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Thermocatalytic analysis of CO_2-CO selective chemisorption mechanism on lithium cuprate (Li_2CuO_2) and oxygen addition effect

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ABSTRACT

In the present work, thermogravimetric and catalytic analyses were performed in order to evidence the chemisorption selective mechanism followed during the CO and CO_2 chemisorption processes on Li_2CuO_2 under different atmosphere conditions. Results were contrasted with some thermodynamic data. According to TG results, when the gas flow was composed by one gas (CO or CO_2), chemisorption occurred through a superficial reaction followed by a volumetric capture. In the CO case, a double process was produced; CO oxidation and subsequent CO_2 chemisorption. Here, Li_2CuO_2, initially, catalyzed the CO oxidation and then it sorbed CO_2. However, as Li_2CuO_2 structure and composition evolves, it could not be strictly considered as a catalyst. On the other hand, when both gases were present (CO-CO_2), a chemisorption competition was observed as a function of temperature, where CO was always selectively chemisorbed. Furthermore, O_2 presence modified positively the chemisorption abilities in binary (CO-O_2 and CO_2-O_2) and ternary (CO-CO_2-O_2) gas systems, in comparison with analogous tests performed in absence of O_2.

1. Introduction

In the last two decades, several papers have reported the CO_2 capture on different materials [1–5], due to the threatening environmental situation. In that sense, alkaline ceramics seem to present good CO_2 sorption properties, mainly at high temperatures ($300 \leq T \leq 850$ °C) [1,6–19]. These alkaline ceramics are able to trap CO_2 chemically, through a double chemisorption process produced at surface and bulk particle sections [20]. The initial reaction process, superficial chemisorption, is produced by an acid-base reaction mechanism as alkaline ceramics present high basic characteristics. On the contrary, CO_2 is an acid molecule, which according to the Lux and Flood acid-base theory [21,22] is able to accept an oxygen anion from the basic component; the alkaline crystal structure in this case, producing CO_3^{2-}. Moreover, as oxygen diffusion is needed to complete the carbonation process of alkaline ceramics, different authors have evidenced the positive effect produced by oxygen addition, where CO_2 and O_2 adsorption competition has been described during the superficial chemisorption process [23–25].

On the other hand, it was recently published that some alkaline ceramics (Li_2CuO_2, Li_5FeO_4, $NaCoO_2$ and Na_2ZrO_3) are able to chemisorb carbon monoxide (CO), through a CO oxidation and subsequent CO_2 chemisorption process [26–28]. In these cases, CO capture process follows a similar superficial and bulk chemisorption mechanism than that described above for CO_2, once CO has been previously oxidized. Such bifunctional application may be of great interest for developing gas separation systems. In that sense, there are several kinds of gas mixtures, such as syngas or biogas [29], where CO and/or CO_2 separation would modify or produce different gas compositions for final applications. For example, there are some biogas or syngas compositions where the amounts of CO_2 and CO are large and similar to methane (CH_4) or hydrogen (H_2) concentrations. In these cases, carbon oxides separation would be ideally desired, in order to obtain gas mixtures with larger heat capacities.

It should be mentioned that lithium cuprate (Li_2CuO_2) has shown some interesting CO_2 and CO capture properties [30–36], although it has not been largely studied. Li_2CuO_2 has an orthorhombic crystalline structure ($a = 3.655$ Å, $b = 2.860$ Å, $c = 9.377$ Å and $Z = 2$, [37]), where lithium atoms are located between the $(CuO_4)^{2-}$ square layers. In the Li_2CuO_2 crystalline structure, lithium atoms have a high diffusion capacity. Moreover, it has to be mentioned that copper is able to change its oxidation state releasing oxygen, which enhances CO_2 and CO

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capture properties, in comparison to other alkaline ceramics.

Based on that, the aim of this work was to analyze the CO_2 and CO selective sorptions on lithium cuprate, one of the most promising alkaline ceramics for CO_2 chemisorption and CO oxidation-chemisorption processes. Thus, different catalytic and thermogravimetric analyses were conducted as an initial approximation for understanding the reaction mechanism. This analysis was performed in presence and absence of oxygen.

2. Experimental section

Li_2CuO_2 ceramic was synthesized by solid-state reaction as it was previously reported in literature [31,35]. Lithium (Li_2O, Aldrich, 99%) and copper (CuO, Meyer, 97%) oxides were used as reagents, mechanically mixed and then calcined in air atmosphere at 800 °C for 6 h. 20 wt% of lithium oxide excess was added in order to compensate Li sublimation at T > 720 °C [37–39]. After, powder X-ray diffraction (XRD) was used to confirm the formation of Li_2CuO_2 crystalline phase (data not shown). Moreover, some microstructural characteristics of Li_2CuO_2 were determined by N_2 adsorption-desorption analysis in a Bel-Japan Minisorp II equipment at 77 K. Prior to analysis, the sample was degassed at room temperature for 12 h in vacuum. Finally, the BET model was used to determine the specific surface area (S_{BET} = 1.9 m^2/g).

