CO$_2$ chemisorption enhancement produced by K$_2$CO$_3$- and Na$_2$CO$_3$-addition on Li$_2$CuO$_2$

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ABSTRACT

This work presents a proposal for enhancing CO$_2$ capture over lithium cuprate (Li$_2$CuO$_2$) by alkaline carbonates addition. Lithium cuprate was synthesized via solid-state reaction. Subsequently, portions of Li$_2$CuO$_2$ were mechanically mixed with 10 wt% of potassium carbonate (K$_2$CO$_3$), sodium carbonate (Na$_2$CO$_3$) or equal amounts of both carbonates (5–5 wt%). All samples were characterized by several techniques and then CO$_2$ chemisorption process was evaluated on different dynamic and isothermal conditions. The presence of K and/or Na carbonates preserves the primary properties of pristine Li$_2$CuO$_2$, such as crystalline phase (DRX) and microstructure (SEM), also allowing to increase textural properties (N$_2$ physisorption) and modifying CO$_2$ desorption abilities (TPD), in comparison with pure material. In general, carbonates addition induces some changes during CO$_2$ chemisorption, depending on the type of carbonate used. On the isothermal tests, it was observed that between 400 and 600 °C the sample containing both carbonates presented the best capture performance, capturing between 25.7 and 31.8 wt% of CO$_2$ (63.9–79.1% of efficiency). On the other hand, at 700 °C, Na-Li$_2$CuO$_2$ sample presented the best capture ability, capturing 30.6 wt% of CO$_2$ (76.1% of efficiency). Meanwhile at 650 °C, K-Li$_2$CuO$_2$ presented the highest sorption capacity with 40.4 wt% of CO$_2$ captured, which represents ~100% of efficiency. The above results showed that in the same thermal conditions, samples modified with alkaline carbonates improved the CO$_2$ capture process. This enhancement was attributed to the formation of eutectic phases (observed in DSC analysis) between sodium and potassium carbonates added mechanically and lithium carbonate (Li$_2$CO$_3$) formed as result of CO$_2$ chemisorption process. Finally, it was observed that carbonate addition is a feasible way to increase CO$_2$ capture in Li$_2$CuO$_2$ material by means of eutectic phase formation.

1. Introduction

Nowadays, increased rates of human population growth and advancements in technology have brought adverse effects on the environment, amongst these, greenhouse effect and global warming. Over the last decades, reducing the amounts of greenhouse gases (GHGs) released to the atmosphere, particularly carbon dioxide (CO$_2$) emissions [1–5], has been one of the greatest challenges for attempting slows down global warming and prevents drastic climate change. Amongst different methods for mitigating CO$_2$ emissions, the use of alkaline ceramics for CO$_2$ sequestration through a process of chemisorption is one of the most used options [1,6]. These CO$_2$ sorbents must satisfy different characteristics, e.g. good physicochemical properties, high surface basicity, mechanical strength, thermal stability, high regeneration ability, multicycle durability, adequate sorption–desorption kinetics and also good selectivity in a wide temperature range.

For this purpose a variety of alkaline ceramics have shown good CO$_2$ capture abilities, among them lithium and sodium zirconates (Li$_2$ZrO$_3$ and Na$_2$ZrO$_3$ [7–13]), lithium orthosilicate (Li$_4$SiO$_4$ [14–19]), lithium aluminate (Li$_5$AlO$_4$ [20,21]), lithium ferrites (Li$_5$FeO$_4$ and LiFeO$_2$ [22]) and lithium cuprate (Li$_2$CuO$_2$ [23,24]). In particular, Li$_2$CuO$_2$ has been already studied as a CO$_2$ captor in a temperature range of 120 to 650 °C [25–28], with a theoretical capture value of 0.401 g of CO$_2$ per gram of ceramic. Li$_2$CuO$_2$ presents an orthorrombic phase with the following unit cell parameters: a = 3.655 Å, b = 2.860 Å, c = 9.377 Å and Z = 2 [29].

In order to enhance the performance of different sorbents during CO$_2$ chemisorption process, it has been proposed several physical and chemical modifications [30,31]. One of them consists in modification ceramics by mixing mechanically small amounts of alkaline carbonates with the aim to promote the eutectic phase formation between residual carbonate (formed during CO$_2$ chemisorption) and alkaline carbonates
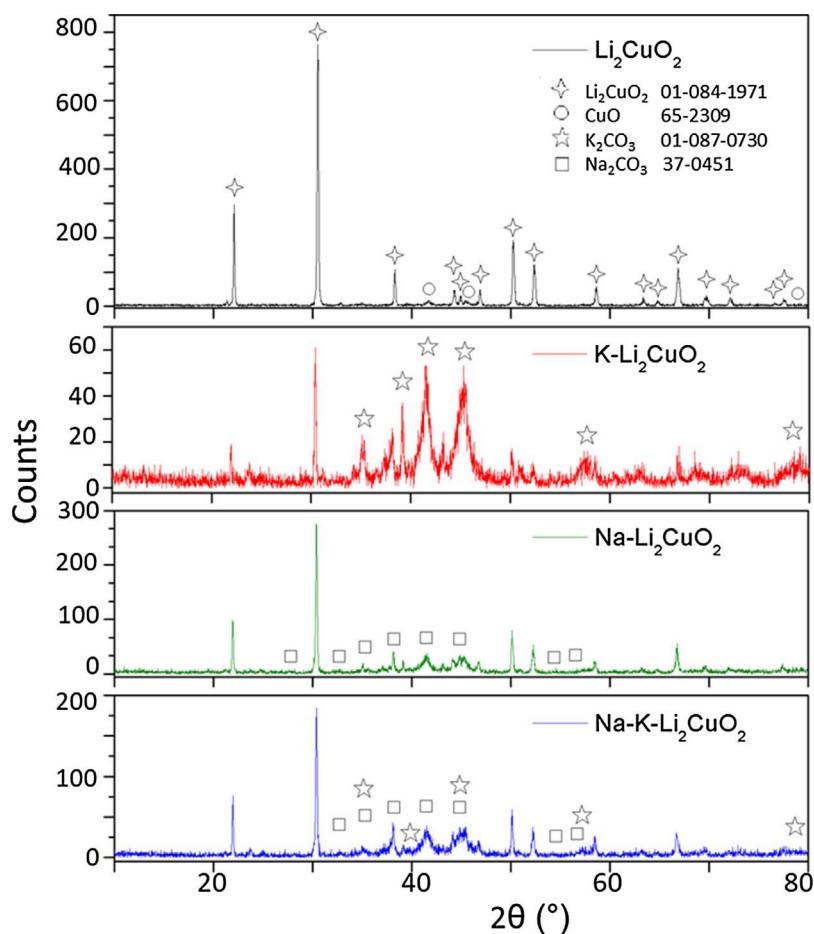

Fig. 1. XRD patterns of Li$_2$CuO$_2$ materials prepared with or without (K-, Na- and K-Na-) carbonates.

added during the synthesis. In this line, some studies have been focus on the effect of carbonates addition in different alkaline ceramics [7,32–34]. For example, in lithium oxosilicate (Li$_8$SiO$_6$) [35] and lithium aluminate (Li$_5$AlO$_4$) [36] cases, it was found that the presence of potassium and sodium carbonates not only produced changes in the temperature range where ceramic can act as a CO$_2$ captor, but also augmented the capacity of CO$_2$ captured in terms of mass. Also, it has been reported that lithium orthosilicate (Li$_4$SiO$_4$) sorbent was doped with K$_2$CO$_3$ [37,38] or Na$_2$CO$_3$-NaF [39], resulting in the formation of different low-temperature eutectic phases during CO$_2$ sorption process. However, there is not any report in literature about the effect of carbonates addition in lithium cuprate over its physicochemical characteristics and CO$_2$ capture abilities. Considering the above information, the aim of the present work was to elucidate the effect of adding K and/or Na carbonates in Li$_2$CuO$_2$ ceramic in order to improve CO$_2$ chemisorption rates due to the formation of Li$_2$CO$_2$-K$_2$CO$_3$, Li$_2$CO$_3$-Na$_2$CO$_3$ or Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ eutectic phases, resulting in a partial molten shell that allow to promote CO$_2$ diffusion.

