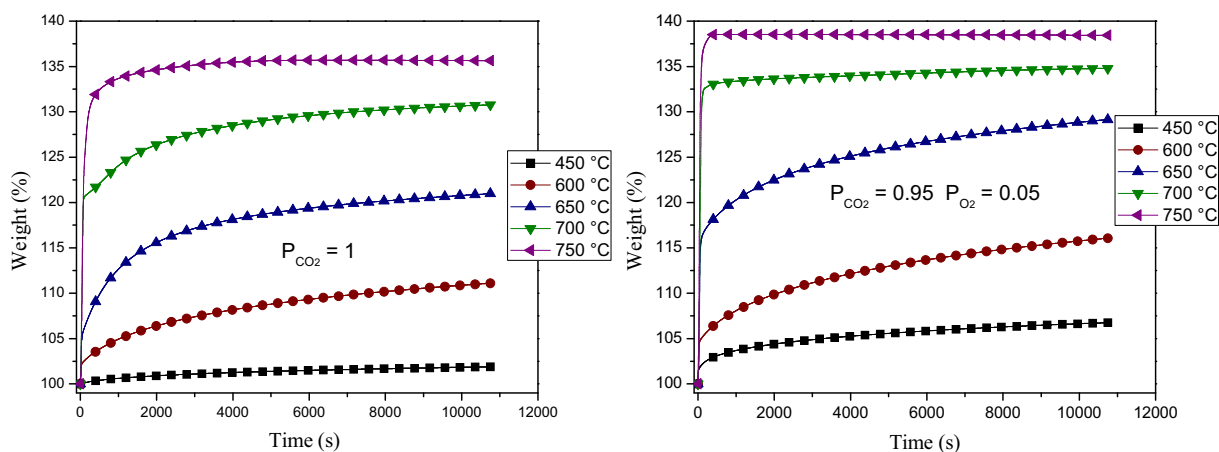


Fig. 4. Chemisorption thermogravimetric isotherms performed with CO_2 saturated atmospheres in the absence and presence of O_2 .

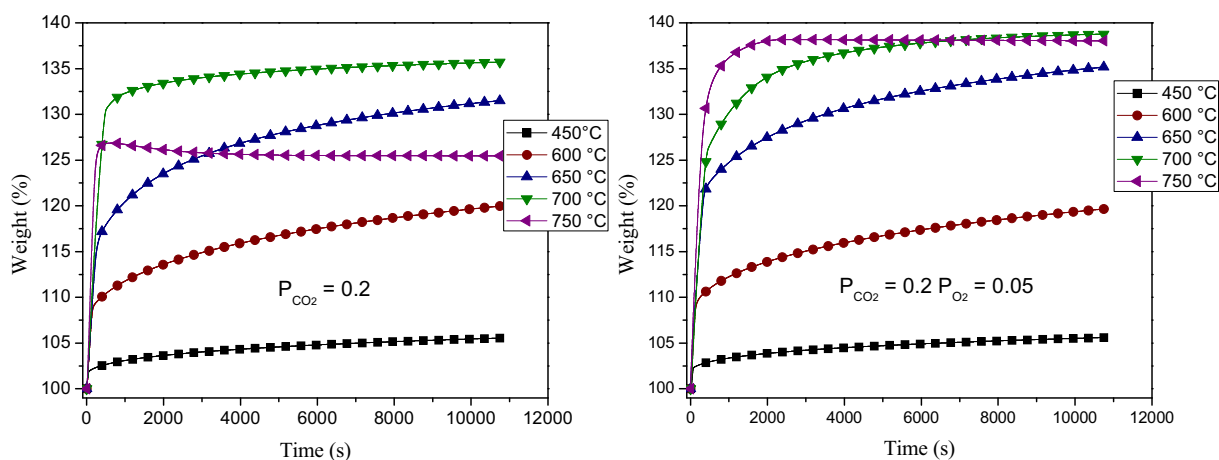


Fig. 5. Chemisorption thermogravimetric isotherms performed with $P_{CO_2} = 0.2$ and $P_{CO_2} = 0.2$ and $P_{O_2} = 0.05$.