Carbon monoxide (CO) and carbon dioxide (CO_2) chemisorption capabilities were evaluated simultaneously in a TA Instruments Q500 thermobalance (~50 mg of sample) and in a catalytic reactor (Bel-Japan, model Bel-Rea, 200 mg of sample). In both analyses, samples were dynamically heated from 30 to 900 °C at 2 °C/min, using 4 mL/min of each gas in the following atmospheres: *i*) CO_2 (Praxair, grade 3.0), *ii*) CO (5 vol% in N_2, Praxair certificate standard), *iii*) CO-CO_2, *iv*) CO-O_2 (Praxair, grade 2.6), *v*) CO_2-O_2 and *vi*) CO-CO2-O_2, all diluted in N_2 to complete 100 mL/min. In TG analysis (Q500HR, from TA Instruments), chemisorption-desorption processes were evaluated following changes in the sample weight; whereas in reactor analysis, gas products were analyzed with a GC-2014 gas chromatograph (Shimadzu) with a Carboxen-1000 column. Then, some isothermal experiments were performed with ~100 mg of sample at different selected temperatures (350, 550 and 700 °C). For isothermal tests, samples were heated rapidly from room temperature to specified temperature, using N_2 (40 mL/min) as carrier gas; once the desired temperature was achieved, the flow gas was switched to desired gas mixture (CO-CO_2 or CO-CO_2-O_2) during 3 h. Isothermal products were analyzed by powder XRD to identify the crystal phases produced by different atmospheres and temperature conditions. XRD patterns were recorded in the $5° \leq 2\Theta \leq 80°$ range, using a goniometer speed of 0.02°(2Θ)/min, with a Siemens D5000 diffractometer coupled to a cobalt anode (λ = 1.7889 Å). Crystal phases were identified using the Joint Committee Powder Diffraction Standards (JCPDS).

Temperature programmed desorption (TPD) analyses were performed in a chemisorption analyzer (Belcat, Bel-Japan) with 50 mg of sample. Sample was pre-treated at 850 °C under a He flow (30 mL/min). The sample was then cooled to 200 °C and saturated with 5 mL/min of CO or CO_2. In both cases, gases were diluted in N_2 up to 100 mL/min during 60 min. Afterwards, TPD analyses were carried out by heating the sample up to 900 °C at 2 °C/min, in a He flow, quantifying data with a thermal conductivity detector (TCD).

3. Results and discussion

In order to analyze the CO_2-CO sorption mechanism on Li_2CuO_2, different thermogravimetric and catalytic experiments were performed using the following gas mixtures: CO_2, CO, CO_2-O_2, CO-O_2, CO_2-CO and CO_2-CO-O_2. Initially, dynamic thermograms of CO_2 and CO gases, as well as the CO_2-O_2 and CO-O_2 gas mixtures, are shown in Fig. 1. CO_2 and CO_2-O_2 dynamic experiments presented the typical behavior previously reported for Li_2CuO_2 (Fig. 1A) [24,30,33–36]. For the CO_2 case, Li_2CuO_2 presented an initial weight increment of 4 wt% between 350 and 600 °C, where superficial CO_2 chemisorption occurred, producing an external shell composed by lithium carbonate (Li_2CO_3) and copper oxide (CuO). Then, a second CO_2 chemisorption process was produced between 660 and 750 °C, where sample gained a total weight

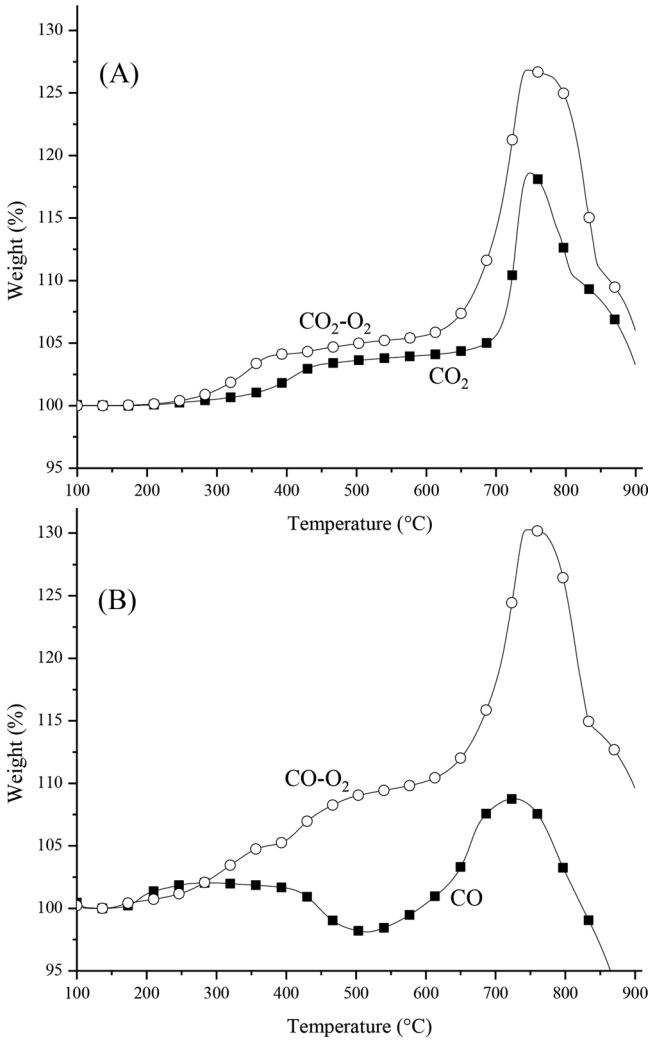

Fig. 1. Thermograms of Li_2CuO_2 sample treated under different carbon oxide atmospheres: (A) CO_2 and CO_2-O_2, (B) CO and CO-O_2.