2. Experimental section

Lithium cuprate (Li$_2$CuO$_2$) was synthesized by well-known solid-state reaction [22,23]. Lithium oxide (Li$_2$O, Aldrich, 99%) and copper oxide (CuO, Meyer, 97%) powders were used as reagents, mechanically mixed and calcined in air atmosphere up to 800 °C for 12 h at a heating rate of 5 °C/min. Considering lithium sublimation (T > 720 °C [40,41]), a 25 wt% excess of lithium oxide was used to compensate this lost during heat treatment. Then, the formation of Li$_2$CuO$_2$ phase was confirmed by powder X-ray diffraction (XRD) technique. XRD pattern was recorded in the 10° ≤ 2Θ ≤ 70° range, using a goniometer speed of 1°(2Θ) min^{-1}, with a Siemens D5000 diffractometer coupled to a cobalt

anode (λ = 1.789 Å) X-ray tube. Once crystalline structure was confirmed, Li$_2$CuO$_2$ was divided in four sections. Each set was mechanically mixed with different amounts of sodium and/or potassium carbonates as follows: i) 10 wt% of potassium carbonate (K$_2$CO$_3$, Sigma-Aldrich), ii) 10 wt% of sodium carbonate (Na$_2$CO$_3$, Aldrich) and iii) equal amounts of potassium and sodium carbonates (5–5 wt%). Meanwhile, last portion was used as reference with no added carbonates. Hereinafter, samples are labeled as K-Li$_2$CuO$_2$, Na-Li$_2$CuO$_2$, Na-K-Li$_2$CuO$_2$ and Li$_2$CuO$_2$, respectively. Samples modified with carbonates were studied by XRD in order to confirm the presence of Li$_2$CuO$_2$ and respective carbonates phases, using the same conditions described above. Also, samples were analyzed using scanning electron microscopy (SEM) in a FE SEM JEOL JSM-7600F equipment.

The microstructural characteristics were determined by N$_2$ adsorption-desorption analyses in a Bel-Japan Minisorp II equipment at −196 °C. For this purpose, samples were degassed at room temperature for 12 h in vacuum prior to analysis. The BET model was used to determine the surface area (S$_{BET}$). Moreover, endothermic and exothermic transitions, as function of temperature, were determined by differential scanning calorimetry (DSC). These experiments were performed using 5–10 mg of sample and heating it from 30 to 600 °C at 10 °C/min, in a N$_2$ (Praxair, grade 4.8) or CO$_2$ (Praxair, grade 3.0) atmospheres in a pressure DSC equipment from Instruments Specialist Incorporated. Then, CO$_2$ sorption ability was evaluated performing thermogravimetric analyses (TGA) in a TA Instruments Q500HR thermobalance. In this technique, samples were dynamically heated from 30 to 900 °C at a heating rate of 5 °C/min, under a saturated flow of CO$_2$ (60 mL/min). Then, some isothermal experiments were performed at different temperatures (400, 500, 600, 650 and 700 °C). In these tests, samples were heated (5 °C/min) from 30 °C to specified temperature, using N$_2$ (40 mL/min) as carrier gas; once desired temperature was achieved, the
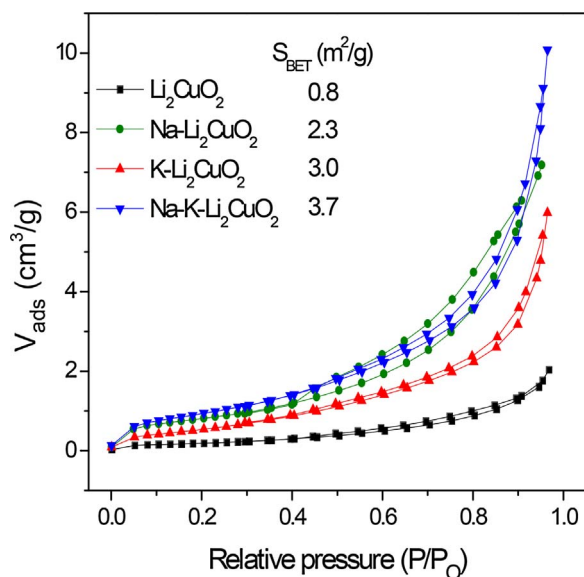
Fig. 2. N_2 adsorption-desorption isotherms for pristine and (K-, Na-, Na-K)-Li_2CuO_2 samples. The S_{BET} values are reported within the figure.

flow gas was switched to CO_2 (60 mL/min) and maintained during 180 min. Afterwards, isothermal products were analyzed by SEM and XRD with the aim to elucidate changes produced by the CO_2 chemisorption on the different materials. Finally, CO_2 temperature-programmed desorption (TPD) analyses were performed using a chemisorption analyzer (Belcat, Bel-Japan). Before each analysis, approximately 50 mg were introduced into a quartz cell and pretreated at 850 °C under a He flow (30 mL/min). Each sample was then cooled to 200 °C and saturated with a 60 mL/min flow of CO_2 for 60 min. Afterwards, CO_2-TPD analyses were performed by heating each sample up to 850 °C (heating rate of 2 °C/min) in a He flow, and the data were quantified by a thermal conductivity detector (TCD).

3. Results and discussion

3.1. (K-, Na-, Na-K-)-Li_2CuO_2 physicochemical characterization

Powder XRD patterns for pristine Li_2CuO_2 and samples mixed with sodium and/or potassium carbonates are shown in Fig. 1. Lithium cuprate X-ray diffraction shows signals related to crystalline planes of Li_2CuO_2 (JCPDS 01-084-1971, orthorhombic phase), but also reflections from residual CuO (JCPDS 65-2309, monoclinic phase) that did

not react during the synthesis stage. As expected, X-ray diffraction patterns of materials modified with carbonates, showed reflections for Li_2CuO_2 crystalline structure and also signals related to carbonates addition: Na_2CO_3 (JCPDS 37-0451, monoclinic phase) and K_2CO_3 (JCPDS 01-087-0730, monoclinic phase). In a further characterization, N_2 physisorption technique was applied in order to determinate textural characteristics for (K-, Na- and Na-K-)-Li_2CuO_2 samples. Nitrogen adsorption-desorption isotherms are show in Fig. 2. According to IUPAC classification, all materials present isotherms type II corresponding to nonporous materials [42]. In these materials, no significant hysteresis loops were observed. Additionally, specific surface areas (S_{BET}) were determined from N_2 adsorption curves, using the BET model. The S_{BET} value for pristine Li_2CuO_2 ceramic was 0.8 m²/g, which is in good agreement with previous reports for lithium cuprate synthetized by solid-state method [23,25]. Afterwards, carbonate additions in Li_2CuO_2 produces an increase in the S_{BET} values up to 3.7 m²/g. These results are totally related to composition changes occurred when carbonates were added on Li_2CuO_2, meaning that 10 wt% of carbonates contributes with 1.5–2.9 m²/g, depending on type and amounts of each carbonate.