the final weight increments at 450 and 600 °C did not seem to present variation due to the oxygen addition. Nevertheless, at higher temperatures (650–750 °C) the final weights did increase by the oxygen addition. The three final weights at 650, 700 and 750 °C in the absence of oxygen were 32, 35 and 25 wt%, while in the oxy-

gen presence the final weights were 35, 38 and 37.5 wt%. As the CO_2 chemisorption rate seems to be faster in the oxygen presence, the CO_2 desorption is kinetically reduced. All these results confirmed that oxygen addition does enhance the CO_2 chemisorption process in Li_2CuO_2 . In fact this enhancement must be attributed

Table 1
Table 1. Kinetic constant values obtained from the first order reaction model for the CO₂ chemisorption on Li₂CuO₂ into a CO₂ saturated atmosphere, in the oxygen absence (k_{CO_2}) or presence ($k_{\text{CO}_2\text{-O}_2}$).

T (°C)	k_{CO_2} (1/s)	R ²	$k_{\text{CO}_2\text{-O}_2}$ (1/s)	R ²
450	2.24×10^{-5}	0.9991	2.88×10^{-3}	0.9849
600	9.47×10^{-4}	0.9632	2.49×10^{-3}	0.9962
650	1.61×10^{-3}	0.9612	2.62×10^{-3}	0.9848
700	1.97×10^{-3}	0.9647	3.49×10^{-3}	0.9971
750	2.23×10^{-3}	0.9815	5.49×10^{-3}	0.9809

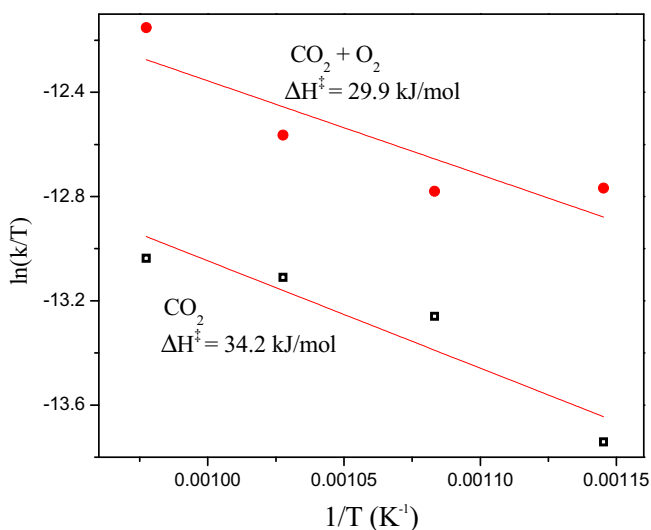


Fig. 6. Eyring-type plot of $\ln(k/T)$ vs $1/T$ for data obtained assuming a first-order reaction of $[\text{Li}_2\text{CuO}_2]$.

to the oxygen accessibility during the reaction process instead oxygen lattice atoms must diffuse and react with CO₂ to produce Li₂CO₃. These reaction rates and mechanism are further supported and described below.

To further analyze the isothermal curves shown in Fig. 4, these data were fitted to a first-order reaction model [32]. This model was selected because there are several processes involved in this reaction mechanism, for example different CO₂ chemisorption processes and the addition of the oxygen into the flow. Therefore, it was not possible to fit the data to the exponential model [32–34]. However, during the first moments of the CO₂ chemisorption process, it can be assumed that a first-order reaction occurred with respect to Li₂CuO₂ surface particles because CO₂ was present in excess (P_{CO_2} of 1 or 0.95). Therefore, the rate law can be described as:

