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Water steam effect during the high CO$_2$ chemisorption in lithium cuprate (Li$_2$CuO$_2$) at moderate temperatures: experimental and theoretical evidences

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Abstract. Li$_2$CuO$_2$ was evaluated as CO$_2$ captor at moderate temperatures, using water vapor into the gas flow. Different water vapor sorption experiments were performed using N$_2$ or CO$_2$ as carrier gases. If N$_2$ was used as carrier gas, it was evidenced that Li$_2$CuO$_2$ is able to trap water physically and chemically, producing in the second case Li–OH superficial species. Moreover, when CO$_2$ was used as carrier gas, Li$_2$CuO$_2$ continued trapping water, as in the previous case, but in this case CO$_2$ was mainly trapped, forming Li$_2$CO$_3$ and CuO phases. Additionally, the microstructure change importantly when CO$_2$ and H$_2$O were chemically trapped in Li$_2$CuO$_2$. Li$_2$CO$_3$ and CuO seemed to segregate changing the morphology and the specific surface area. Li$_2$CuO$_2$ sample was able to capture up to 6.7 mmoles of CO$_2$ per gram of ceramic at 80 °C, a considerably high CO$_2$ amount. Furthermore, all these experiments were theoretically supported by different thermodynamic calculations. Experimental and theoretical results show that H$_2$O acts as a catalytic intermediate, diminishing the activation energy of the whole CO$_2$ chemisorption.
process. Therefore, the presence of water vapor strongly favored the CO$_2$ chemisorption on Li$_2$CuO$_2$ at moderate temperatures (30-80 °C).

**Keywords;** CO$_2$ capture; Lithium cuprate; Thermal analysis, ab initio thermodynamics

1. Introduction

Nowadays, a main contributor to global warming and climate change problems is believed to be carbon dioxide (CO$_2$) produced due human activities, mainly from industrial gas streams.$^{1,2}$ It is necessary to reduce the amounts of CO$_2$ gas produced. Numerous techniques (e.g., adsorption, chemisorption, cryogenic distillation, membrane separation) have been applied in order to reduce the amount of CO$_2$ emitted from large exhaust sources such as fossil fuel power plants, cement industries, iron and steel mills and other industry sectors which account for about 60 % of total CO$_2$ emissions.$^{1,3}$

Many studies have been focused on the development of solid CO$_2$ sorbents with high CO$_2$ sorption capacity and kinetics, good selectivity at low (30-200 °C), moderate (200-400 °C) or high temperature (>400 °C) and excellent regeneration ability.$^2$ In that way, some materials have been tested as CO$_2$ captors at low and moderate temperatures, such as carbon-based adsorbents, zeolites, hydrotalcites-like materials, metal–organic frameworks (MOFs), CaO-based sorbents and alkaline ceramics, among others.$^{2,4-5}$ Among alkaline ceramics, lithium and sodium ceramics are the most studied at a wide temperature range (30-800 °C), for example zirconates, aluminates and silicates.$^{6-34}$

In addition, typical flow gas composition post-combustion contain approximately 65-75% N$_2$, 7-15% CO$_2$, 2-12% O$_2$, 5-15% H$_2$O, and smaller concentrations of other polluting species.$^3$ Since water vapor is present in the flue gas post-combustion some works have been performed to understand the capture of CO$_2$ in different CO$_2$-H$_2$O compositions.
Particularly, among alkaline and earth alkaline ceramics, there are a few papers showing the effects of water vapor during de CO₂ absorption at low temperatures (30-80 °C).34-40 Most of these works mention that water vapor improve the CO₂ chemisorption due to the superficial hydroxylation processes. For example, it was recently published that CO₂ capture in Li₄SiO₄ is improved under the water vapor presence because the presence of steam enhances Li⁺ diffusion and reactivity between Li₄SiO₄ and CO₂.40

On the other hand, lithium cuprate (Li₂CuO₂) presents interesting electronic and magnetic properties, so it has been used for different electrical applications such as cathodes for lithium-ion batteries and as a superconductor material, owing to the excellent lithium diffusion.41-44 Some of these diffusion properties have been attributed to the Li₂CuO₂ layered crystalline structure, where the lithium atoms are located between the layers (Figure 1).45 The Li₂CuO₂ presents an orthorhombic phase with the following unit cell parameters: a=3.655 Å, b=2.860 Å, c=9.377 Å and Z = 2.