Materials were characterized by differential scanning calorimetry (DSC) technique in two different atmospheres (N_2 and CO_2, Fig. 3), with the aim of elucidate if it is possible to produce a partial melts by means of eutectic phase formation between carbonates added (K_2CO_3 and Na_2CO_3) and the one produced (Li_2CO_3) during CO_2 chemisorption on Li_2CuO_2. Fig. 3-A shows the thermograms obtained for each sample treated under nitrogen atmosphere. In all cases, excepting for Na-Li_2CuO_2 material, a first endothermic peak between 50 and 60 °C was observed, which corresponds to the dehydration process of adsorbed water weakly physisorbed over ceramic surface. Subsequently, samples modified with carbonates presented a second endothermic peak between 80 and 100 °C, which increases as function of K_2CO_3 content. Thus, Na-Li_2CuO_2 profile presented a low intense signal, which began approximately 50 °C earlier than that well defined peak observed in K-Li_2CuO_2 material. This signal can be related to loss of intercrystalline water molecules that require a higher energy for being released from crystalline structure of sodium and potassium carbonates. After, between 300 and 500 °C, all samples exhibit an endothermic peak related to carbonates fusion processes, even pristine Li_2CuO_2, meaning a partial carbonation. It is possible noticing that independently of which carbonate was added, the melting process started at lower temperatures in comparison with original Li_2CuO_2 material. This result showed that carbonates addition decreases the energy needed to bring this melting process on ceramic surface. Despite Na-Li_2CuO_2 presents the lowest temperature, it requires the highest amount of heat flow for carrying out this process. Also, this temperature increases as function of K_2CO_3 content, thus the material modified with both carbonates, Na-K-
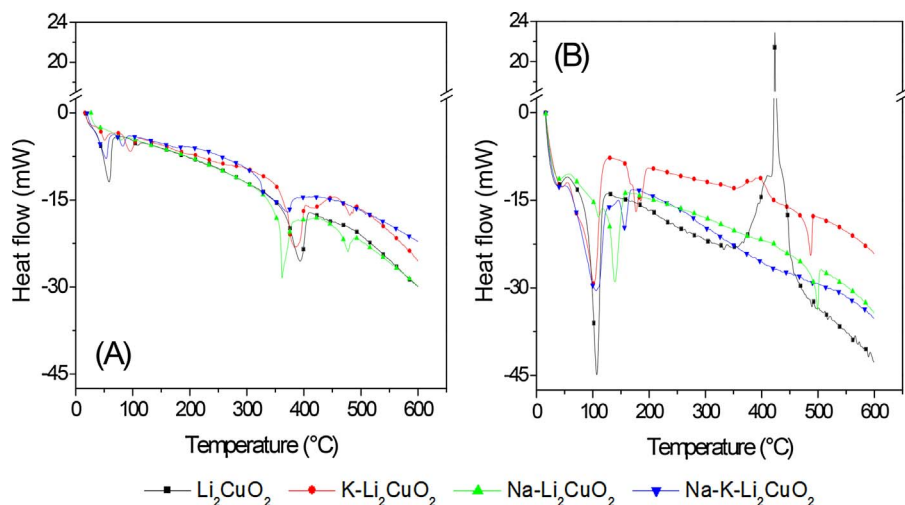

Fig. 3. DSC analyses in N_2 (A) and CO_2 (B) atmospheres for pristine and modified (K-, Na- and K-Na-)-Li_2CuO_2 samples.

Table 1

Specific enthalpy (ΔH) calculated in J/g from DSC analyses in N_2 and CO_2 atmospheres.

Atmosphere	Sample	Temperature range			
		30–60 °C	70–115 °C	330–420 °C	450–500 °C
N_2	Li_2CuO_2	96.7	–	202.4	–
	$K\text{-}Li_2CuO_2$	12.7	28.9	204.3	20.5
	$Na\text{-}Li_2CuO_2$	5.7	–	168.4	36.9
	$Na\text{-}K\text{-}Li_2CuO_2$	42.6	11.4	56.2	–
		40–120 °C	120–200 °C	330–420 °C	450–500 °C
CO_2	Li_2CuO_2	498.4	–	−725.5	–
	$K\text{-}Li_2CuO_2$	659.4	88.8	−73.4	46.1
	$Na\text{-}Li_2CuO_2$	–	195.3	–	38.5
	$Na\text{-}K\text{-}Li_2CuO_2$	435.6	32.0	–	–

Li_2CuO_2, showed an intermediate temperature behavior. On the other hand, a further endothermic peak was observed in $K\text{-}Li_2CuO_2$ and $Na\text{-}Li_2CuO_2$ profiles at around 480 °C. This can be attributed to a second fusion process between Na or K carbonates that did not intervene during first fusion process and Li_2CO_3 formed after the first diffusive capture process. This endothermic peak was not observed in $Na\text{-}K\text{-}$

Li_2CuO_2 profile maybe due to the fact that this sample was mechanical mixed with half amount from each carbonate. After N_2 tests, DSC experiments with CO_2 were performed at atmospheric pressure (Fig. 3-B). Thermograms show that endothermic and exothermic processes are influenced by the atmosphere used. In this case, thermal profiles presented greater signals than in N_2 atmosphere. As expected, all samples presented the same endothermic processes between 50 and 150 °C and 485–500 °C that were described above in Fig. 3-A. Then, in the intermediate temperature range between 300 and 430 °C, it can be noticed that endothermic signals, observed in N_2 tests, are not present in CO_2 profiles. Furthermore, only pure Li_2CuO_2 material presented a well-defined exothermic peak between 350 and 450 °C. According to literature [34,37,43], this signal is related to the CO_2 chemisorption reaction over alkaline ceramic surface. This result for Li_2CuO_2 sample showed that exothermic CO_2 chemisorption is energetically higher than endothermic carbonate fusion observed in N_2 test (Fig. 3-A). Despite, modified samples did not present a signal in this temperature range, it can be established that energy released due to CO_2 sorption must be equal to energy required for melting process during the eutectic phase formation. This can be possible considering that in CO_2 atmosphere endothermic processes requires higher amount of energy in order to do so, as it was described above. Finally, Table 1 shows specific enthalpies calculated for all the processes described above for both atmospheres.
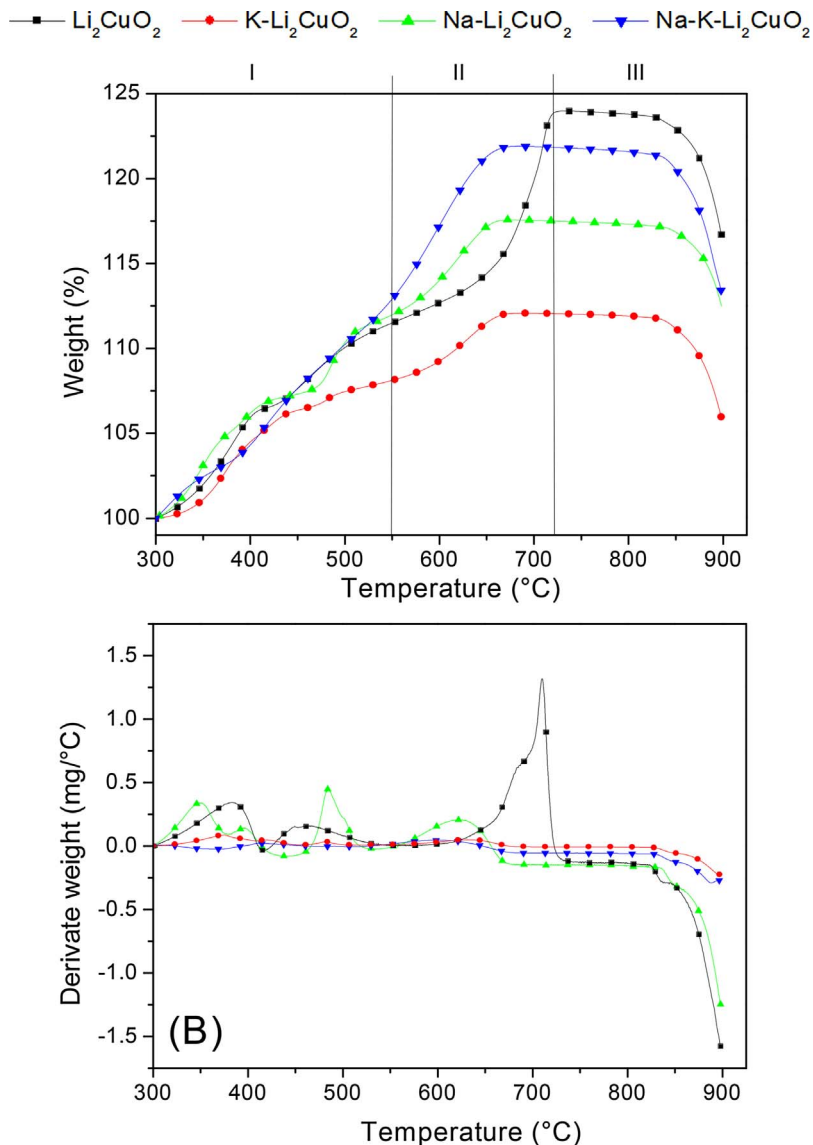