$$\ln[\text{Li}_2\text{CuO}_2] = -kt \quad (2)$$

where k is the reaction rate constant, t is the time, and $[\text{Li}_2\text{CuO}_2]$ is the molar concentration of the unreacted ceramic. Assuming a superficial Li₂CuO₂ carbonation reaction, data presented linear trends over a very short time periods (~15 s). Table 1 shows the k values obtained for both isothermal sets, in presence or absence of oxygen. In the oxygen absence, k_{CO_2} values tend to increase between 450 and 750 °C. On the other hand, $k_{\text{CO}_2\text{-O}_2}$ decrease between 450 and 600 °C, but after that, $k_{\text{CO}_2\text{-O}_2}$ values tend to increase. However, the k values for the CO₂ chemisorption in presence of oxygen are always higher than those obtained in the oxygen absence ($k_{\text{CO}_2\text{-O}_2} > k_{\text{CO}_2}$). It means that oxygen improves the reaction kinetics. Moreover, using Eyring's model (Eq. (3)) for heterogeneous reactions, the activation enthalpy (ΔH^\ddagger , Fig. 6) could be determined.

$$\ln(k/T) = (\Delta H^\ddagger/RT) + (\Delta S^\ddagger/R) + C \quad (3)$$

where R is the universal gas constant and ΔH^\ddagger and ΔS^\ddagger correspond to the activation enthalpy and entropy, respectively.

To obtain ΔH^\ddagger in both cases, it was used the temperature range between 600 and 750 °C, since in a previous report of lithium cuprate, ΔH^\ddagger could not be determined at temperatures below 600 °C, due to other thermodynamic or diffusion factors are influencing the reaction [25]. ΔH^\ddagger value in presence or absence of oxygen were 29.9 and 34.2 kJ/mol, respectively. Hence, the oxygen addition tends to decrease, slightly, the CO₂ chemisorption temperature dependence. Additionally, ΔH^\ddagger values are in the range of the same range than those reported for other alkaline ceramics [32]. All this results confirms that addition of oxygen enhances the CO₂ chemisorption on lithium cuprate.

After the isothermal analysis, the CO₂ chemisorption was evaluated cyclically under P_{CO_2} and P_{O_2} of 0.2 and 0.05, respectively. The chemisorption process was performed at 700 °C for 1 h, while desorptions were conducted at 700 °C for 1 or 2 h into a N₂ flow with the same oxygen addition ($P_{\text{O}_2} = 0.05$), otherwise the desorption process was not produced (Fig. 7). In both cyclic experiments the first CO₂ chemisorption reached 33–35 wt%, meaning an 85% of efficiency. However, when the desorption process was limited to one hour (Fig. 7-A) the sample did not completely the decarbonation process. In this case, only half of the initial CO₂, previously trapped, was desorbed. Then, in the subsequent cycles, the CO₂ chemisorption was limited to half of the initial CO₂ captured, although the procedure was stable. Therefore, in the second cyclic experiment desorption process was set to two hours (Fig. 7-B). Under this condition, the desorption process went almost to completion, as 85–88% of the initial CO₂ trapped was desorbed. Again, using two hours of desorption cycles presented a very good stability. The total CO₂ cycled and the stability of these cycles is shown on the Fig. 7-C, where it is clear that around 4 or 6 mmol_{CO2}/gr_{ceram} can be cycled under low P_{CO_2} and in the presence of small amounts of oxygen, depending on the desorption time.

In order to further understand the Li₂CuO₂-CO₂ chemisorption process in the presence of oxygen, the final cyclic products were analyzed by XRD. These results are presented in the Fig. 8, where the initial Li₂CuO₂ was included for comparison purposes. The cyclic products were analyzed by XRD after one or two hours of desorption. The XRD pattern of the two hours desorption cyclic product showed the presence of different crystalline phases (Fig. 8-b); Li₂CO₃ (22-1141 PDF file), Li₃Cu₂O₄ (42-0477 PDF file) and CuO (48-1548 PDF file). The formation of Li₂CO₃ and CuO are in good agreement with the CO₂ chemisorption proposed in the reaction 1. Moreover, as it is a partially desorbed product, their presence is justified. On the other hand, the presence of Li₃Cu₂O₄ phase indicates that Li₂CuO₂ recrystallizes through intermediate crystalline phases. To prove this hypothesis, a total desorbed cycle experiment was analyzed via XRD. In this case the XRD pattern fitted very well with the 20-0623 PDF file, corresponding to Li₂CuO₂. This result confirms the Li₂CuO₂ carbonation and subsequent decarbonation processes, where the Li₂CuO₂ is recovered through an intermediate; Li₃Cu₂O₄.