Recently, it has been reported that the Li₂CuO₂ is able to trap CO₂ in a wide range of temperatures (120-650 °C).46-49 These papers show that Li₂CuO₂ is able to chemisorb CO₂, where the maximum theoretical CO₂ chemisorption capacity is 9.11 mmoles of CO₂ per gram of Li₂CuO₂ (0.401 g_{CO₂}/g_{ceramic}). These reports show that Li₂CuO₂ begins to react with CO₂ at around 120 °C in dry conditions. Thus, the presence of water vapor may improve the CO₂ chemisorption at low temperatures in this lithium ceramic. Therefore, the aim of the work reported here was to study the CO₂-H₂O capture process in Li₂CuO₂ at a low temperature range (30-80 °C).

2. Experimental section

Lithium cuprate (Li₂CuO₂) was synthesized by solid-state method. Initially, lithium
oxide (Li$_2$O, Aldrich) and copper oxide (CuO, Across Organics) were mixed mechanically, in order to get a good homogeneity of the reagents. The mixtures were prepared using a lithium excess of 10 wt%, based on the stoichiometric lithium content on Li$_2$CuO$_2$, as lithium tends to sublimate during high thermal treatments. Then, the powders were calcined at 800 °C for 6 h in air.

A diffractometer (Siemens D-5000) coupled to an X-ray tube was used to identify the phases obtained. The phase was identified using the Joint Committee Powder Diffraction Standards (JCPDS) files. The microstructural characteristics of the Li$_2$CuO$_2$ sample was determined via N$_2$ adsorption-desorption and scanning electron microscopy (SEM). N$_2$ adsorption (Bel-Japan Minisorp II) was used to determine the sample surface area using the BET model. Then, the sample morphology was analyzed by SEM, which was performed on a JEOL JMS-7600F.

The CO$_2$-H$_2$O sorption process was evaluated dynamic and isothermally in a humidity-controlled thermobalance (TA Instruments, model Q5000SA) at different temperatures and relative humidity (RH). The experiments were performed using distilled water and two different flow gases: nitrogen (N$_2$, Praxair grade 4.8) or carbon dioxide (CO$_2$, Praxair grade 3.0). The total flow gas used in all the experiments was 100 mL/min and the RH percentages were controlled automatically by the Q5000SA equipment. Dynamic water vapor sorption/desorption experiments were generated at different temperatures (between 30 and 80 °C), varying the RH from 0 to 80 % (sorption) and then from 80 to 0 % (desorption) at a rate of 0.5 %/min, using 100 mL of N$_2$ or CO$_2$ as flow gas during the entire experiment. Additionally, different isothermal experiments were
performed at specific temperatures (20, 40, 60 and 80 °C) setting the RH at different values (20, 40, 60 and 80 %) for 180 min, using CO₂ as carrier gases.

Afterwards, the CO₂ isothermal products (~40mg) were characterized to identify and quantify the products. The samples were analyzed using XRD, infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). XRD characterization was performed as described above. For FTIR spectroscopy samples were analyzed in an Alpha-Platinum spectrometer from Bruker, using the ATR mode. The TG measurements were performed under a nitrogen atmosphere using a TA Instruments model Q500HR thermobalance from 30 to 930 °C at a rate of 5°C/min. Additionally, to elucidate if these products presented changes in their microstructural characteristics, the isothermal products were analyzed via N₂ adsorption-desorption and scanning electron microscopy (SEM) using the same methods described above.

Since the thermodynamic properties of the Li₂CuO₂ are not available in the literature, we performed the ab initio thermodynamics calculations on these CO₂ capture reactions by Li₂CuO₂ based on combining density functional theory (DFT) with lattice phonon dynamics. The detailed descriptions of the calculation method can be found in previous studies. The CO₂ and/or H₂O capture reactions of Li₂CuO₂ can be expressed generically in the form (for convenient description, we normalized the reaction to 1 mole of CO₂ or H₂O):

$$\sum_{R_i} n_{R_i} SolidR_i + CO_2 + H_2O \leftrightarrow \sum_{P_j} n_{P_j} SolidP_j$$

(1)

where \(n_{R_i}\), \(n_{P_j}\) are the reagents \((R_i)\) and products \((P_j)\) moles involved in the capture reactions. We treat the gas phase CO₂ or H₂O as an ideal gas. By assuming that the difference between the Gibbs free energy (\(\Delta G^\circ\)) of the solid phases of reactants \((R_i)\) and
products \((P)\) can be approximated by the difference in their total energies \((\Delta E_{\text{DFT}})\), obtained directly from DFT calculations, and the vibrational free energy of the phonons and by ignoring the PV contribution terms for solids, the variation of the chemical potential \((\Delta \mu)\) for reaction with temperature and pressure can be written as:

\[
\Delta G(T, P) = \Delta G^0(T) - RT \ln \frac{P_{\text{gas}}}{P_0}
\]

where,

\[
\Delta G^0(T) \approx \Delta E_{\text{DFT}} + \Delta E_{\text{ZP}} + \Delta F_{\text{PH}}(T) - G^0_{\text{gas}}(T)
\]