Fig. 4. (A) TGA and (B) DTG profiles for (K-, Na-, Na-K)-Li_2CuO_2 samples tested dynamically in a saturated CO_2 atmosphere. TGA were normalized at 100 wt%, after the dehydration weight loss of each sample (around 1 wt %).
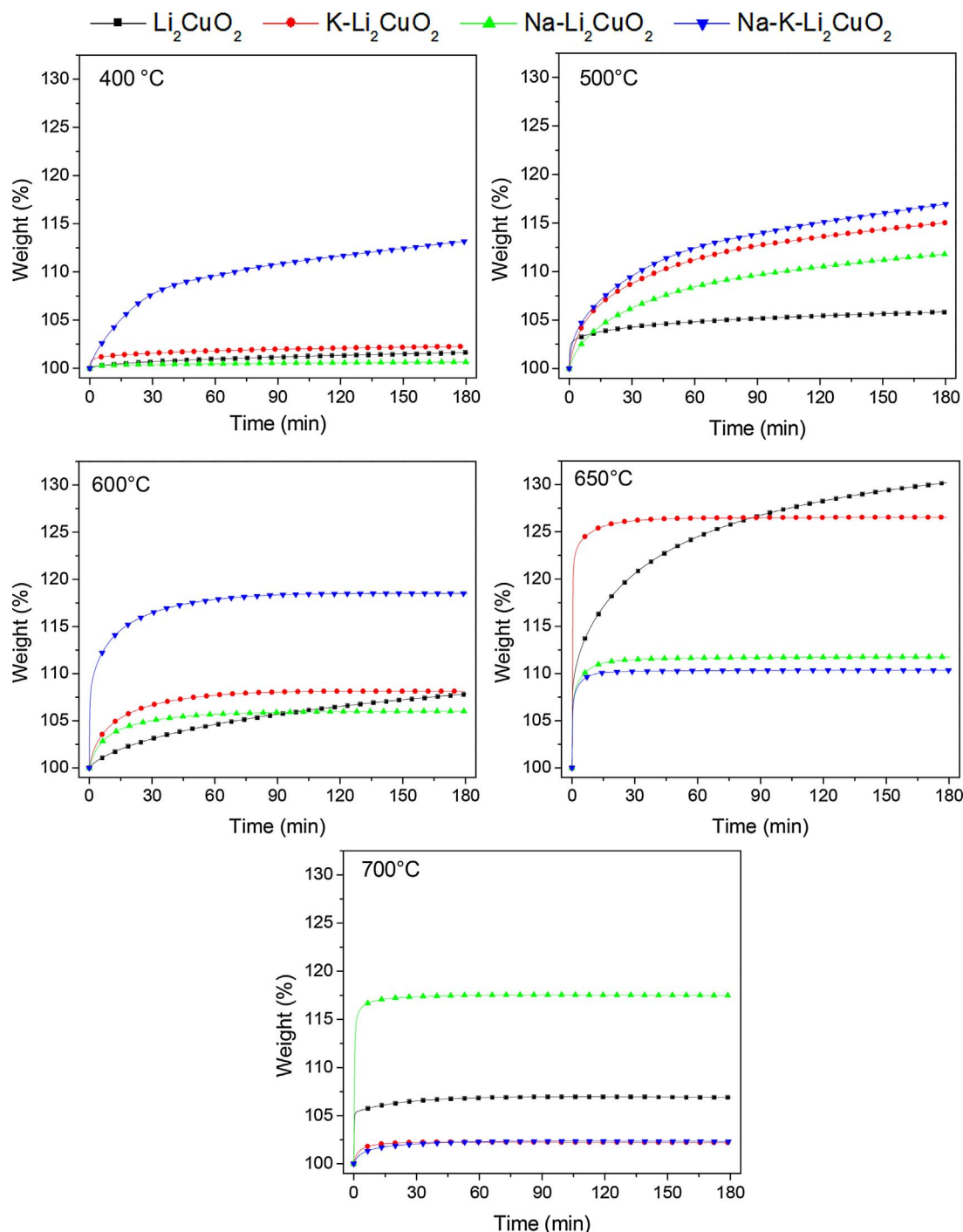
Fig. 5. Isotherm profiles for (K-, Na-, Na-K-)-Li$_2$CuO$_2$ samples tested at different temperatures (400–700 °C) in a saturated CO$_2$ atmosphere.

As it can be seen, an exothermic process (CO$_2$ capture) was observed only in two samples (Li$_2$CuO$_2$ and K- Li$_2$CuO$_2$) under CO$_2$ atmosphere. In these cases, carbonate addition induces the formation of a eutectic phase by means of reducing drastically the exothermic character observed in pure Li$_2$CuO$_2$, decreasing ten times its value when potassium carbonate was added or avoiding completely when Na- or Na-K- carbonates were aggregated. Meanwhile, the rest of ΔH correspond to endothermic processes, namely dehydration at T < 200 °C or carbonates fusion between 450 and 500 °C.

3.2. CO$_2$ sorption and desorption tests

After physicochemical characterization, all materials were thermally treated under carbon dioxide flow (60 mL/min). The thermogram profiles evidenced the chemisorption process described in reaction 1 (Fig. 4-A), by the weight increase as function of temperature. Thermograms have been dived in three sections according to changes observed in differential thermogravimetric curves (DTG, Fig. 4-B). It has to be mentioned that all samples presented at low temperatures (30–300 °C), dehydration and dehydroxylation processes, resulting in a loss of almost 1 wt% (data not shown).

$$Li_2CuO_{2(s)} + CO_{2(g)} \leftrightarrow Li_2CO_{3(s)} + CuO_{(s)} \qquad (1)$$
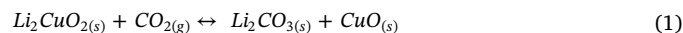
Regarding to pure Li$_2$CuO$_2$, thermogravimetric profile at 300 °C begins the surface capture [44], which was evident with a weight increase of 12 wt% at 550 °C (Process I). Subsequently, between 550 and
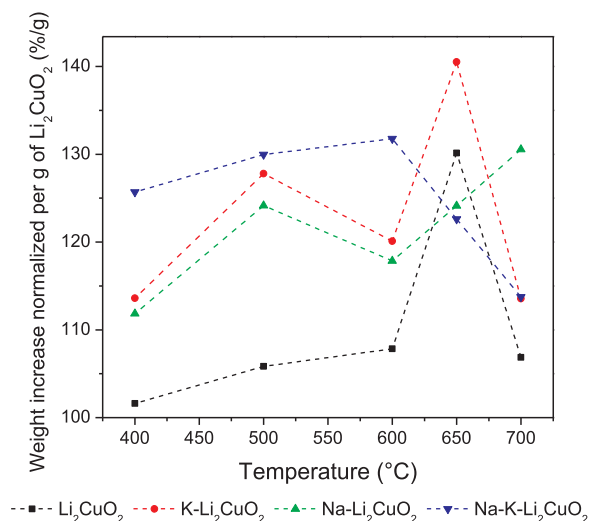
Fig. 6. CO₂ maxima chemisorption for pristine and modified Li₂CuO₂ samples tested isothermically between 400 and 700 °C in a saturated CO₂ atmosphere. Dash lines indicate possible lineal tendency between experimental data obtained at every temperature.
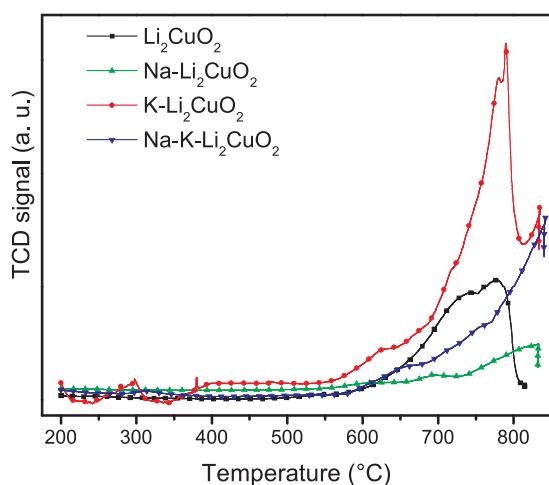

Fig. 7. CO₂-TPD desorption profiles for (K-, Na-, Na-K)-Li₂CuO₂ samples heat treated from 200 to 850 °C in a He flow.

700 °C, volumetric capture process took place producing a drastically weight increment and reaching at 730 °C, the maximum CO₂ chemisorption (24.0 wt%, Process II). This amount of CO₂ corresponds to an efficiency of 59.7% in comparison to theoretical maximum capture value of 40.2 wt% [23]. DTG curve for this material presented the greatest changes among all profiles. The first change occurs at 390 °C and it is related to the formation of an outer layer composed by Li₂CO₃ and CuO as a secondary phase. This outer layer obstructs a subsequent CO₂ sorption, then the capture mechanism changes and it is performed by means of diffusion processes in material bulk. This phenomenon was observed since 550 °C, where the outer layer becomes saturated. In this case, diffusion processes continue CO₂ capture and a weight increment of 12 wt% was registered in this stage. Finally, at temperatures between 700 and 800 °C, no changes in material weight were observed; whereas at T > 800 °C a significant decrease in weight percentage was observed due to CO₂ desorption (Process III) through Li₂CO₃ decomposition, which was formed during carbon dioxide capture [41].