Cyclic results indicates that Li₂CuO₂ can be regenerated using oxygen, observing similar desorption temperatures than other

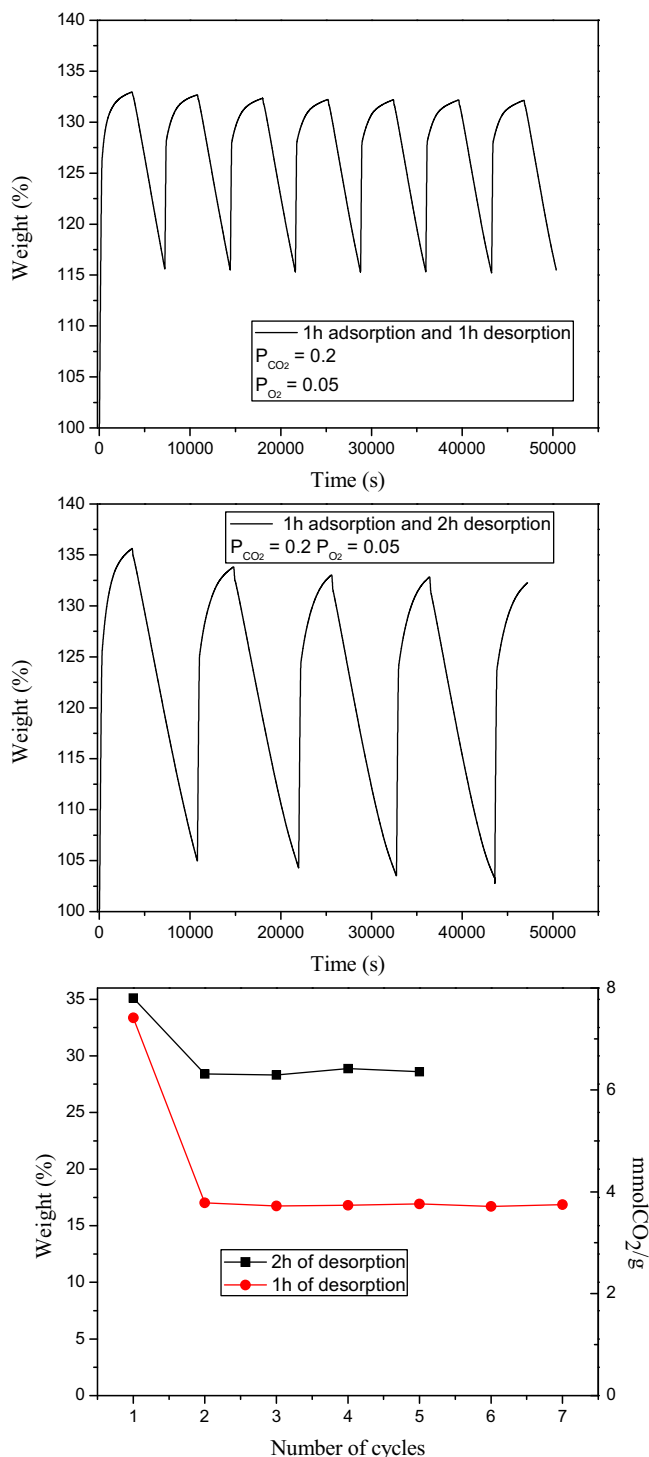


Fig. 7. Cyclability experiments performed with $P_{\text{CO}_2} = 0.2$ and $P_{\text{O}_2} = 0.05$, using different desorption times; 1 h (a), 2 h (b) and cycle efficiency (c).

alkaline ceramics, such as Na_2ZrO_3 (550–800 °C) [35], Li_5AlO_4 (750 °C) [36], and Li_4SiO_4 (600–850 °C) [33,36,37]. In any case, the use of oxygen shows the desorption viability in this material, which suggests that other alkaline ceramics may be benefited by using oxygen during the cyclic desorption process.