(3)

Here, \(\Delta E_{\text{DFT}}\) is the DFT energy difference between the reactants and products of the reaction \(\Delta E_{\text{ZP}}\) is the zero point energy difference between the reactants and products and can be obtained directly from phonon calculations. \(\Delta F_{\text{PH}}\) is the phonon free energy change excluding zero-point energy (which is already counted into the \(\Delta E_{\text{ZP}}\) term) between the solids of products and reactants. \(P_{\text{gas}}\) is the partial pressure of \(\text{CO}_2\) or \(\text{H}_2\text{O}\) in the gas phase and \(P_0\) is the standard state reference pressure taken to be 1 bar. The heat of reaction \((\Delta H^{\text{cal}}(T))\) can be evaluated through the following equation:

\[
\Delta H^{\text{cal}}(T) = \Delta G^0(T) + T[\Delta S_{\text{PH}}(T) - S_{\text{CO}_2}(T)]
\]

(4)

where, \(\Delta S_{\text{PH}}(T)\) is the difference of entropies between product solids and reactant solids. The free energy of \(\text{CO}_2\) or \(\text{H}_2\text{O}\) \((G^0_{\text{gas}})\) can be obtained from standard statistical mechanics, and its entropy \((S_{\text{gas}})\) can be found in the empirical thermodynamic databases. The DFT calculations with plane-wave basis sets and pseudopotential approximation were done to describe the structural, energetic and electronic properties of solids considered in this study. All calculations were performed using the Vienna \(ab\text{-initio}\) simulation package (VASP). In this study, the PAW pseudo-potentials and PW91 exchange-correlation

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functional were used in all of the calculations. Plane wave basis sets were used with a kinetic energy cutoff of 520 eV and an augmentation charge cutoff of 605.4 eV. The k-point sampling grids of $m \times n \times l$, obtained using the Monkhorst-Pack method,\textsuperscript{57} are used for these bulk calculations, where $m$, $n$, and $l$ are determined with a spacing of about 0.028 Å\textsuperscript{-1} along the reciprocal axes of their unit cells. In the phonon calculations, for each generated supercell, the displacements of 0.03 Å of non-equivalent atoms were generated. Then, for each supercell, the DFT calculations were performed again to obtain the force on each atom due to the displacements. These forces are carried back to PHONON package\textsuperscript{58} to calculate the phonon dispersions and densities from which the partition function can be carried out and used to obtain free energies and entropies as shown in Equations 3 and 4.

3. Results and discussion

Figure 2 shows the XRD pattern of the Li$_2$CuO$_2$ synthesized by solid state reaction. The diffraction pattern fitted to the 00-084-1971 JCPDS file, and no other phases were detected. After the structural confirmation, the sample microstructure was analyzed by N$_2$ adsorption and SEM. The Li$_2$CuO$_2$ morphological characteristics are shown in the Figure 3. The size of the Li$_2$CuO$_2$ agglomerates is around 5-15 μm, but a closer analysis indicated that these agglomerates are formed by polyhedral particles of 0.5 μm in average. Additionally, the N$_2$ adsorption-desorption isotherm for this sample corresponded to a type II isotherm according to the IUPAC classification (data shown below)\textsuperscript{59} and the isotherm did not presented hysteresis. Additionally, the surface area of the sample was estimated to be 0.2 m$^2$/g using the BET model. This behavior corresponds to a nonporous, dense aggregate of particles, which is in good agreement with the synthesis method (solid-state reaction) and SEM observations.

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Experimentally, Li$_2$CuO$_2$-N$_2$-H$_2$O and Li$_2$CuO$_2$-CO$_2$-H$_2$O systems were evaluated at different temperatures (30-80 °C). The Li$_2$CuO$_2$-N$_2$-H$_2$O system was analyzed seeking for any possible reaction between lithium cuprate and water vapor. Figure 4 shows water vapor sorption-desorption isotherms. It is clearly evident that all of the sorption isotherms corresponded to type III according to the IUPAC classification. Water sorption varied as a function of the temperature, and it was not completed or limited to the increasing relative humidity section ramp (0−80% RH) because during some part of the decreasing RH section ramp (80−0% RH), the samples continued gaining weight. This effect was highly evidenced in the isotherm performed at 80 °C. Therefore, as these curves are dynamic experiments the water sorption equilibrium has not been reached. Final weight increments into the N$_2$-H$_2$O flow did not vary importantly. While the Li$_2$CuO$_2$ sample treated at 40 °C gained 10.3 wt %, the final weight increment at 80 °C was 15.5 wt %. However, the sorption process began at a much lower RH when temperature was increased. At 40 °C, the weight increased at around 38 % of RH, while the sorption process began with 14 % of RH at 80 °C. It must be mentioned that the weight decrement observed in the sample thermally treated at 80 C during the desorption process between 35 and 14 wt% must be attributed to water evaporation. In previous works, the final weight increments observed during the N$_2$-H$_2$O flow experiments has been attributed to a surface hydroxylation process, where different species are produced.