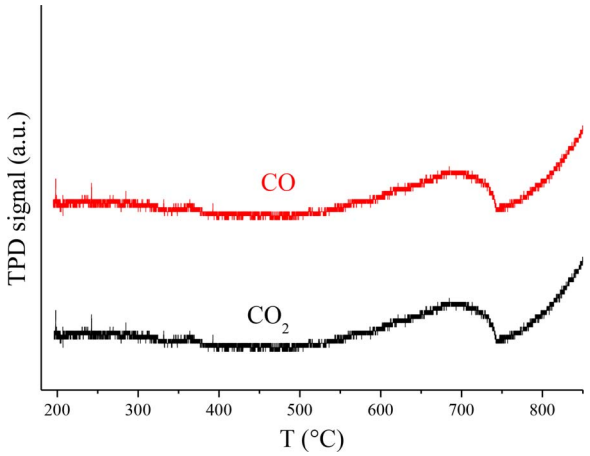

Fig. 2. Temperature programmed desorption of CO_2 or CO on Li_2CuO_2.

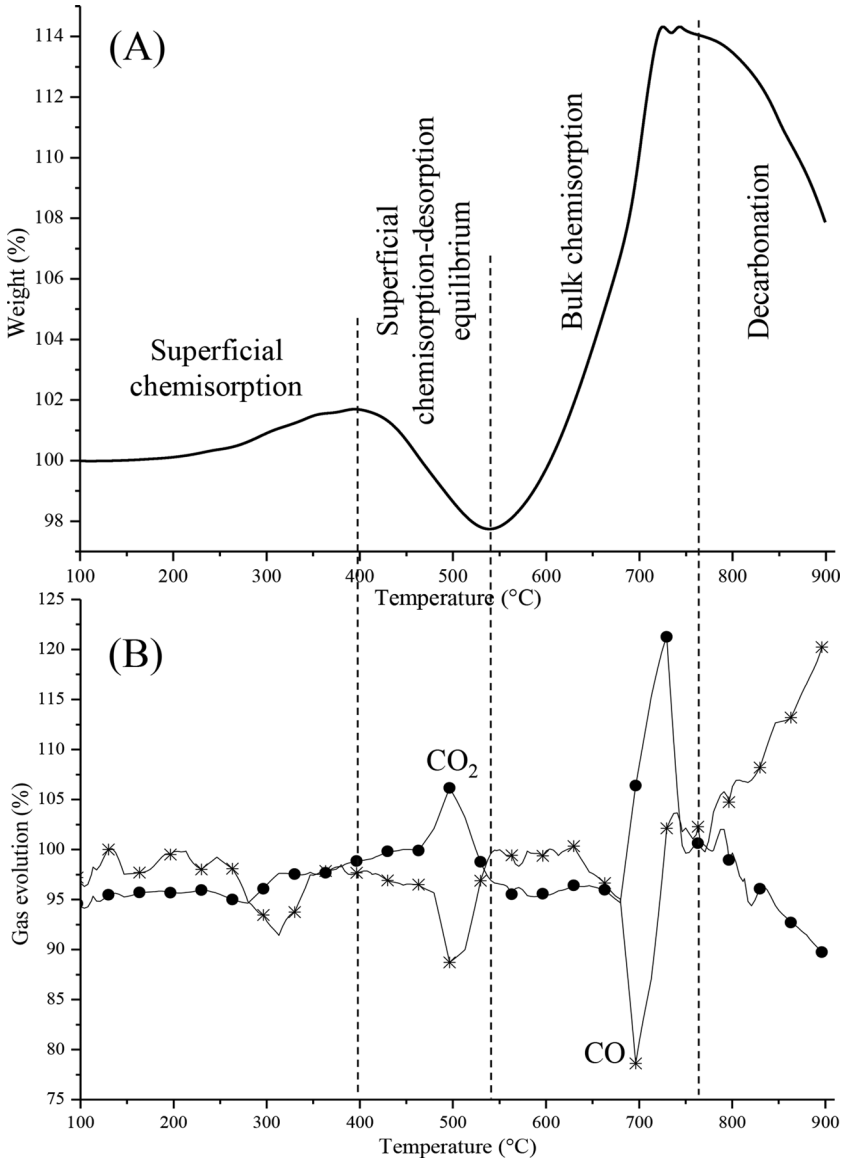

Fig. 3. Thermogravimetric profile (A) and catalytic evolution (B) of Li_2CuO_2 sample treated on CO-CO_2 atmosphere.