Based in all these results the following reaction mechanism can be proposed for the CO_2 chemisorption on Li_2CuO_2 in the oxygen absence or presence. In both cases, CO_2 must initially interact with the lithium atoms of Li_2CuO_2 , through an acid-base interaction.

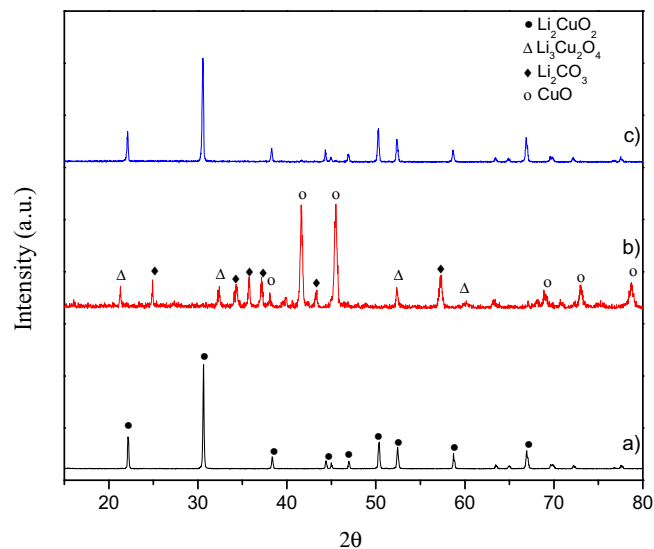
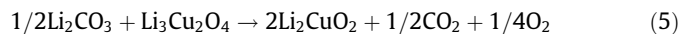
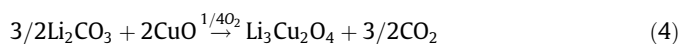


Fig. 8. XRD patterns of the pristine Li_2CuO_2 (a) and products of the cycles; after an unfinished desorption (b) and after a total desorption (c) processes.

Thus, Li_2CO_3 production depends on the CO_3^{2-} ion formation, which seems to highly depend on the oxygen viability. In the first case, oxygen has to be released from the Li_2CuO_2 crystalline structure, while in the second case oxygen can be obtained, more easily, from the gas flow. Moreover, the presence of copper facilitates the oxygen dissociation, as it has been report [28]. In such a case, the oxygen surplus, present in the Li_2CuO_2 structure, must be released without affecting the kinetic reaction mechanism.

On the contrary, the Li_2CuO_2 recrystallization, produced during the decarbonation process, follows an alternative way by the $\text{Li}_3\text{Cu}_2\text{O}_4$ intermediate formation. In this case, the $\text{Li}_3\text{Cu}_2\text{O}_4$ intermediate phase is produced by the partial reincorporation of lithium liberated after the Li_2CO_3 decomposition into the CuO structure. In this case, half of the total copper atoms have to be further oxidized, from 2+ to 3+. It seems that $P_{\text{O}_2} = 0.05$ produces the partial copper oxidation and subsequently the $\text{Li}_3\text{Cu}_2\text{O}_4$ stabilization. After that, if all the Li_2CO_3 is decomposed $\text{Li}_3\text{Cu}_2\text{O}_4$ evolves to Li_2CuO_2 by the lithium reincorporation (reactions 4 and 5). Finally, it must be mentioned that $\text{Li}_3\text{Cu}_2\text{O}_4$ was not observed during the carbonation process at none of the physicochemical conditions used in the present work, as all the isothermal products were analyzed by XRD (data not show).



4. Conclusions

Lithium cuprate was produced via a solid state reaction to study the CO_2 capture under different partial pressures of CO_2 and O_2 . The CO_2 chemisorption process was dynamically and isothermally analyzed using thermogravimetric analysis. Initially, the use of different CO_2 partial pressures (P_{CO_2} between 0.03 and 0.2) did not show any important difference during the CO_2 chemisorption in comparison to the experiment performed with CO_2 saturated atmosphere ($P_{\text{CO}_2} = 1$). Then, when oxygen was added to the gas flow (P_{O_2} between 0.03 and 0.2) the CO_2 chemisorption process was importantly enhanced at different levels, even when different CO_2 saturated atmospheres were used ($P_{\text{CO}_2} + P_{\text{O}_2} = 1.0$, where $P_{\text{O}_2} \leq 0.2$); 1) The CO_2 capture temperature was shifted to lower

temperatures, 2) the CO₂ capture rate was improved and 3) Li₂-CuO₂ could perform a carbonation-decarbonation process.