Figure 5 shows the Li$_2$CuO$_2$-CO$_2$-H$_2$O sorption-desorption curves. Again, the sorption curves were type III, as in the previous case, but the water desorption process and the final weight increments were noticeably different. In all these cases, the weight gain increased as a function of the temperature, from 4.9 to 30.2 wt % at 30 and 80 °C, respectively. It means that the final weight gained is twice larger in the CO$_2$-H$_2$O system (at
80 °C) in comparison to the N₂-H₂O case. Therefore, the CO₂-H₂O system produces different reactions than N₂-H₂O, where hydration, hydroxylation, and carbonation processes must be performed.

Table 1 and Figures 6 and 7 show the calculated thermodynamic properties of CO₂ reactions with Li₂CuO₂ and LiOH (reactions 5 and 7), as well as the Li₂CuO₂ hydroxylation reaction (reaction 6), because lithium hydroxide seems to be the real responsible of the CO₂ capture under humidity conditions.

\[
\begin{align*}
\text{Li}_2\text{CuO}_2 + \text{CO}_2 & \rightarrow \text{Li}_2\text{CO}_3 + \text{CuO} & (5) \\
\text{Li}_2\text{CuO}_2 + \text{H}_2\text{O} & \rightarrow 2 \text{LiOH} + \text{CuO} & (6) \\
2 \text{LiOH} + \text{CO}_2 & \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O} & (7)
\end{align*}
\]

As shown in Figure 6A, the heat of reactions (ΔH) involved in these three reactions, obey the Hess’s law, and all of them are exothermic reactions. For example at 27 °C, the Li₂CuO₂ carbonation reaction (reaction 5) has a ΔH value of -185 kJ/mol, whilst the Li₂CuO₂ hydroxylation and subsequent carbonation processes (reactions 6 and 7) have ΔH values equal to -86 and -98 kJ/mol, respectively. In other words, the total ΔH value of reactions 6 and 7 is -184 kJ/mol, the alike energy required in reaction 5. The same tendency is observed in the whole temperature range. On the other hand, and according the ΔG values (Figure 6B), the Li₂CuO₂ hydroxylation and LiOH carbonation reactions (reactions 6 and 7) are less stable than Li₂CuO₂ direct carbonation. Thus, ΔG values indicate that Li₂CuO₂-CO₂-H₂O reaction system is stabilized as Li₂CO₃ and CuO, where H₂O simply acts as a catalytic intermediate. In other words, these thermodynamic data confirm that water acts as intermediate specie in the Li₂CuO₂-CO₂-H₂O system diminishing the activation energy of the whole reaction process.
Moreover, Figure 7 shows T and P graphs describing where the chemical potential is equal to zero for the reactions 5-7, where $\Delta G = 0$. Around $\text{Li}_2\text{CuO}_2$-$\text{CO}_2$ and $\text{LiOH}$-$\text{CO}_2$ reaction lines are determined the chemisorption and desorption regions with optimal conditions because of the minimum energy costs at the respective temperature and pressure conditions. Additionally, in the $\text{Li}_2\text{CuO}_2$-$\text{H}_2\text{O}$ reaction curve, the hydroxylation and dehydroxylation regions are determined. All these reactions are thermodynamically favorable over a certain range of temperatures and $P_{\text{CO}_2}$ or $P_{\text{H}_2\text{O}}$, which means that under such conditions $\text{CO}_2$ and $\text{H}_2\text{O}$ are thermodynamically favored to be reacted with $\text{Li}_2\text{CuO}_2$ or $\text{LiOH}$. However, it is evident that the $\text{CO}_2$ capture is more favored than the dehydroxylation process under the experimental conditions of temperature and $\text{CO}_2$ pressure. Based in the theoretical and experimental results, the most feasible reaction mechanism is the $\text{Li}_2\text{CuO}_2$ hydroxylation process subsequently followed by the $\text{LiOH}$ carbonation process. Nevertheless, at standard pressures the $\text{CO}_2$ chemisorption in both materials ($\text{Li}_2\text{CuO}_2$ or $\text{LiOH}$) is favored over the $\text{Li}_2\text{CuO}_2$ hydroxylation process.