Thermogravimetric profiles for materials mixed with alkaline carbonates present the same general behavior than that observed with pure Li₂CuO₂. However, some specific variations were observed as function of type of carbonate and temperature. Between 300 and 550 °C, it was observed that surface capture was not improved by

carbonates addition. Similar than Li₂CuO₂, modified samples reached a weight increase of 12 wt%; excepting for K-Li₂CuO₂ sample, which presents the lowest CO₂ capture (7.5 wt%) at 550 °C. According to literature [45], the changes in sample weight during this stage must be related to corresponding CO₂ surface capture and subsequent saturation of the outer layer. Furthermore, during volumetric capture (process II), it was observed that K₂CO₃ addition did not allow to obtaining a better performance in the capture process, while Na₂CO₃ and Na₂CO₃-K₂CO₃ containing samples benefit the CO₂ capture process between 550 and 700 °C. The material modified with both carbonates (Na-K-Li₂CuO₂) presented the highest enhancement, capturing more CO₂ between 500 and 690 °C than the original material. This phenomenon can be due to the formation of a eutectic phase between the carbonate Li₂CO₃ formed during the CO₂ capture process and the carbonates mechanically added during the synthesis, as it was observed during DSC analysis in CO₂ (Fig. 3-B). This result has been already observed in CO₂ capture with other alkaline ceramics mechanically mixed with Na and K carbonates [34,36]. Furthermore, samples added with sodium or potassium carbonates reach the maximum capture at around 660 °C and they can be arranged as follows: K-Li₂CuO₂ (12 wt%) < Na-Li₂CuO₂ (17.5 wt %) < Na-K-Li₂CuO₂ (22.3 wt%). Considering the theoretical value for CO₂ capture with Li₂CuO₂, these amounts correspond to efficiencies of 33.6, 47.7 and 61.9%, respectively. In addition, the presence of carbonates activates the sorption-desorption equilibrium at least 50 °C earlier than that observed on the pure Li₂CuO₂ at 730 °C. In the last stage, no significant changes were observed among modified samples. All materials showed at T > 850 °C, the same CO₂ desorption process registered by pure Li₂CuO₂ [35,41]. The above qualitative results show that adding sodium carbonate or equal amounts of Na and K carbonates seems to improve the CO₂ chemisorption in Li₂CuO₂ by means of the volumetric capture process.

According to TG dynamic analyzes, the effect induced by carbonates addition in lithium cuprate can be observed mainly between 400 and 700 °C. Thus, the following temperatures were selected for performing isothermal tests: 400, 500, 600, 650 and 700 °C. Fig. 5 shows CO₂ sorption isotherms for pure Li₂CuO₂ and materials modified with carbonates at selected temperatures. All profiles present a weight exponential increase as function of time due to the CO₂ chemisorption over the materials. At 400 °C, a similar behavior was observed for Li₂CuO₂, K-Li₂CuO₂ and Na-Li₂CuO₂ samples, reaching less than 2.5 wt % after 3 h. In contrast, Na-K-Li₂CuO₂ exhibits the best ability for capturing CO₂ at this temperature (13.2 wt%). When CO₂ capture tests were performed at 500 and 600 °C, the following trend was obtained: Na-K-Li₂CuO₂ sample presents the highest CO₂ captures (between 17 and 19 wt%), followed by K-Li₂CuO₂, Na-Li₂CuO₂ and pure Li₂CuO₂. These results indicate that carbonates addition improves the CO₂ capture process between 500 and 600 °C, regardless which carbonate was mixed with the pristine Li₂CuO₂ material. However, at 600 °C and long times (t > 80 min) a change in the above trend was observed. Li₂CuO₂ sample presented a faster weight increase than Na-Li₂CuO₂, and after 3 h of reaction, Li₂CuO₂ was able to capture the same amount of CO₂ (8.2 wt%) than that obtained with K-Li₂CuO₂. At 650 °C contrary to previous isotherms, Na-K-Li₂CuO₂ material shows the lowest CO₂ captured (10.3 wt%), followed by the sample mixed with sodium carbonate (Na-Li₂CuO₂, 11.7 wt%). On the other hand, at t < 80 min, the material with the best ability was that modified with K₂CO₃. However, this material reaches very fast the maximum amount of CO₂ chemisorbed (26.6 wt%, at t > 20 min) and then the sorption-desorption equilibrium takes place avoiding further CO₂ capture. Furthermore, at 650 °C, it was observed that at t < 80 min the weight increase registered for Li₂CuO₂ sample remains below than K-Li₂CuO₂. However, pure Li₂CuO₂ continues capturing CO₂ until 30.2 wt% after 180 min of reaction. Finally, at 700 °C, a very different trend was observed. In this thermal condition, Na-Li₂CuO₂ is the material with the highest CO₂ capture (17.5 wt%), followed by pure Li₂CuO₂, Na-K-Li₂CuO₂ and K-Li₂CuO₂ with 6.9, 2.3 and 2.2 wt%, respectively.
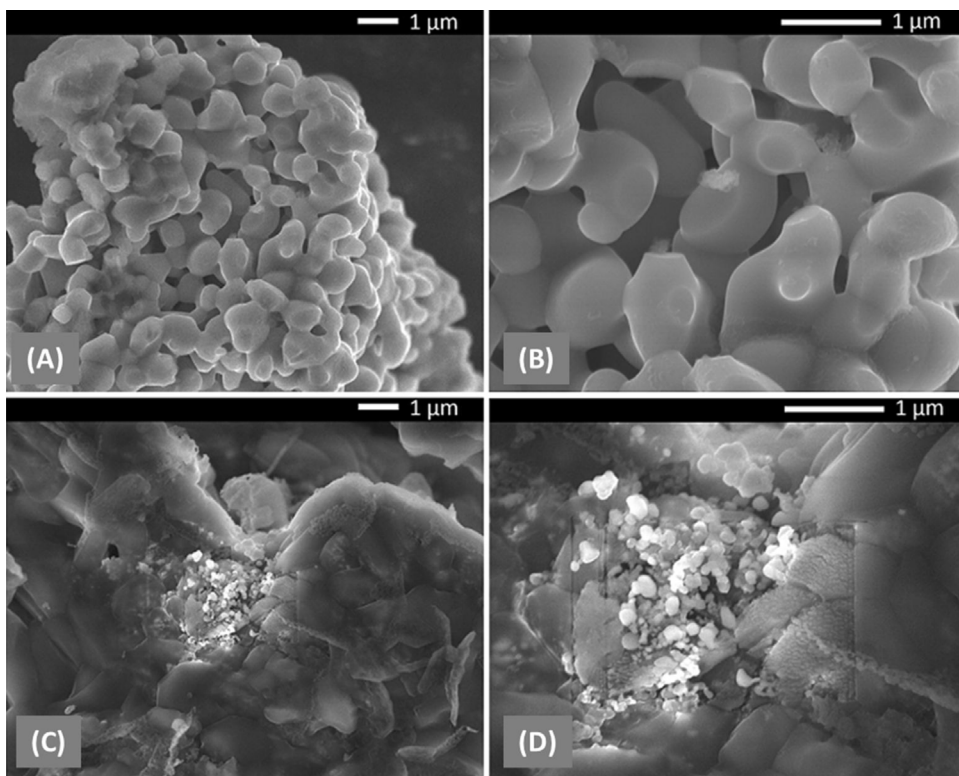
Fig. 8. SEM images for pristine Li_2CuO_2 (charts A and B) and Li_2CuO_2 material obtained after 3 h of CO_2 capture at 500 °C (charts C and D).
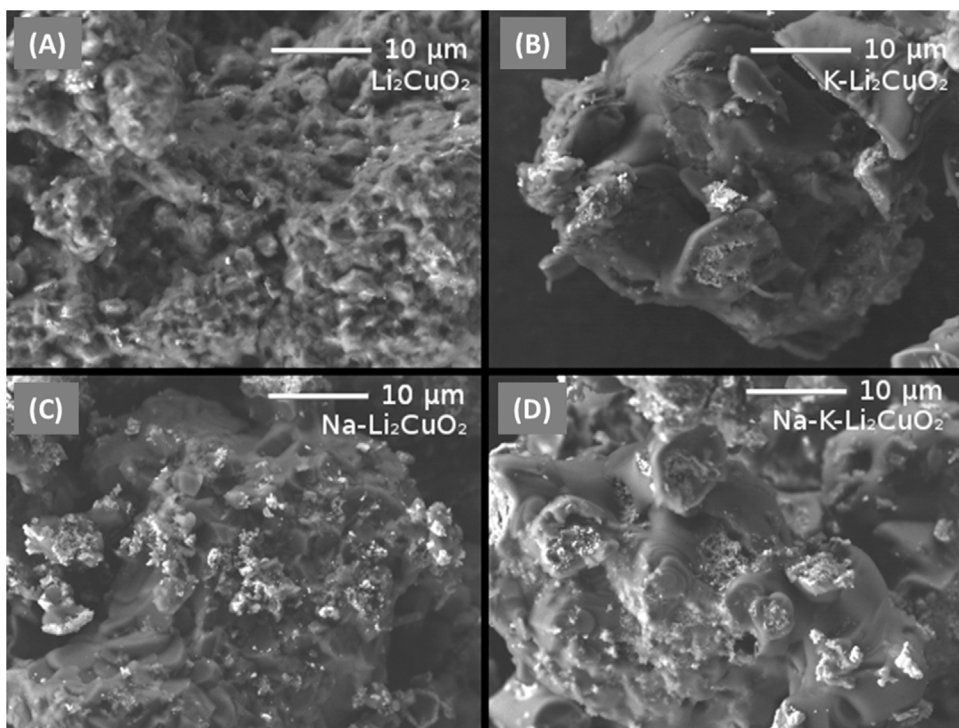