A kinetic analyses were performed assuming first order reaction. The kinetic constant values obtain when oxygen was added ($k_{CO_2-O_2}$) were higher than without oxygen (k_{CO_2}). Then, the reaction kinetics is improved with the addition of oxygen. Furthermore, ΔH^\ddagger values ($\Delta H^\ddagger_{CO_2+O_2} = 29.9$ kJ/mol and $\Delta H^\ddagger_{CO_2} = 34.2$ kJ/mol), showed that oxygen addition decreases the reaction temperature dependence. Therefore, CO₂ chemisorption strongly depends on the oxygen viability. In the oxygen absence, oxygen atoms have to be released from the Li₂CuO₂ crystalline structure. Then an anionic crystalline diffusion has to be performed, limiting the whole carbonation process. On the contrary, if oxygen is supplied through the gas flow, the carbonation process is facilitated. In this case, the presence of copper in lithium cuprate crystalline must facilitate the oxygen dissociation, which can be taken from the gas flow without any crystalline diffusion process dependency. The oxygen remaining in the Li₂CuO₂ decomposed crystalline structure must be released without affecting the kinetic reaction mechanism, producing the CuO.

Finally, it has to be taken into account the Li₂CuO₂ recrystallization is performed by a different reaction mechanism, where Li₃Cu₂O₄ phase is produced as an intermediate during the decarbonation process. This intermediate phase was observed when only half, or less, of the lithium atoms had been reincorporated to the cuprate structure. The Li₃Cu₂O₄ formation implies a partial copper oxidation, which must be induced by the P_{O₂}. Nonetheless, a further lithium reincorporation enables a total Li₂CuO₂ regeneration.

These results show the importance of the oxygen viability during the carbonation process of lithium cuprate and perhaps of other alkaline ceramics used for the CO₂ capture. It seems that oxygen addition into the gas flow strongly enhances the ceramic carbonation and decarbonation processes.