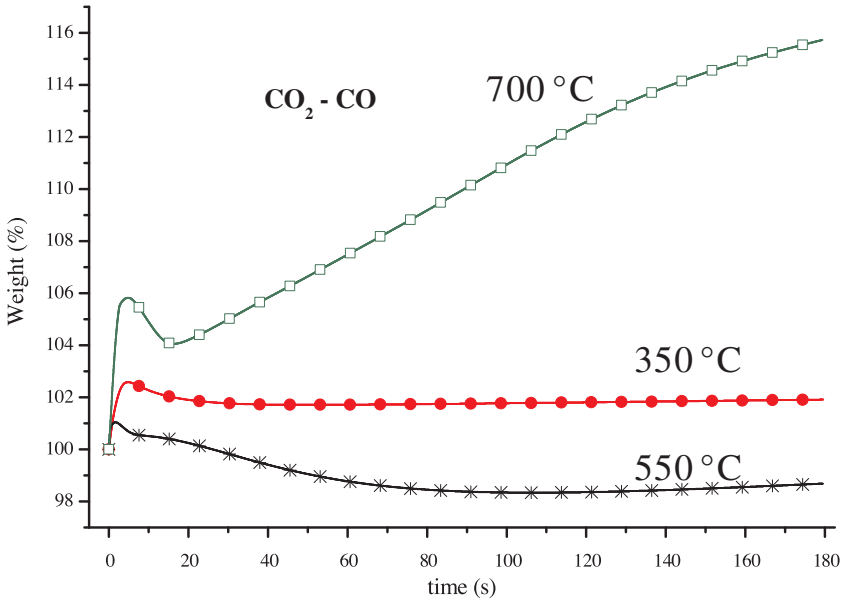

Fig. 4. Isothermal experiments for Li_2CuO_2 sample tested using a CO-CO_2 atmosphere at different temperatures (350, 550 and 700 °C).

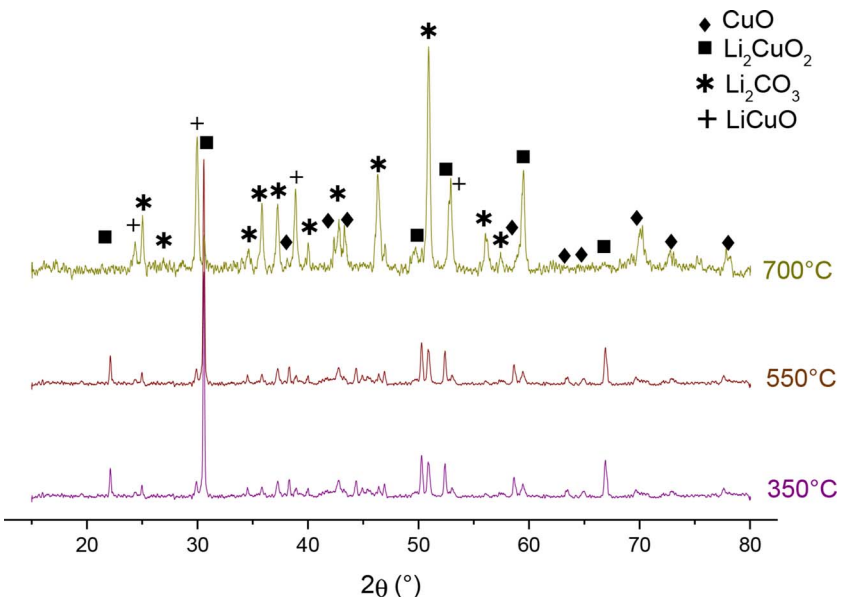

Fig. 5. XRD patterns for Li_2CuO_2-CO-CO_2 isothermal products obtained at different temperatures.

of 18.8 wt%. In this temperature range, lithium and oxygen diffusion processes are activated for CO_2 bulk chemisorption (reaction (1)). Finally, at temperatures higher than 750 °C CO_2 desorption was activated. CO_2-O_2 thermogram presented the same trend than that observed on the CO_2 case, but oxygen addition improved CO_2 superficial and bulk capture processes. In the CO_2-O_2 case, superficial and total (superficial + bulk) CO_2 chemisorption were equal to 6 and 27 wt%, respectively. In a previous work, Lara-García et al. [24] showed that CO_2 chemisorption is strongly enhanced by oxygen addition. When oxygen is supplied through the gas flow, copper atoms facilitate homolytic oxygen dissociation, where two free radical oxygen atoms are produced (reaction (2)). Then, dissociated oxygen atoms can be taken from the gas flow for carbonation without any crystalline diffusion process. Later, oxygen atoms, from Li_2CuO_2 crystalline structure, can diffuse and release at any moment as oxygen molecules (reaction (3)).

$$Li_2CuO_2 + CO_2 \rightarrow Li_2CO_3 + CuO \quad (1)$$

$$O_2 \xrightarrow{Li_2CuO_2} 2O° \quad (2)$$

$$Li_2CuO_2 + CO_2 + 2O\cdot \rightarrow Li_2CO_3 + CuO + O_2 \quad (3)$$

In reaction (3), $O\cdot$ are the oxygen atoms taking part during the Li_2CO_3 formation, while the O_2 molecule, presented on the product side of this reaction, corresponds to the oxygen atoms diffused and released from the Li_2CuO_2 crystalline structure.

Fig. 1B shows the CO and CO-O_2 dynamic thermograms. Both curves evidenced weight increments, which can be attributed to carbonation processes. In the CO case, the thermogram showed a weight increment (2.2 wt%) between 150 and 320 °C, associated to CO superficial chemisorption. Then, between 320 and 500 °C a superficial desorption was produced. At higher temperatures, a second weight increment was produced between 530 and 720 °C, which can be attributed to CO bulk chemisorption process. In this case, CO is being trapped chemically and structural oxygen atoms are used to produce Li_2CO_3. Consequently, copper cations in Li_2CuO_2 must be partially or totally reduced, as it is proposed in reaction (4). A similar behavior was already observed for Li_5FeO_4-CO system, where partial iron reduction was detected from Fe^{3+} to Fe^{2+} or even more to Fe^0 [32]. On the contrary, when oxygen is added (reaction (5)), carbonation generates the same final products as those obtained during Li_2CuO_2 carbonation using carbon dioxide. In fact, thermodynamic analysis shows that reaction (5) is favored over the double reaction process; CO oxidation and subsequent lithium cuprate carbonation [27].