To further understand and analyze the influence of water during the $\text{CO}_2$ capture in $\text{Li}_2\text{CuO}_2$, different kinetic experiments are presented in Figure 8, and these isothermal products were re-characterized to determine and quantify the species produced. Isothermal experiments were performed between 40 and 80 ºC at different RH (20, 40, 60, and 80%). Weight increment rates and amounts increased as a function of the RH, as it could be expected. At 40 ºC the samples treated with 20 and 40% of RH only increased their weights in 0.2 and 1.2 wt % after 3 h, respectively. When the RH was increased to 60 and 80 %, the final weights were 9.2 and 20.5 wt %, respectively. Similar trends were observed at 60 and 80 ºC. Nevertheless, the final weight increments increased as a function of temperature and
RH. It can be well represented if the isotherms with 80 % of RH are compared at different temperatures. The final weights in these cases were 20.5, 24.1 and 37.6 wt% at 40, 60 and 80 ºC, respectively. It must be mentioned that after the experimental times none of these isothermal conditions reached the equilibrium. So the CO2 capture must continue at longer times.

To confirm the CO2 chemical capture and to quantify the CO2 through the Li2CO3 formation under the different thermal and RH conditions, all the isothermal products were characterized using XRD and TGA, through decomposition thermograms. Figure 9 shows the XRD pattern of one specific isothermal product as an example (80 ºC and 80 % of RH), where the CO2 chemical capture was confirmed by the Li2CO3 and CuO formation (see reactions 5-7). In this XRD pattern LiOH was not identified. This result strongly suggest that most of the LiOH reacted with CO2, producing Li2CO3. In fact, this qualitative evidence was corroborated by the TG decomposition analysis described now. Figure 10 shows the TG and DTG decomposition curves of isothermal products treated at 80 ºC with different RH. These thermograms show three different decomposition processes. Initially, between room temperature and 120 ºC, the samples lost small quantities of weight (around 1 and 2.5 wt%), which could be attributed to dehydration processes. The second weight decrement was observed between 350 and 470 ºC, and it can be attributed to the dehydroxylation process. In fact, the samples treated at lower RH presented lower dehydroxylations than those observed at high HR. Additionally, the DTG dehydroxylation peaks were shifted to higher temperatures as a function of the RH, which may be related to the carbonation process. If the Li2CO3 shell amounts are higher, the dehydroxylation may become slower due to diffusion processes. In fact, this assumption is in good agreement with the decarbonation process, which was produced at T ≥ 600 ºC. The decarbonation
process was produced in two steps between 610 and 760 °C and between 760 and 925 °C. These two processes can be described as superficial and bulk decarbonation processes. Based on these results the amounts of CO$_2$, trapped as Li$_2$CO$_3$ (weight lost at T $\geq$ 600 ºC), were quantified and plotted in Figure 11. From these curves it is obvious that when the RH increased from 20 to 80%, the CO$_2$ chemisorbed increased, independently of the temperature, although the CO$_2$ chemisorptions at 80 ºC presented the best results, where the maximum weight increment (29.5 wt%) was obtained at 80 ºC and 80 % of RH. This weight increment corresponds to a 72.2 % of the total efficiency, although the equilibrium was not reached. So the CO$_2$ chemisorption may be increased as a function of time. The efficiency obtained after 3 hours corresponds to 6.6 mmoles of CO$_2$ per gram of Li$_2$CuO$_2$. In addition, it could be mentioned that if Li$_2$CuO$_2$ reacted totally with CO$_2$, the maximum theoretical CO$_2$ capture value would correspond to 9.13 mmoles/g (see reaction 5).