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References

- [1] J. Wang, L. Huang, R. Yang, Z. Zhang, J. Wu, Y. Gao, Q. Wang, D. O'Hare, Z. Zhong, Recent advances in solid sorbents for CO₂ capture and new development trends, *Energy Environ. Sci.* 7 (2014) 3478–3518.
- [2] X. Lu, D. Jin, S. Wei, Z. Wang, C. An, W. Guo, Strategies to enhance CO₂ capture and separation based on engineering adsorbent materials, *J. Mater. Chem. A* 3 (2015) 12118–12132.
- [3] M. Olivares-Marín, M. Maroto-Valer, Development of adsorbents for CO₂ capture from waste materials: a review, *Greenhouse Gases Sci. Technol.* 2 (2012) 20–35.
- [4] Q. Wang, J. Luo, Z. Zhong, A. Borgna, CO₂ capture by solid adsorbents and their applications: current status and new trends, *Energy Environ. Sci.* 4 (2011) 42–55.
- [5] L. Fu, G. Qi, O. Shekhah, Y. Belmabkhout, L. Estevez, M. Eddaoudi, E.P. Giannelis, Synthesis and carbon dioxide sorption of layered double hydroxide/silica foam nanocomposites with hierarchical mesostructure, *ChemSusChem* 7 (2014) 1035–1039.
- [6] S.D. Kenarsari, D. Yang, G. Jiang, S. Zhang, J. Wang, A.G. Russell, Q. Wei, M. Fan, Review of recent advances in carbon dioxide separation and capture, *RSC Adv.* 3 (2013) 22739–22773.
- [7] P. Wattanaphan, T. Sema, R. Idem, Z. Liang, P. Tontiwachwuthikul, Effects of flue gas composition on carbon steel (1 0 2 0) corrosion in MEA-based CO₂ capture process, *Inter. J. Greenhouse Gas Control* 19 (2013) 340–349.
- [8] E.S. Rubin, H. Mantripragada, A. Marks, P. Versteeg, J. Kitchin, The outlook for improved carbon capture technology, *Prog. Energy Combust. Sci.* 38 (2012) 630–671.
- [9] S. Choi, J.H. Drese, C.W. Jones, Adsorbent materials for carbon dioxide capture from large anthropogenic point sources, *ChemSusChem* 2 (2009) 796–854.
- [10] S. Wang, C. An, Q.H. Zhang, Syntheses and structures of lithium zirconates for high-temperature CO₂ absorption, *J. Mater. Chem. A* 1 (2013) 3540–3550.
- [11] S.M. Amorim, M.D. Domenico, T.L.P. Dantas, H.J. José, R.F.P.M. Moreira, Lithium orthosilicate for CO₂ capture with high regeneration capacity: kinetic study and modeling of carbonation and decarbonation reactions, *Chem. Eng. J.* 283 (2016) 388–396.
- [12] K.M. Ooi, S.P. Chai, A.R. Mohamed, M. Mohammadi, Effects of sodium precursors and gelling agents on CO₂ sorption performance of sodium zirconate, *Asia-Pac. J. Chem. Eng.* 10 (2015) 565–579.
- [13] C. Gauer, W. Heschel, Doped lithium orthosilicate for absorption of carbon dioxide, *J. Mater. Sci.* 41 (2006) 2405–2409.
- [14] A. Gaur, J.W. Park, J.H. Jang, S. Maken, J. Lee, H.J. Song, Characteristics of alkaline wastewater neutralization for CO₂ capture from landfill gas, *Energy Fuels* 23 (2009) 5467–5473.
- [15] A. Castillo Villa, J. Salinas Gutiérrez, C.J. Navarro Gómez, G.S. Aquino de los Rios, M. Rentería Villalobos, L. Cortés Palacios, A. López Ortiz, V. Collins-Martínez, Kinetic study of the CO₂ desorption process by carbonated Na₂ZrO₃ solid adsorbent, *Inter. J. Hydrogen Energy* 40 (2015) 17338–17343.
- [16] B.N. Nair, R.P. Burwood, V.J. Goh, K. Nakagawa, T. Yamaguchi, Lithium based ceramic materials and membranes for high temperature CO₂ separation, *Prog. Mater. Sci.* 54 (2009) 511–541.
- [17] H.R. Radfarnia, M.C. Iliuta, Application of surfactant-template technique for preparation of sodium zirconate as high temperature CO₂ sorbent, *Sep. Purif. Technol.* 93 (2012) 98–106.
- [18] H.G. Jo, H.J. Yoon, C.H. Lee, K.B. Lee, Citrate sol-gel method for the preparation of sodium zirconate for high-temperature CO₂ sorption, *Ind. Eng. Chem. Res.* 55 (2016) 3833–3839.
- [19] Q. Xiao, X. Tang, Y. Liu, Y. Zhong, W. Zhu, Citrate route to prepare K-doped Li₂ZrO₃ sorbents with excellent CO₂ capture properties, *Chem. Eng. J.* 174 (2011) 231–235.