$$Li_2CuO_2 + CO \rightarrow Li_2CO_3 + Cu \quad (4)$$

$$Li_2CuO_2 + CO + \frac{1}{2}O_2 \rightarrow Li_2CO_3 + CuO \quad (5)$$

In the last case (CO-O_2), superficial (9 wt%) and bulk (30.5 wt%) weight increments were the highest among different gas mixtures analyzed. Thus, Li_2CuO_2 is able to catalyze the conversion of CO to CO_2 and chemisorbs the product, although Li_2CuO_2 could not be establish as a catalyst as it evolves chemically during the CO_2 chemisorption process. Moreover, Li_2CuO_2 chemical change modifies particle microstructural evolution, enhancing final CO_2 chemisorption.

In order to verify if CO and CO_2 sorption processes are produced at the same Li_2CuO_2 actives sites, TPD-CO_2 experiments were performed with both gases (Fig. 2). In both cases, the TPD curves showed two CO_2 desorption process at 500–750 °C and T > 750 °C. These processes can be associated to CO_2 molecules strongly sorbed on Li_2CuO_2 particles and Li_2CuO_2 decarbonation process, respectively. It must be pointed out that TPD experiments presented exactly the same behavior, independently of the sorbed gas, CO or CO_2. Thus, sorption process and Li_2CuO_2 superficial active sites are the same for CO and CO_2.

After CO_2 and CO chemisorption evaluation on Li_2CuO_2, in presence and absence of oxygen, CO_2-CO and CO_2-CO-O_2 systems were analyzed. In both cases, thermograms presented similar trends as those obtained previously. However, gas evolution was followed in order to determine whether CO_2 or CO were selectively chemisorbed. On the CO_2-CO case (Fig. 3), thermogram showed four different sections; *i*) superficial chemisorption, *ii*) superficial chemisorption-desorption equilibrium, *iii*) bulk chemisorption and *iv*) decarbonation, where all these processes fit well to previous references on Li_2CuO_2 [31]. Initially, superficial chemisorption process was observed between 250 and 400 °C, with a weight increment of 1.9 wt% (Fig. 3A). In the same temperature range, gas evolution analysis did not evidence which carbon oxide would be associated to superficial chemisorption, although CO evolution suggested a partial consumption at around 320 °C (Fig. 3B). At higher temperatures (400–540 °C), a superficial desorption was produced, inducing a chemisorption-desorption equilibrium. In this temperature range, gas evolution curve clearly showed CO consumption and CO_2 production. Thus, Li_2CuO_2 must be catalyzing CO to CO_2, but it is not trapped, as CO_2 is detected in excess. Moreover, CO_2 detection must be a consequence of CO oxidation and CO_2 desorption. Once the bulk chemisorption is activated (T > 540 °C), this thermogram showed an

