

CO₂ chemisorption enhancement produced by K₂CO₃- and Na₂CO₃-addition on Li₂CuO₂



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ABSTRACT

This work presents a proposal for enhancing CO₂ capture over lithium cuprate (Li₂CuO₂) by alkaline carbonates addition. Lithium cuprate was synthesized via solid-state reaction. Subsequently, portions of Li₂CuO₂ were mechanically mixed with 10 wt% of potassium carbonate (K₂CO₃), sodium carbonate (Na₂CO₃) or equal amounts of both carbonates (5–5 wt%). All samples were characterized by several techniques and then CO₂ chemisorption process was evaluated on different dynamic and isothermal conditions. The presence of K and/or Na carbonates preserves the primary properties of pristine Li₂CuO₂, such as crystalline phase (DRX) and microstructure (SEM), also allowing to increase textural properties (N₂ physisorption) and modifying CO₂ desorption abilities (TPD), in comparison with pure material. In general, carbonates addition induces some changes during CO₂ 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 CO₂ (63.9–79.1% of efficiency). On the other hand, at 700 °C, Na-Li₂CuO₂ sample presented the best capture ability, capturing 30.6 wt% of CO₂ (76.1% of efficiency). Meanwhile at 650 °C, K-Li₂CuO₂ presented the highest sorption capacity with 40.4 wt% of CO₂ captured, which represents ~100% of efficiency. The above results showed that in the same thermal conditions, samples modified with alkaline carbonates improved the CO₂ 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 (Li₂CO₃) formed as result of CO₂ chemisorption process. Finally, it was observed that carbonate addition is a feasible way to increase CO₂ capture in Li₂CuO₂ 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 (CO₂) 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 CO₂ emissions, the use of alkaline ceramics for CO₂ sequestration through a process of chemisorption is one of the most used options [1,6]. These CO₂ 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 CO₂ capture abilities, among them lithium and sodium zirconates (Li₂ZrO₃ and Na₂ZrO₃ [7–13]), lithium orthosilicate (Li₄SiO₄ [14–19]), lithium aluminate (Li₅AlO₄ [20,21]), lithium ferrites (Li₅FeO₄ and LiFeO₂ [22]) and lithium cuprate (Li₂CuO₂ [23,24]). In particular, Li₂CuO₂ has been already studied as a CO₂ captor in a temperature range of 120 to 650 °C [25–28], with a theoretical capture value of 0.401 g of CO₂ per gram of ceramic. 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 [29].

In order to enhance the performance of different sorbents during CO₂ 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 CO₂ chemisorption) and alkaline carbonates

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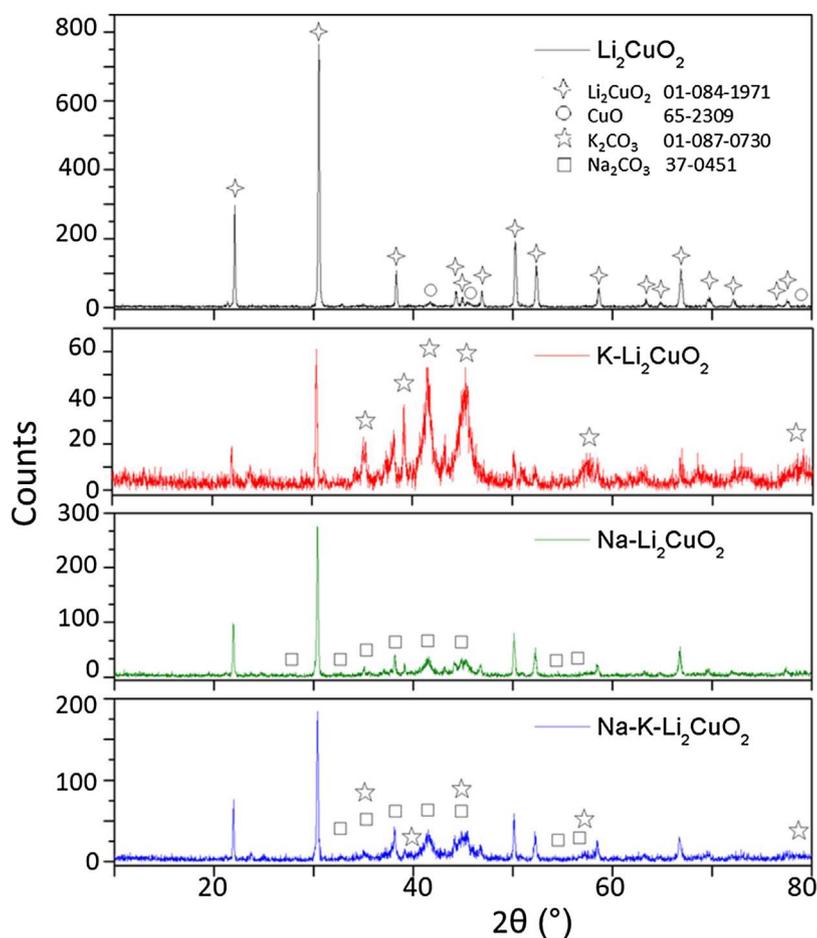


Fig. 1. XRD patterns of Li_2CuO_2 materials prepared with or without (K-, Na- and K-Na-) carbonates.

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 ($\text{Li}_8\text{Si}_6\text{O}_6$) [35] and lithium aluminate (Li_5AlO_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_4SiO_4) sorbent was doped with K_2CO_3 [37,38] or Na_2CO_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_2CuO_2 ceramic in order to improve CO_2 chemisorption rates due to the formation of Li_2CO_3 - K_2CO_3 , Li_2CO_3 - Na_2CO_3 or Li_2CO_3 - Na_2CO_3 - K_2CO_3 eutectic phases, resulting in a partial molten shell that allow to promote CO_2 diffusion.

2. Experimental section

Lithium cuprate (Li_2CuO_2) was synthesized by well-known solid-state reaction [22,23]. Lithium oxide (Li_2O , 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_2CuO_2 phase was confirmed by powder X-ray diffraction (XRD) technique. XRD pattern was recorded in the $10^\circ \leq 2\theta \leq 70^\circ$ range, using a goniometer speed of $1^\circ(2\theta) \text{ min}^{-1}$, with a Siemens D5000 diffractometer coupled to a cobalt

anode ($\lambda = 1.789 \text{ \AA}$) X-ray tube. Once crystalline structure was confirmed, Li_2CuO_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_2CO_3 , Sigma-Aldrich), ii) 10 wt% of sodium carbonate (Na_2CO_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_2CuO_2 , Na- Li_2CuO_2 , Na-K- Li_2CuO_2 and Li_2CuO_2 , respectively. Samples modified with carbonates were studied by XRD in order to confirm the presence of Li_2CuO_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

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