Li$_2$CuO$_2$ and other alkaline ceramics have shown good CO$_2$ capture properties at moderate temperatures in the presence of water steam; in comparison to dry conditions. The explanation given for this effect has been associated to the ceramic hydroxylation process, which promotes the CO$_2$ reactivity. On the other hand, different microstructural characteristics may have been modified during the CO$_2$ chemisorption process. So, the Li$_2$CuO$_2$-CO$_2$-H$_2$O isothermal products were analyzed by SEM and N$_2$ adsorption. Figure 12 show some secondary and backscattered electron images (BSEI) of the Li$_2$CuO$_2$-CO$_2$-H$_2$O isothermal products treated at 80 ºC with 80 % of RH. The morphology of the sample changed importantly in comparison to the Li$_2$CuO$_2$ initial appearance (see Figure 3). The particles seem to be still agglomerated but the polyhedral particles decreased in size importantly, from 15 µm to 200 nm. Additionally, BSEI analysis evidenced the presence of
two different phases by the particle contrasts observed in the corresponding image. These two phases must correspond to Li$_2$CO$_3$ and CuO, because they are the main Li$_2$CuO$_2$ carbonation products (excluding the possible hydroxide formation). Thus, the contrast differences arise from the differences in mean atomic number ($\bar{Z}$) of Li$_2$CO$_3$ and CuO, 6 and 18.5, respectively. Therefore, the backscattered electron coefficient ($\eta$)$^{60}$ of these phases increases from 0.064 to 0.212 for Li$_2$CO$_3$ (dark phase) and CuO (light phase), respectively. From this backscattered electron image, it can be observed that CuO nanoparticles (≤ 200 nm) seem to be dispersed over the Li$_2$CO$_3$ phase. Finally, the N$_2$ adsorption-desorption isotherm of the pristine Li$_2$CuO$_2$ sample and the isothermal product treated at 80 °C and 80 % of RH are presented in the Figure 13. Both samples are isotherms type II, to the IUPAC classification,$^{59}$ but only the isothermal product presented hysteresis, H3 type. The presence of hysteresis and the large difference in the N$_2$ adsorbed volume clearly indicate high variations in the textural properties of these samples. Additionally, the surface areas of these samples were determined using the BET model. While the surface area of the pristine Li$_2$CuO$_2$ sample was 0.2 m$^2$/g, the isothermal product had a surface area of 11.3 m$^2$/g. The large difference observed between these samples may be associated Li$_2$CO$_3$-CuO external shell, which resulted to have porous and the formation of CuO nanoparticles, determined by SEM. Similar results have been published for other alkaline ceramics during the CO$_2$ capture.$^{6-34}$ Nevertheless, these textural modifications have been observed at much higher temperatures (450-550 °C) during the CO$_2$ capture process under dry conditions. In any case, the presence of porosity and/or the nanoparticles formation allows CO$_2$ or CO$_2$-H$_2$O diffusion, favoring the CO$_2$ chemisorption without the necessity of intercrystalline processes. All these results are in good agreement with the SEM and isothermal results.
All these results clearly show that CO\textsubscript{2} chemisorption in Li\textsubscript{2}CuO\textsubscript{2} is importantly improved by the presence of water vapor in moderate temperatures (30-80 °C), in comparison to the dry conditions, as Li\textsubscript{2}CuO\textsubscript{2} only chemisorbs CO\textsubscript{2} at higher temperatures than 250 °C under dry conditions.\textsuperscript{46-49} If these amounts of CO\textsubscript{2} trapped are compared with other materials, the results seem to be highly encouraging. For example, several materials including activated carbons, zeolites, hydrotalcites, and amines, are able to trap, physically or chemically, around 4–6 mmoles/g in the same temperature range.\textsuperscript{4,5,61,62} In addition, other alkaline ceramics (Li\textsubscript{5}AlO\textsubscript{4} and Na\textsubscript{2}ZrO\textsubscript{3}, among others) tested as CO\textsubscript{2} captors in similar thermal and humid conditions have shown similar properties.\textsuperscript{35-39} Nevertheless, the Li:Al molar ratio on Li\textsubscript{5}AlO\textsubscript{4} is importantly higher (4:1) than those of Na\textsubscript{2}ZrO\textsubscript{3} and Li\textsubscript{2}CuO\textsubscript{2} (2:1). Hence, the high CO\textsubscript{2} chemisorption in Li\textsubscript{5}AlO\textsubscript{4} at low temperatures may be attributed to the high lithium content, while in the Li\textsubscript{2}CuO\textsubscript{2} case could be attributed to the high lithium accessibility presented due to its layered crystalline structure. In fact the Na\textsubscript{2}ZrO\textsubscript{3} has the same alkaline:metal atomic molar ratio as well as the layered crystalline structure. Consequently, it seems that layered crystalline structures highly favor the CO\textsubscript{2} reactivity with Li\textsubscript{2}CuO\textsubscript{2}. Thus, this kind of ceramics may be considered as feasible materials for the CO\textsubscript{2} capture at moderate temperatures.

4. Conclusions

The Li\textsubscript{2}CuO\textsubscript{2}-CO\textsubscript{2}-H\textsubscript{2}O system was evaluated at moderate temperatures (30–80 °C). Li\textsubscript{2}CuO\textsubscript{2} sample was prepared by solid-state reaction. Initial results, using N\textsubscript{2} as carrier gas, showed that Li\textsubscript{2}CuO\textsubscript{2} traps water physically and chemically, where the water vapor adsorption and/or chemisorption depended on temperature and relative humidity. When CO\textsubscript{2} was used as carrier gas, important changes appeared in the results. Although Li\textsubscript{2}CuO\textsubscript{2}
mainly trapped CO\textsubscript{2} chemically, producing Li\textsubscript{2}CO\textsubscript{3} and CuO. In fact, different isothermal analyses and the characterization of the isothermal products confirmed this statement. Li\textsubscript{2}CuO\textsubscript{2} was able to chemisorb 6.7 mmoles of CO\textsubscript{2} per gram of ceramic.