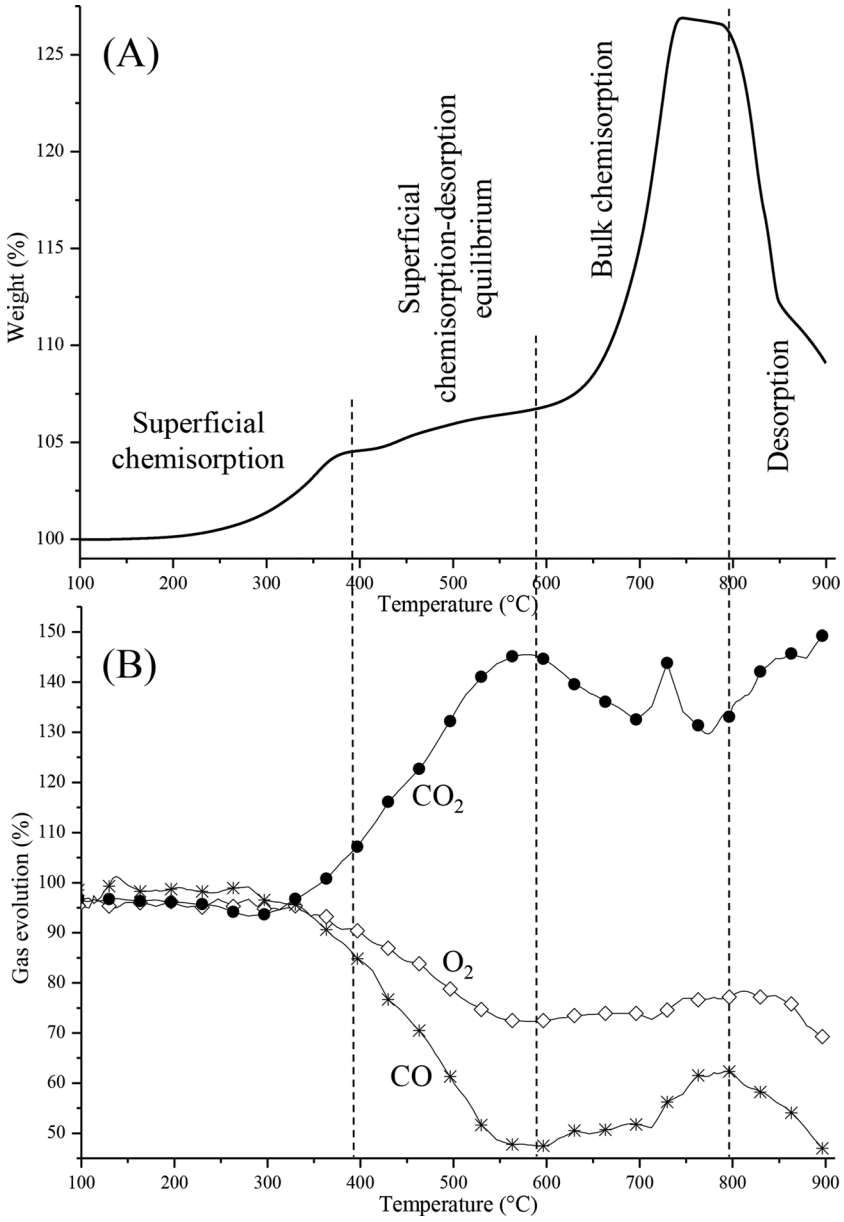

Fig. 6. Thermogravimetric profile (A) and catalytic evolution (B) of Li_2CuO_2 sample treated on CO-CO_2-O_2 atmosphere.

important weight increment of 14.7 wt%. At the same time, gas evolution curve shows that CO is consumed, while CO_2 is being produced. These results show that CO is the gas consumed, where part of it is used for bulk chemisorption and the other part is only oxidized to CO_2. Therefore, in the CO_2-CO system, CO seems to be the most reactive specie, where the carbonation process must follow the reaction (4). In fact, the metallic copper production explains the last process; decarbonation. In this case, CO_2 is consumed while CO is produced. Here, CO_2 is partially reduced, producing a CO excess (between 760 and 900 °C), through copper re-oxidation or Li_2CuO_2 regeneration.

In order to further analyze the Li_2CuO_2-CO_2-CO reaction mechanism, three specific isothermal experiments were performed at 350, 550 and 700 °C to represent superficial chemisorption, superficial chemisorption-desorption and bulk chemisorption processes, respectively. Moreover, isothermal products were analyzed by XRD to determine composition and structural changes produced by CO and CO_2 chemisorption-desorption. Fig. 4 shows Li_2CuO_2-CO_2-CO isotherms. The isotherm performed at 350 °C showed an initial weight increment of 2.6 wt% after five minutes. This weight increment is similar to that observed in the dynamic experiment. After that, isotherm tends to reach a chemisorption-desorption equilibrium, stabilizing the weight gained in 1.8 wt%. Final weight increment and temperature correspond to a superficial process. Then, isotherm performed at 550 °C chemically increased its weight by only 1.1 wt% after three minutes. After that, isotherm desorbed even more weight than that present at the beginning of this isotherm. This weight should be correlated to continuous CO oxidation process evidenced on the gas evolution curve (Fig. 3B). In this case, part of oxygen atoms, present into the Li_2CuO_2 crystalline structure, are released to react with CO; producing CO_2. Thus, Li_2CuO_2 should be partially decomposed through copper reduction. Finally, when isotherm was performed at 700 °C, an initial weight increment was observed (5.8 wt%) after five minutes, which corresponds to superficial chemisorption process. Then, superficial chemisorption-desorption and bulk chemisorption are activated, reaching a final weight increment of 15.8 wt%. As in the previous case (550 °C), chemisorption process must be produced through the copper reduction, according to thermogravimetric and gas evolution results (see Fig. 3). In order to probe this reaction mechanism, isothermal products were analyzed by powder XRD (Fig. 5). As it could be expected, X-ray diffraction patterns of isothermal products obtained at 350 and 550 °C mainly depicted the

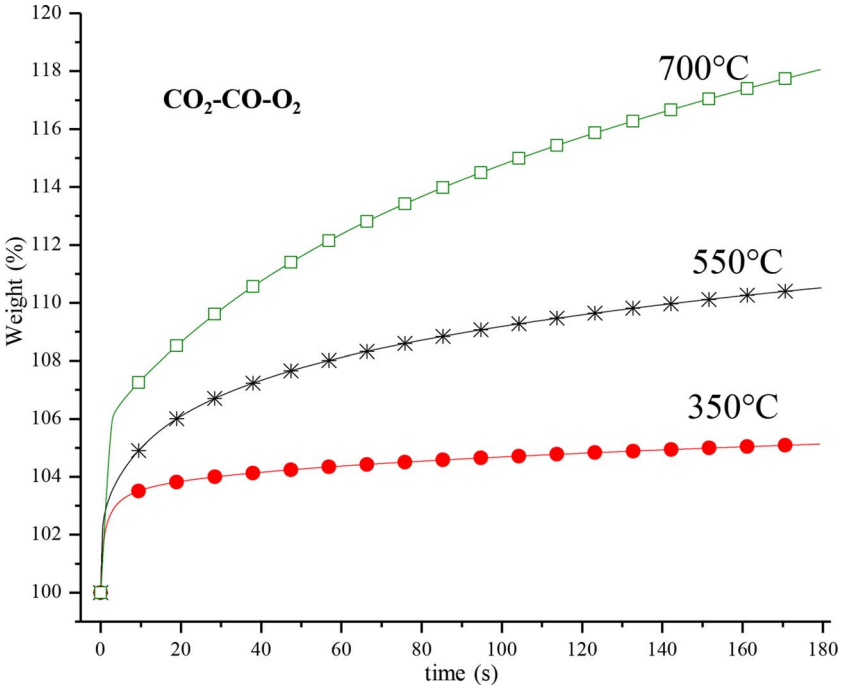

Fig. 7. Isothermal experiments for Li_2CuO_2 sample tested using a CO-CO_2-O_2 atmosphere at different temperatures (350, 550 and 700 °C).