Fig. 9. SEM images for Li_2CuO_2 ceramic (A) and modified materials with K_2CO_3 (B), Na_2CO_3 (C) and Na_2CO_3- K_2CO_3 (D) after CO_2 capture at 500 °C.

Further observations in isothermals tests were made considering that in modified materials only 90% of the sample is able to chemisorb CO_2 and the rest (10% composed by Na or K carbonates) is not capable for performing this chemical process. Thus, Fig. 6 presents the weight increase reached with each material in 3 h, normalized by gram of Li_2CuO_2 used. It was observed that pure Li_2CuO_2 has a positive trend as temperature increases from 400 to 600 °C. Thereafter between 600 and 650 °C, the highest weight increase was observed, indicating that this

thermal condition is the best for pristine sample. After this temperature, a significant weight decrease was obtained as result of the activation of sorption-desorption equilibrium previously described in dynamic tests (Fig. 4-A). Regarding to modified samples with carbonates, between 400 and 600 °C, all exhibit greater weight increments than pure lithium cuprate, due to the diffusion promotion provided by the partial melted phase composed by Li_2CO_3 and corresponding carbonates added. In particular, Na-K-Li_2CuO_2 presented the highest enhancements (~23%)
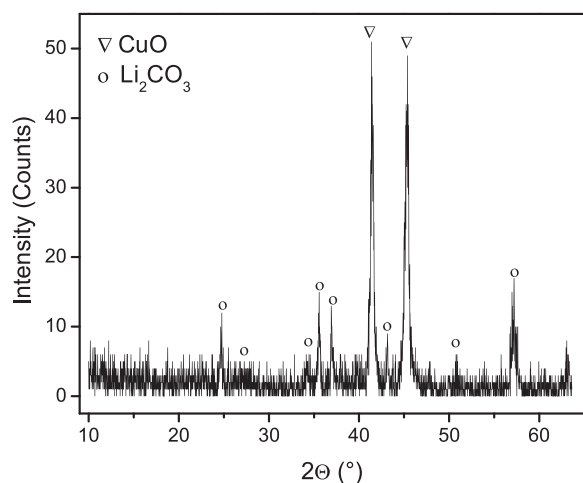
Fig. 10. XRD pattern for Na-K-Li$_2$CuO$_2$ material tested in CO$_2$ capture at 500 °C during 3 h.

in this temperature range in comparison with pure Li$_2$CuO$_2$, showing that combining equal amounts of both carbonates can promote a synergic effect, providing a significant benefit during the CO$_2$ chemisorption. At 650 °C a different trend was obtained, in this case only K-Li$_2$CuO$_2$ presented a higher weight increment than pure Li$_2$CuO$_2$. This result pointed out that adding potassium carbonate and 650 °C is the best combination among all conditions proved for obtaining a complete CO$_2$ capture per gram of ceramic (40.4 wt%). On the other hand, despite Na-K-Li$_2$CuO$_2$ sample presented the best capture between 400 and 600 °C, when temperature increases from 600 to 700 °C, a lineal weight decrease was registered due to a sintering process in the outer layer. This behavior has been already reported for other lithium ceramics-CO$_2$ systems, such as: Li$_8$SiO$_6$ [35] and α-Li$_5$AlO$_4$ [36]. In contrast, Na-Li$_2$CuO$_2$ showed a lineal weight increase between 600 and 700 °C, obtaining its best performance in the last thermal condition (30.4 wt%). Summarizing, it can be established that CO$_2$ chemisorption not only depends on temperature and reaction time as it was previous reported [46,47], but also on the type and mass ratio between carbonates added during the synthesis, which are the principal responsible for increasing the diffusion processes by means the eutectic phase formation with Li$_2$CO$_3$ produced during CO$_2$ capture process.

Afterwards, CO$_2$-TPD experiments were performed in order to determinate the effect of carbonates addition on CO$_2$ desorption abilities (Fig. 7). Desorption signals in a low temperature range (250–350 °C) related to a superficial chemisorption on ceramic, were observed only in the sample modified with potassium. Meanwhile, a second signal at T > 550 °C was detected in all profiles, indicating a stronger bound CO$_2$ sorption over ceramic particles. Pure Li$_2$CuO$_2$ showed a CO$_2$ desorption between 600 and 810 °C with a maximum located at 775 °C. For this process, it was observed some differences in CO$_2$ desorption temperature depending on the carbonate added. As consequence of K$_2$CO$_3$ addition; CO$_2$ desorption began at least 50 °C earlier and presented higher amount of gas desorbed than pure sample, indicating that K$_2$CO$_3$ decomposition also can be taken place. On the contrary, Na- and combine Na-K- additions resulted in an increase of desorption temperature (T > 800 °C), showing a stronger bound between CO$_2$ and modified ceramics. These increments must be related with the formation of Li$_2$CO$_3$-Na$_2$CO$_3$ or Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ eutectic phases which retard CO$_2$ desorption from ceramic, obtaining a partial CO$_2$ storage in temperatures lower than 700 °C. This characteristic allowed to obtain better CO$_2$ captures than that on pure material during dynamic tests (Fig. 4-A).

Finally, SEM and XRD techniques were employed in order to determinate changes in microstructure and composition of products obtained after CO$_2$ isothermal tests at 500 °C. In this temperature, it was

observed the highest difference in CO$_2$ capture between pure Li$_2$CuO$_2$ and those materials modified with carbonates. Thus, Fig. 8 presents SEM images from pure lithium cuprate before and after CO$_2$ capture. It can be seen that pristine material morphology (Charts A and B) consists on aggregates of granular particles in coral polyps form with different sizes; between 0.7 and 1.1 μm. After CO$_2$ tests (Charts 8-C and -D), it can be distinguee two phases well-defined by contrast. In this case, they must correspond to the carbonation products (Li$_2$CO$_3$ and CuO) obtained as consequence of chemical reaction between Li$_2$CuO$_2$ and CO$_2$ (reaction 1). Considering this contrast difference, it can be established that dark phase corresponds to Li$_2$CO$_3$, whereas the bright one is related to CuO. In further observations, it was found that dark phase (Li$_2$CO$_3$) presents dense agglomerates with particle size between 0.7 and 2.4 μm, while the other phase (CuO) consists mainly by small round particles with sizes around 0.2–0.4 μm. Also, this technique was used to observe the microstructure changes in carbonate-modified Li$_2$CuO$_2$ samples after CO$_2$ capture (Fig. 9). As it could expect, these samples are composed by the same two phases described above for pure Li$_2$CuO$_2$ case. In line with SEM observations, Fig. 10 shows the XRD pattern for Na-K-Li$_2$CuO$_2$ product treated at 500 °C, corroborating that Li$_2$CO$_3$ and CuO are the only products obtained after CO$_2$ capture, as it was previously described in reaction 1. Then, these results pointed out that CO$_2$ chemisorption process was produced. Also, it can be observed that carbonate addition did not produce any change in products obtained after CO$_2$ chemisorption.