Additionally, all previous results were corroborated based on the theoretical thermodynamic data for the Li\textsubscript{2}CuO\textsubscript{2}-CO\textsubscript{2}, Li\textsubscript{2}CuO\textsubscript{2}-H\textsubscript{2}O and LiOH-CO\textsubscript{2} reaction systems. \(\Delta H\) and \(\Delta G\) values clearly showed the different thermal stability of each reaction process at different temperature ranges, but lithium cuprate carbonation is the most plausible process at moderate temperatures. All the experimental and theoretical results showed that H\textsubscript{2}O acts as catalytic intermediate specie, which must diminish the activation energy of the whole CO\textsubscript{2} chemisorption process. Thus, Li\textsubscript{2}CuO\textsubscript{2} must be considered as a possible option for the CO\textsubscript{2} capture process at moderated or environmental temperatures.

**Acknowledgements**

This work was financially supported by the projects PAPIIT-UNAM (IN-102313) and SENER-CONACYT (150358). H. Lara-García thanks CONACYT for financial support. The authors thank to Adriana Tejeda and Omar Novelo for technical help.

**References**


Figure captions

Figure 1. Crystal structure of Li₂CuO₂ in space group Immm (No. 71). Red stands for oxygen, purple stands for lithium, and gray stands for copper.

Figure 2. X-ray diffraction pattern of the Li₂CuO₂ synthesized by solid state reaction.

Figure 3. Secondary electron images of the Li₂CuO₂ sample.

Figure 4. Li₂CuO₂-N₂-H₂O sorption-desorption curves where different weight increments are shown as a function temperatures (40-80 °C).

Figure 5. Li₂CuO₂-CO₂-H₂O sorption-desorption curves where different weight increments are shown as a function temperatures (40-80 °C).

Figure 6. The calculated thermodynamic data of different reactions of Li₂CuO₂ and LiOH capturing CO₂ versus temperatures, as well as the Li₂CuO₂ hydroxylation reaction: (A) heat of reaction (ΔH) and (B) free energy (ΔG).

Figure 7. The calculated vant’ Hoff Plots of the relationships among the free energy (ΔG), temperature (T) and gas pressure (P in logarithmic scale). It has to be mentioned that only the ΔG=0 curves are presented here. For Li₂CuO₂ + CO₂ = Li₂CO₃ + CuO, P=Pₐₐ₆/P₀, where P₀ is the reference pressure set to 1 bar; For 2LiOH + CO₂ = Li₂CO₃ + H₂O, For Li₂CuO₂ + H₂O = 2LiOH + CuO, P=Pₐ₆/P₀, where P₀ is the reference pressure set to 1 bar. For each reaction, above the curve, the sorbent absorbs CO₂ and the reaction goes forward to form Li₂CO₃, whereas below the curve, the carbonate releases CO₂ and the reaction goes backward to regenerate the sorbent.
Figure 8. Li$_2$CuO$_2$-CO$_2$-H$_2$O thermogravimetric kinetic isotherms performed at different temperatures (40, 60 and 80 °C) and RH (20, 40, 60 and 80 %).

Figure 9. XRD pattern of the Li$_2$CuO$_2$-CO$_2$-H$_2$O isothermal product treated at 80 °C with 80 % of RH.

Figure 10. TG and DTG decomposition curves of Li$_2$CuO$_2$-CO$_2$-H$_2$O products treated isothermally at 80 °C and different RH (20-80 %).

Figure 11. Quantification of the CO$_2$ desorbed during the TG analyses from Li$_2$CO$_3$ by Li$_2$CuO$_2$ varying temperature and RH.

Figure 12. Secondary (A) and backscattered (B) electron images of the Li$_2$CuO$_2$-CO$_2$-H$_2$O isothermal products treated at 80 °C with 80 % of RH.