- [20] A. Iwan, H. Stephenson, W.C. Ketchie, A.A. Lapkin, High temperature sequestration of CO₂ using lithium zirconates, *Chem. Eng. J.* 146 (2009) 249–258.
- [21] M.R. Quddus, M.B.I. Chowdhury, H.I. de Lasa, Non-isothermal kinetic study of CO₂ sorption and desorption using a fluidizable Li₄SiO₄, *Chem. Eng. J.* 260 (2015) 347–356.
- [22] M.B.I. Chowdhury, M.R. Quddus, H.I. de Lasa, CO₂ capture with a novel solid fluidizable sorbent: thermodynamics and temperature programmed carbonation-decarbonation, *Chem. Eng. J.* 232 (2013) 139–148.
- [23] K. Oh-Ishi, Y. Matsukura, T. Okumura, Y. Matsunaga, R. Kobayashi, Fundamental research on gas-solid reaction between CO₂ and Li₂CuO₂ linking application for solid CO₂ absorbent, *J. Solid State Chem.* 211 (2014) 162–169.
- [24] L.M. Palacios-Romero, H. Pfeiffer, Lithium cuprate (Li₂CuO₂): a new possible ceramic material for CO₂ chemisorption, *Chem. Lett.* 37 (2008) 862–863.
- [25] L.M. Palacios-Romero, E. Lima, H. Pfeiffer, Structural analysis and CO₂ chemisorption study on non-stoichiometric lithium cuprates (Li_{2+x}CuO_{2+x/2}), *J. Phys. Chem. A* 113 (2009) 193–198.
- [26] Y. Matsukura, T. Okumura, R. Kobayashi, K. Oh-Ishi, Synthesis and CO₂ absorption properties of single-phase Li₂CuO₂ as a CO₂ absorbent, *Chem. Lett.* 39 (2010) 966–967.
- [27] H.A. Lara-García, B. Alcántar-Vázquez, Y. Duan, H. Pfeiffer, Water steam effect during high CO₂ chemisorption in lithium cuprate (Li₂CuO₂) at moderate temperatures: experimental and theoretical evidence, *RSC Adv.* 5 (2015) 34157–34165.
- [28] H.A. Lara-García, B. Alcántar-Vázquez, Y. Duan, H. Pfeiffer, CO chemical capture on lithium cuprate, through a consecutive CO oxidation and chemisorption bifunctional process, *J. Phys. Chem. C* 120 (2016) 3798–3806.
- [29] H.A. Lara-García, M.J. Ramírez-Moreno, J. Ortiz-Landeros, H. Pfeiffer, CO₂ chemisorption in Li₂CuO₂ microstructurally modified by ball milling: study performance with different physicochemical CO₂ capture conditions, *RSC Adv.* 6 (2016) 57880–57888.
- [30] J. Ortiz-Landeros, T.L. Ávalos-Rendón, C. Gómez-Yáñez, H. Pfeiffer, Analysis and perspectives concerning CO₂ chemisorption on lithium ceramics using thermal analysis, *J. Therm. Anal. Calorim.* 108 (2012) 647–655.
- [31] L. Martínez-díCruz, H. Pfeiffer, Effect of oxygen addition on the thermokinetic properties of CO₂ chemisorption on Li₂ZrO₃, *Ind. Eng. Chem. Res.* 49 (2010) 9038–9042.
- [32] F. Durán-Muñoz, I.C. Romero-Ibarra, H. Pfeiffer, Analysis of the CO₂ chemisorption reaction mechanism in lithium oxosilicate (Li₈SiO₆): a new option for high-temperature CO₂ capture, *J. Mater. Chem. A* 1 (2013) 3919–3925.
- [33] H. Kim, H.D. Jang, M. Choi, Facile synthesis of macroporous Li₄SiO₄ with remarkably enhanced CO₂ adsorption kinetics, *Chem. Eng. J.* 280 (2015) 132–137.
- [34] K. Wang, Z. Yin, P. Zhao, Synthesis of macroporous Li₄SiO₄ via a citric acid-based sol-gel route coupled with carbon coating and its CO₂ chemisorption properties, *Ceram. Inter.* 42 (2016) 2990–2999.
- [35] L. Martínez-díCruz, H. Pfeiffer, Cyclic CO₂ chemisorption-desorption behavior of Na₂ZrO₃: structural, microstructural and kinetic variations produced as a function of temperature, *J. Solid State Chem.* 204 (2013) 298–304.
- [36] T. Ávalos-Rendón, V.H. Lara, H. Pfeiffer, CO₂ chemisorption and cyclability analyses of lithium aluminate polymorphs (α - and β -Li₅AlO₄), *Ind. Eng. Chem. Res.* 51 (2012) 2622–2630.
- [37] M. Olivares-Marín, T.C. Drage, M.M. Maroto-Valer, Novel lithium-based sorbents from fly ashes for CO₂ capture at high temperatures, *Inter. J. Greenhouse Gas Control* 4 (2010) 623–632.