4. Conclusions

The effect of carbonates addition on Li$_2$CuO$_2$ ceramic was evaluated during CO$_2$ capture. For this proposal, Li$_2$CuO$_2$ was synthetized and then mechanically mixed with K and/or Na carbonates. N$_2$ physisorption and XRD analyzes showed that primary characteristics of pristine Li$_2$CuO$_2$ were preserved in all (K-, Na- and Na-K-)-Li$_2$CuO$_2$ samples, although the surface area was increased by carbonate addition. After, DSC-N$_2$ analyzes showed that all samples presented an endothermic carbonate fusion process between 300 and 430 °C, regardless the type of carbonate mechanically mixed. DSC-CO$_2$ tests revealed that in this atmosphere all processes involved require absorb or release higher amounts of energy in comparison with inert atmosphere (N$_2$). Also, it was observed that between 300 and 450 °C, Li$_2$CuO$_2$ is the only sample with a highly exothermic process related to the CO$_2$ sorption over the ceramic. Nevertheless, this exothermic signal was not observed for (Na and Na-K)-Li$_2$CuO$_2$ samples, indicating that eutectic phase formation requires the same energy than that released as a consequences of CO$_2$ capture. In addition, CO$_2$-TPD analyses reveled that carbonate addition modified desorption abilities. When potassium carbonate was added a decrement in desorption temperature was observed; on the contrary, Na- and Na-K- addition resulted in an increase of desorption temperature, indicating a higher CO$_2$-ceramic surface bound.

Afterwards, dynamic thermogravimetric experiments showed that all materials are able to capture CO$_2$ in a wide temperature range through two consecutive processes: superficial capture (300–550 °C) followed by a volumetric chemisorption (550–700 °C). Regarding to CO$_2$ tests, isothermal profiles showed that materials modified with alkaline carbonates presented better capture abilities than pure Li$_2$CuO$_2$ between 400 and 700 °C, except at 650 °C where pure sample presented higher CO$_2$ sorption than Na-Li$_2$CuO$_2$ and Na-K-Li$_2$CuO$_2$ samples. It seems that carbonate addition improves the CO$_2$ chemisorption in Li$_2$CuO$_2$ by means of eutectic phase formation during the volumetric capture stage. However, the selection of an appropriate material depends strongly on the temperature condition used during carbon dioxide capture. Thus, between 400 and 600 °C the ceramic modified with equal amounts of both carbonates (Na-K-Li$_2$CuO$_2$) is the best option for performing CO$_2$ capture. Meanwhile, at 600 and 700 °C, K-Li$_2$CuO$_2$ and Na-Li$_2$CuO$_2$ materials are the materials with the highest volumetric capture, respectively. Furthermore, it was found that at

650 °C, potassium carbonate addition is the best condition for obtaining an eutectic phase composed by K_2CO_3 and Li_2CO_3 carbonates, obtaining a complete CO_2 chemisorption (40.4 wt% per gram of Li_2CuO_2), among all materials tested. This amount corresponds an efficiency of ~100%, in relation with theoretical amount (40.2 wt%) calculated for CO_2 capture over 1.0 g of Li_2CuO_2 ceramic.

Acknowledgements

References

[1] A. Yamasaki, An overview of CO₂ mitigation options for global warming-emphasizing CO₂ sequestration options, J. Chem. Eng. Jpn. 36 (2003) 361–375, http://dx.doi.org/10.1252/jcej.36.361.

[2] E. de Visser, C. Hendriks, M. Barrio, M.J. Mølnvik, G. de Koeijer, S. Liljemark, Y. Le Gallo, Dynamis CO₂ quality recommendations, Int. J. Greenh. Gas Control 2 (2008) 478–484, http://dx.doi.org/10.1016/j.ijggc.2008.04.006.

[3] E. Blomen, C. Hendriks, F. Neele, Capture technologies: improvements and promising developments, Energy Proc. 1 (2009) 1505–1512, http://dx.doi.org/10.1016/j.egypro.2009.01.197.

[4] A.A. Olajire, CO₂ capture and separation technologies for end-of-pipe applications – a review, Energy 35 (2010) 2610–2628, http://dx.doi.org/10.1016/j.energy.2010.02.030.

[5] D.Y.C. Leung, G. Caramanna, M.M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, Renew. Sustain. Energy Rev. 39 (2014) 426–443, http://dx.doi.org/10.1016/j.rser.2014.07.093.

[6] M.M. Abu-Khader, Recent progress in CO₂ capture/sequestration: a review, energy sources, part a recover, Util. Environ. Eff. 28 (2006) 1261–1279, http://dx.doi.org/10.1080/009083190933825.

[7] R. Xiong, J. Ida, Y.S. Lin, Kinetics of carbon dioxide sorption on potassium-doped lithium zirconate, Chem. Eng. Sci. 58 (2003) 4377–4385, http://dx.doi.org/10.1016/S0009-2509(03)00319-1.

[8] B.N. Nair, T. Yamaguchi, H. Kawamura, S.-I. Nakao, K. Nakagawa, Processing of lithium zirconate for applications in carbon dioxide separation: structure and properties of the powders, J. Am. Ceram. Soc. 87 (2004) 68–74, http://dx.doi.org/10.1111/j.1551-2916.2004.00068.x.

[9] D.J. Fauth, E.A. Frommell, J.S. Hoffman, R.P. Reasbeck, H.W. Pennline, Eutectic salt promoted lithium zirconate: novel high temperature sorbent for CO₂ capture, Fuel Process. Technol. 86 (2005) 1503–1521, http://dx.doi.org/10.1016/j.fuproc.2005.01.012.

[10] X.-S. Yin, Q.-H. Zhang, J.-G. Yu, Three-step calcination synthesis of high-purity Li₈ZrO₆ with CO₂ absorption properties, Inorg. Chem. 50 (2011) 2844–2850, http://dx.doi.org/10.1021/ic102035y.

[11] J.A. Mendoza-Nieto, H. Pfeiffer, Thermogravimetric study of sequential carbonation and decarbonation processes over Na₂ZrO₃ at low temperatures (30–80 °C): relative humidity effect, RSC Adv. 6 (2016) 66579–66588, http://dx.doi.org/10.1039/C6RA12533F.

[12] J.A. Mendoza-Nieto, E. Vera, H. Pfeiffer, Methane reforming process by means of a carbonated-Na₂ZrO₃ catalyst, Chem. Lett. 45 (2016) 3–6, http://dx.doi.org/10.1246/cl.160136.

[13] T. Zhao, E. Ochoa-Fernández, M. Rønning, D. Chen, Preparation and high-temperature CO₂ capture properties of nanocrystalline Na₂ZrO₃, Chem. Mater. 19 (2007) 3294–3301, http://dx.doi.org/10.1021/cm062732h.

[14] M. Kato, S. Yoshikawa, K. Nakagawa, Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations, J. Mater. Sci. Lett. 21 (2002) 485–487, http://dx.doi.org/10.1023/A:1015338808533.

[15] K. Essaki, K. Nakagawa, M. Kato, H. Uemoto, CO₂ absorption by lithium silicate at room temperature, J. Chem. Eng. Jpn. 37 (2004) 772–777, http://dx.doi.org/10.1252/jcej.37.772.

[16] R.B. Khomane, B.K. Sharma, S. Saha, B.D. Kulkarni, Reverse microemulsion mediated sol–gel synthesis of lithium silicate nanoparticles under ambient conditions: scope for CO₂ sequestration, Chem. Eng. Sci. 61 (2006) 3415–3418, http://dx.doi.org/10.1016/j.ces.2005.11.065.

[17] T. Okumura, K. Enomoto, N. Togashi, K. Oh-Ishi, CO₂ absorption reaction of Li₄SiO₄ studied by the rate theory using thermogravimetry, J. Ceram. Soc. Jpn. 115 (2007) 491–497, http://dx.doi.org/10.2109/jcersj2.115.491.