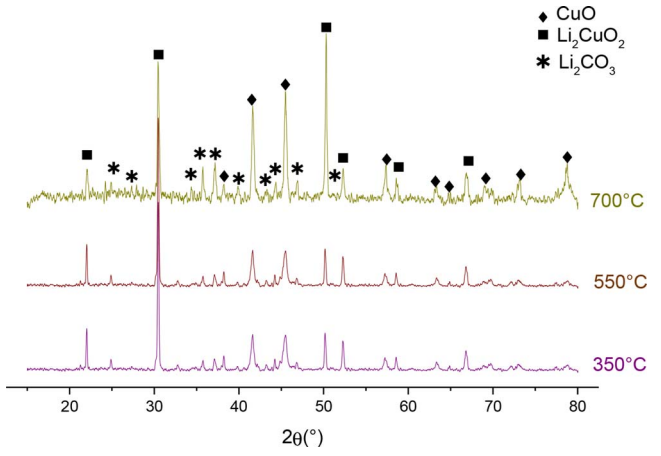

Fig. 8. XRD patterns of Li_2CuO_2-CO-CO_2-O_2 isothermal products obtained at different temperatures.

presence of Li_2CuO_2 (PDF file 01-084-1971) and Li_2CO_3 (PDF file 00-022-1141) as the main carbonation product. Nevertheless, it was possible to determine the presence of a different lithium cuprate phase: LiCuO (PDF file 00-077-1698), where copper cations present a different oxidation state (Cu^{1+}) from that presented on Li_2CuO_2 (Cu^{2+}). XRD pattern of isotherm performed at 700 °C confirmed the formation of Li_2CO_3 and LiCuO, while Li_2CuO_2 phase tended to disappear. Finally, CuO (PDF file 00-045-0937) was also detected in the last XRD pattern, which implies a partial reaction of copper element or a different carbonation reaction mechanism. These results confirmed the carbonation process, in which part of the oxygen atoms present in the Li_2CuO_2 crystal phase are released to react with CO, producing the final carbonation process. However, the presence of small amounts of CuO confirmed that, at least, a small proportion of the carbonation process is produced by the direct CO_2 chemisorption (reaction (1)). On the contrary, released oxygen (from Li_2CuO_2 crystal structure) induces a partial copper reduction, according to following reaction (reaction (6)).

$$2Li_2CuO_2 + CO \rightarrow 2LiCuO + Li_2CO_3 \quad (6)$$

After the CO_2-CO system analysis, oxygen was included (CO_2-CO-O_2) in order to determine variations. Fig. 6 shows the same four chemisorption-desorption sections described above. Initially, superficial chemisorption was produced between 250 and 390 °C, producing a weight increment of 4.6 wt% (Fig. 6A). In this temperature range, gas evolution analysis showed that CO and O_2 are consumed, while CO_2 concentration increased (Fig. 6B). The same gas evolution tendency continued between 390 and 580 °C (superficial chemisorption-desorption equilibrium). Thus, as in the CO_2-CO system, Li_2CuO_2 must catalyze CO to CO_2 (reaction (7)), but CO_2 is not highly chemisorbed as its weight only increased in 2.2 wt%. However, it should be mentioned that oxygen importantly modified the chemisorption-desorption equilibrium in this temperature range, in comparison to CO_2-CO system. Once bulk chemisorption is activated (T > 600 °C), thermogram showed a total weight increment of 26.9 wt%, which is almost twice higher than that observed on O_2 absence (Fig. 3A). In the same temperature range, gas evolution curve shows that CO is consumed as well as O_2, while CO_2 increased. In fact, it can be seen that CO_2 concentration presented the highest production at around 730 °C. Finally, at T ≥ 800 °C decarbonation process was evidenced, with the consequent CO and O_2 consumptions and CO_2 production, meaning that CO oxidation process continued in this temperature range.

$$CO + \frac{1}{2}O_2 \xrightarrow{Li_2CuO_{2(cat)}} CO_2 \quad (7)$$

As in the previous case, three isothermal experiments were performed (350, 550 and 700 °C) on the Li_2CuO_2-CO_2-CO-O_2 system. Fig. 7 shows that isotherms presented an exponential behavior, where the final weights increased as a function of temperature. Isotherm performed at 350 °C presented a weight increment of 5.1 wt% after five minutes. This weight increment was higher than that observed on oxygen absence (2.1 wt%, see Fig. 4). At 550 and 700 °C, the total weigh increments were 10.6 and 18.0 wt%, respectively. As in the lowest temperature (350 °C), oxygen addition favored the carbonation process, independently of temperature. Isothermal products were analyzed by XRD (Fig. 8), and diffractograms only showed the presence of Li_2CuO_2, as unreacted material, and Li_2CO_3 and CuO as carbonation products, according to reactions (3) or (5). It should be mentioned that in the oxygen presence, copper was not partially reduced.