Figure 13. N$_2$ adsorption-desorption isotherm of the pristine Li$_2$CuO$_2$ sample and the Li$_2$CuO$_2$-CO$_2$-H$_2$O isothermal product treated at 80 °C and 80 % of RH.
# TABLES

**Table 1.** The calculated thermodynamic properties of reaction of CO\(_2\) captured by Li\(_2\)CuO\(_2\) and LiOH comparison with Li\(_2\)O. \(T_1\) and \(T_2\) are the turnover temperatures of the CO\(_2\) capture reactions at \(P_{CO_2}=0.1\) bar for post-combustion, \(P_{CO_2}=20\) bar for pre-combustion condition. For LiOH, assuming \(P_{H_2O}=1\) bar.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>CO(_2) wt%</th>
<th>(\Delta E^{DFT}) (kJ/mol)</th>
<th>(\Delta H) (kJ/mol)</th>
<th>(\Delta G) (kJ/mol)</th>
<th>(T_1) (K)</th>
<th>(T_2) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_2)CuO(_2) + CO(_2) = Li(_2)CO(_3) + CuO</td>
<td>59.99</td>
<td>-190.052</td>
<td>-184.516</td>
<td>-135.359</td>
<td>1005</td>
<td>1335</td>
</tr>
<tr>
<td>2LiOH + CO(_2) = Li(_2)CO(_3) + H(_2)O</td>
<td>91.88</td>
<td>-76.659</td>
<td>-98.623</td>
<td>-97.134</td>
<td>H(_t)(^a)</td>
<td>H(_t)</td>
</tr>
<tr>
<td>Li(_2)CuO(_2) + H(_2)O = 2LiOH + CuO</td>
<td>---</td>
<td>-113.393</td>
<td>-85.893</td>
<td>-38.225</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Li(_2)O + CO(_2) = Li(_2)CO(_3)(^b)</td>
<td>142.52</td>
<td>-204.786</td>
<td>-226.731</td>
<td>-179.261</td>
<td>1295</td>
<td>H(_t)</td>
</tr>
</tbody>
</table>

\(^a\) H\(_t\) stands for the temperature out of the range of 1500 K

\(^b\) Taken from Refs 51 and 63.
Figure 1
Figure 2

![Graph showing Intensity (a.u.) vs. 2θ for Li₂CuO₂]
Figure 3
Figure 4

![Diagram showing weight (%) against relative humidity (%) at different temperatures (40°C, 60°C, 80°C).]
Figure 5
Figure 6

(A) 

-70
-80
-90
-100
-110
-120
-130
-140
-150

\( \Delta H \) (kJ/mol)

Temperature (K)

Li\textsubscript{2}CuO\textsubscript{2}+H\textsubscript{2}O \rightarrow 2LiOH+CuO

2LiOH+CO\textsubscript{2} \rightarrow Li\textsubscript{2}CO\textsubscript{3}+H\textsubscript{2}O

Li\textsubscript{2}CuO\textsubscript{2}+CO\textsubscript{2} \rightarrow Li\textsubscript{2}CO\textsubscript{3}+CuO

(B) 

-150
-100
-50
0
50
100
150

\( \Delta G \) (kJ/mol)

Temperature (K)

Li\textsubscript{2}CuO\textsubscript{2}+H\textsubscript{2}O \rightarrow 2LiOH+CuO

2LiOH+CO\textsubscript{2} \rightarrow Li\textsubscript{2}CO\textsubscript{3}+H\textsubscript{2}O

Li\textsubscript{2}CuO\textsubscript{2}+CO\textsubscript{2} \rightarrow Li\textsubscript{2}CO\textsubscript{3}+CuO
Figure 7

\[ \Delta G > 0, \text{H}_2\text{O des region} \]
\[ \Delta G < 0, \text{H}_2\text{O ads region} \]
\[ \Delta G < 0, \text{CO}_2 \text{ capture region} \]
\[ \Delta G > 0, \text{CO}_2 \text{ release region} \]

Li$_2$CuO$_2$ + CO$_2$ → Li$_2$CO$_3$ + CuO

Li$_2$CuO$_2$ + H$_2$O → 2LiOH + CuO

2LiOH + CO$_2$ → Li$_2$CO$_3$ + H$_2$O

\[ \Delta G > 0, \text{H}_2\text{O des region} \]

Temperature (1000/T, K$^{-1}$)

CO$_2$ or H$_2$O Pressure log(P)

Temperature (°C)
Figure 8

40 °C

RH = 80 %
RH = 60 %
RH = 40 %
RH = 20 %

Weight (%)
Time (sec)

Figure 9

60 °C

RH = 80 %
RH = 60 %
RH = 40 %
RH = 20 %

Weight (%)
Time (sec)

80 °C

RH = 80 %
RH = 60 %
RH = 40 %
RH = 20 %

Weight (%)
Time (sec)
Figure 10
Figure 11
Figure 12

(A) 

(B)
Figure 13
Li$_2$CuO$_2$ is able to chemisorb high quantities of CO$_2$ in the presence of water steam at low temperatures.