[18] M.J. Venegas, E. Fregoso-Israel, R. Escamilla, H. Pfeiffer, Kinetic and reaction mechanism of CO₂ sorption on Li₄SiO₄: study of the particle size effect, Ind. Eng. Chem. Res. 46 (2007) 2407–2412, http://dx.doi.org/10.1021/ie061259e.

[19] K. Essaki, M. Kato, H. Uemoto, Influence of temperature and CO₂ concentration on the CO₂ absorption properties of lithium silicate pellets, J. Mater. Sci. 40 (2005) 5017–5019, http://dx.doi.org/10.1007/s10853-005-1812-3.

[20] 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, http://dx.doi.org/10.1007/s10973-011-2063-y.

[21] P.V. Korake, A.G. Gaikwad, Capture of carbon dioxide over porous solid adsorbents lithium silicate, lithium aluminate and magnesium aluminate at pre-combustion

[22] H.A. Lara-García, E. Vera, J.A. Mendoza-Nieto, J.F. Gómez-García, Y. Duan, H. Pfeiffer, Bifunctional application of lithium ferrites (Li₅FeO₄ and LiFeO₂) during carbon monoxide (CO) oxidation and chemisorption processes. A catalytic, thermogravimetric and theoretical analysis, Chem. Eng. J. 327 (2017) 783–791, http://dx.doi.org/10.1016/j.cej.2017.06.135.

[23] L.M. Palacios-Romero, H. Pfeiffer, Lithium cuprate (Li₂CuO₂): a new possible ceramic material for CO₂ chemisorption, Chem. Lett. 37 (2008) 862–863, http://dx.doi.org/10.1246/cl.2008.862.

[24] 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, http://dx.doi.org/10.1246/cl.2010.966.

[25] H.A. Lara-García, H. Pfeiffer, High and efficient Li₂CuO₂-CO₂ chemisorption using different partial pressures and enhancement produced by the oxygen addition, Chem. Eng. J. 313 (2017) 1288–1294, http://dx.doi.org/10.1016/j.cej.2016.11.029.

[26] H.A. Lara-García, M.J. Ramírez-Moreno, J. Ortiz-Landeros, H. Pfeiffer, CO₂ chemisorption in Li₂CuO₂ microstructurally modified by ball milling: study performed with different physicochemical CO₂ capture conditions, RSC Adv. 6 (2016) 57880–57888, http://dx.doi.org/10.1039/C6RA06895B.

[27] L.M. Palacios-Romero, E. Lima, H. Pfeiffer, Structural analysis and CO₂ chemisorption study on nonstoichiometric lithium cuprates (Li₂₊ₓCuO₂₊ₓ/₂), J. Phys. Chem. A 113 (2009) 193–198, http://dx.doi.org/10.1021/jp808521f.

[28] 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, http://dx.doi.org/10.1016/j.jssc.2013.12.018.

[29] F. Sapiña, J. Rodríguez-Carvajal, M.J. Sanchis, R. Ibáñez, A. Beltrán, D. Beltrán, Crystal and magnetic structure of Li₂CuO₂, Solid State Commun. 74 (1990) 779–784, http://dx.doi.org/10.1016/0038-1098(90)90934-4.

[30] A. Samanta, A. Zhao, G.K.H. Shimizu, P. Sarkar, R. Gupta, Post-combustion CO₂ capture using solid sorbents: a review, Ind. Eng. Chem. Res. 51 (2012) 1438–1463, http://dx.doi.org/10.1021/ie200686q.

[31] M.K. Mondal, H.K. Balsora, P. Varshney, Progress and trends in CO₂ capture/separation technologies: a review, Energy 46 (2012) 431–441, http://dx.doi.org/10.1016/j.energy.2012.08.006.

[32] K. Nakagawa, T. Ohashi, Reversible change between lithium zirconate and zirconia in molten carbonate, Electrochemical 67 (1999) 618–621.

[33] G. Pannocchia, M. Puccini, M. Seggiani, S. Vitolo, Experimental and modeling studies on high-temperature capture of CO₂ using lithium zirconate based sorbents, Ind. Eng. Chem. Res. 46 (2007) 6696–6706, http://dx.doi.org/10.1021/ie0616949.

[34] P. Sánchez-Camacho, I.C. Romero-Ibarra, H. Pfeiffer, Thermokinetic and microstructural analyses of the CO₂ chemisorption on K₂CO₃–Na₂ZrO₃, J. CO₂ Util. 3–4 (2013) 14–20, http://dx.doi.org/10.1016/j.jcou.2013.08.003.

[35] I.C. Romero-Ibarra, F. Durán-Muñoz, H. Pfeiffer, Influence of the K-, Na- and K-Na-carbonate additions during the CO₂ chemisorption on lithium oxosilicate (Li₈SiO₆), Greenh. Gases Sci. Technol. 4 (2014) 145–154, http://dx.doi.org/10.1002/ghg.1402.

[36] M.T. Flores-Martínez, H. Pfeiffer, CO₂ chemisorption and cyclability analyses in α-Li₅AlO₄: effects of Na₂CO₃ and K₂CO₃ addition, Greenh. Gases Sci. Technol. 5 (2015) 802–811, http://dx.doi.org/10.1002/ghg.1526.

[37] Z. Zhou, K. Wang, Z. Yin, P. Zhao, Z. Su, J. Sun, Molten K₂CO₃-promoted high-performance Li₄SiO₄ sorbents at low CO₂ concentrations, Thermochim. Acta 655 (2017) 284–291, http://dx.doi.org/10.1016/j.tca.2017.07.014.

[38] K. Kanki, H. Maki, M. Mizuhata, Carbon dioxide absorption behavior of surface-modified lithium orthosilicate/potassium carbonate prepared by ball milling, Int. J. Hydrogen Energy 41 (2016) 18893–18899, http://dx.doi.org/10.1016/j.ijhydene.2016.06.158.

[39] K. Wang, Z. Zhou, P. Zhao, Z. Yin, Z. Su, J. Sun, Molten sodium-fluoride-promoted high-performance Li₄SiO₄-based CO₂ sorbents at low CO₂ concentrations, Appl. Energy 204 (2017) 403–412, http://dx.doi.org/10.1016/j.apenergy.2017.07.072.

[40] J.-W. Kim, Y.-D. Lee, H.-G. Lee, Decomposition of Li₂CO₃ by interaction with SiO₂ in mold flux of steel continuous casting, ISIJ Int. 44 (2004) 334–341, http://dx.doi.org/10.2355/isijinternational.44.334.

[41] J.-W. Kim, H.-G. Lee, Thermal and carbothermic decomposition of Na₂CO₃ and Li₂CO₃, Metall. Mater. Trans. B 32 (2001) 17–24, http://dx.doi.org/10.1007/s11663-001-0003-0.

[42] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Springer, Netherlands, Dordrecht, 2004, http://dx.doi.org/10.1007/978-1-4020-2303-3.

[43] T. Ohashi, K. Nakagawa, Effect of Potassium Carbonate additive on CO₂ absorption in lithium zirconate powder, MRS Proc. 547 (1998) 249, http://dx.doi.org/10.1557/PROC-547-249.

[44] J. Ida, Y.S. Lin, Mechanism of high-temperature CO₂ sorption on lithium zirconate, Environ. Sci. Technol. 37 (2003) 1999–2004, http://dx.doi.org/10.1021/es0259032.

[45] P. Sánchez-Camacho, I.C. Romero-Ibarra, Y. Duan, H. Pfeiffer, Thermodynamic and kinetic analyses of the CO₂ chemisorption mechanism on Na₂TiO₃: experimental and theoretical evidences, J. Phys. Chem. C 118 (2014) 19822–19832, http://dx.doi.org/10.1021/jp504922e.

[46] S. Kumar, S.K. Saxena, A comparative study of CO₂ sorption properties for different oxides, Mater. Renew. Sustain. Energy 3 (2014), http://dx.doi.org/10.1007/s40243-014-0030-9.

[47] D.M. D'Alessandro, B. Smit, J.R. Long, Carbon dioxide capture: prospects for new materials, Angew. Chem. Int. Ed. 49 (2010) 6058–6082, http://dx.doi.org/10.1002/anie.201000431.