Comparing these results with theoretical Gibbs free energy (ΔG), the following facts can be seen (Fig. 9): 1) CO_2 capture is always higher

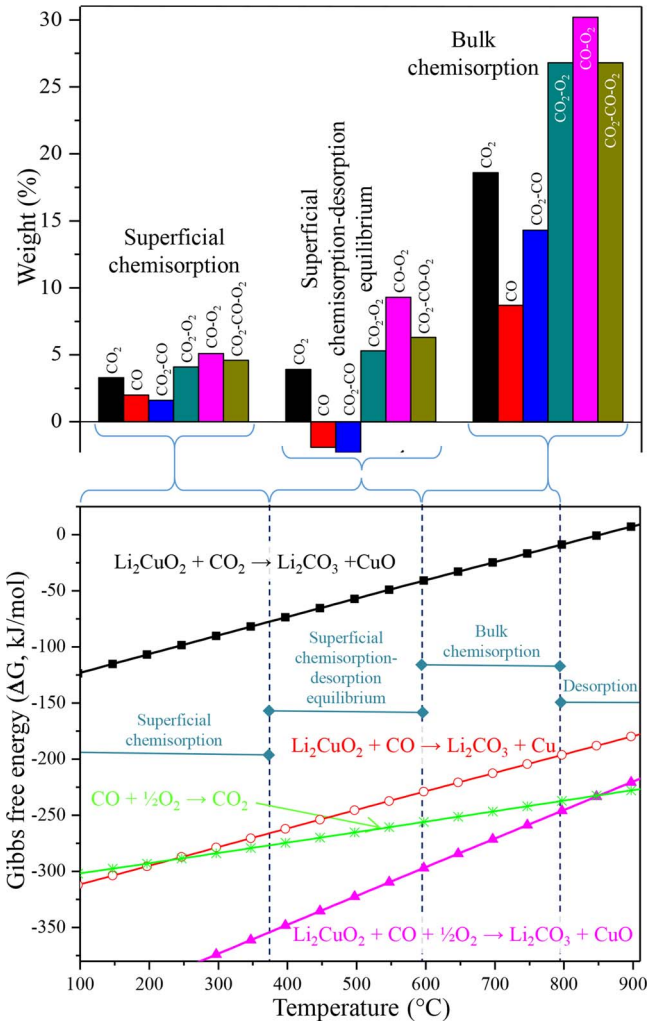

Fig. 9. Comparison between experimental data and theoretical calculations [27] for different CO_2 and CO chemisorption-desorption processes occurred on Li_2CuO_2. Thermodynamic data was obtained for each reaction independently, and reaction data were presented to show which of them was the most suitable process at the different temperature ranges.

than that of CO at superficial chemisorption, superficial chemisorption-desorption equilibrium and bulk chemisorption temperature ranges, although the Gibbs free energies suggest a higher stability of CO chemisorption reaction. Therefore, CO chemisorption process must be slower, kinetically, than that of CO_2. It may be generated by oxygen release from Li_2CuO_2 crystal structure producing lithium carbonate and LiCuO. 2) On the contrary, once oxygen is added, chemisorption of CO_2 and CO are importantly improved. This result is in very good agreement with ΔG values obtained for the Li_2CuO_2-CO-O_2 system, which presents the highest thermodynamic stability. Moreover, from ΔG data, it can be seen that at $T < 845\,^{\circ}C$ CO catalytic conversion to CO_2 is less stable than CO-O_2 chemisorption, confirming that Li_2CuO_2 reaction with CO varies as a function of oxygen presence (reaction (5)) or absence (reaction (6)). 3) Finally, when CO_2 and CO_2-CO systems are compared, all chemisorption processes decreased on the CO_2-CO case in oxygen absence, but enhanced in the presence of oxygen. As it could be expected, in oxygen absence, CO_2 presence on CO_2-CO mixture must modify the CO catalytic conversion to CO_2, according to Le Chatelier's equilibrium law, reducing the chemisorption process due to low CO_2 partial pressure in addition to the oxygen release necessity. On the contrary, once oxygen is added, reaction mechanism changes and CO oxidation (reaction (7)) is not the preponderant reaction.

4. Conclusions

Li_2CuO_2 was synthetized and then tested for CO and CO_2 chemisorption processes on presence or absence of O_2. Based on the results obtained, it was possible to establish different reaction mechanisms for each gas condition. Reaction mechanisms were corroborated through thermodynamic calculations (ΔG). According to TG experiments, CO_2 chemisorption process was achieved using Li_2CuO_2 as chemical sorbent (18.8 wt%) in a wide temperature range (400–750 °C). This effect was significant enhanced by O_2 addition; especially during bulk chemisorption stage (27.0 wt%, between 600 and 800 °C), where lithium and oxygen diffusion processes are active. Regarding to CO oxidation reaction, it can be established that it is slower than CO_2 chemisorption on O_2 absence, but it is highly enhanced by O_2 addition (CO-O_2). In the CO cases, it always presented a higher selectivity chemisorption on Li_2CuO_2 than CO_2. Moreover, a bifunctional process took place during the CO chemisorption: 1) CO oxidation to CO_2 and 2) CO_2 chemisorption. According to all these results, CO-O_2 system is the best condition for obtaining the highest chemical capture, among all gas compositions tested. Thus, oxygen addition avoids direct carbon monoxide chemisorption observed in O_2 absence, while it significantly enhances the following processes; superficial chemisorption (~5 wt%), superficial chemisorption-desorption equilibrium (~10 wt%) and bulk adsorption (~30 wt%).

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