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

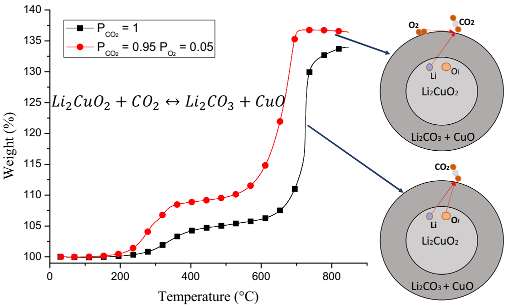
Hugo A. Lara-García, Heriberto Pfeiffer *

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

HIGHLIGHTS

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

GRAPHICAL ABSTRACT



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ABSTRACT

CO_2 chemisorption in Li_2CuO_2 was studied under different CO_2 and O_2 partial pressures, through thermogravimetric analysis. Results showed that using low P_{CO2} (0.05–0.2) did not impact in the final CO_2 chemisorption, in comparison to the $P_{CO2} = 1$. When oxygen was added to the flow (P_{O2} between 0.03 and 0.2) the CO_2 chemisorption presented different modifications: The CO_2 chemisorption is produced at lower temperatures; the CO_2 carbonation kinetics is improved and the material is able to perform CO_2 carbonation-decarbonation cycles. CO_2 chemisorption kinetic parameters were determined assuming a first order reaction between 450 and 750 °C, where k and $\Delta H^{\ddagger}$ values confirmed that CO_2 carbonation on Li_2CuO_2 is importantly enhanced with oxygen addition. If oxygen is not present in the flow gas, it has to be released from the Li_2CuO_2 crystalline structure to complete the carbonation process, while if oxygen is supplied in the flow gas the carbonation process is strongly facilitated, as the carbonation does not depend on the oxygen crystalline diffusion. Additionally, results evidenced that Li_2CuO_2 recrystallization, during the cyclic process, is performed by a different reaction mechanism. During the decarbonation process, partial lithium reincorporation, to the cuprate phase, produces $Li_3Cu_2O_4$. The formation of this secondary phase ($Li_3Cu_2O_4$) implies a partial copper oxidation, which must be induced by the P_{O2}. When a total decarbonation is produced, Li_2CuO_2 is totally recovered.

1. Introduction

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

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

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pressure [1–4]. Pre-combustion systems basically separate the CO_2 from the flue [5,6]. Post-combustion capture involves separating the CO_2 from other exhaust gases after combustion of the fossil fuel. Typical post-combustion flow gases contain approximately N_2 (65–75%), CO_2 (7–15%), O_2 (2–12%), H_2O (5–15%) and smaller concentrations of other polluting species [7]. Oxyfuel combustion technology involves the combustion of coal with the use of pure oxygen. Therefore, the major composition of the flue gases is CO_2, water, particulates and SO_2. The concentration of carbon dioxide is major in the oxyfuel process that the others [3,5,8].

Among these processes, several materials have been studied as CO_2 captors and some of them are used now in the industry. Nevertheless, all these materials may present several disadvantages such as saturation, corrosion, etc [1,4,9]. Numerous factors describe the quality or utility of CO_2 captors; fast sorption and desorption kinetics, large sorption capacities, infinite regenerability and stability, and a wide range of operating temperatures [9]. One of the most studied materials, for high temperature CO_2 capture, are the alkaline ceramics. It has been proved that this kind of materials exhibits some of the CO_2 capture properties described above [10–16]. However, most of the reports presented for these ceramics were performed under a saturated CO_2 atmosphere, which is far from the real industrial CO_2 concentrations. However, there are some reports using alkaline ceramics as CO_2 captors under non-saturated CO_2 atmospheres (P_{CO2}), for example; sodium and lithium zirconates (Na_2ZrO_3 and Li_2ZrO_3) [10,17–20], lithium silicates (Li_2SiO_3, Li_4SiO_4 and Li_8SiO_6) [11,21,22] and lithium cuprate (Li_2CuO_2) [23]. Most of these reports mentioned that CO_2 chemisorption tends to importantly decrease when CO_2 partial pressure decreases. Nevertheless, the CO_2 chemisorption ability of Li_2CuO_2 does not seem to present any important variation on the CO_2 capture process, even using $P_{CO2} = 0.05$ [23]. However this result was only analyzed dynamically. Thus, it is necessary to perform a deepest study. Additionally, lithium cuprate (Li_2CuO_2) has been reported as a material able to trap chemically CO_2 with saturated atmospheres according to the reaction (1), in a wide range of temperatures (40–750 °C) under different physicochemical conditions [23–29].

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

Among the alkaline ceramics studied as possible CO_2 captors it has been proposed different models to explain their reaction mechanism. Most of these reports assumed that the chemisorption process is composed of two main steps; i) the CO_2 superficial chemisorption and ii) the CO_2 bulk chemisorption controlled by ion-diffusion, meaning that once CO_2 reacts with the ceramic on the solid surface forming an external shell of Li_2CO_3 and CuO (for the Li_2CuO_2 case). Thus, Li^{1+} and O^{2-} ions have to diffuse through the product layer in order to continue the carbonation process [30]. Most of these studies mention that ion diffusion seems limit the whole reaction process. However, there is only one reported including oxygen into the flow gas. The Li_2ZrO_3-CO_2-O_2 system described that the activation enthalpy ($\Delta H^{\neq}$) of the CO_2 bulk chemisorption process is reduced when oxygen is added into the gas flow [31], indicating that oxygen addition somehow helps to the CO_2 chemisorption in that case. Therefore, the aim of this work was to study, dynamic and isothermally, the CO_2 chemisorption and cyclability in the Li_2CuO_2 under different partial pressure of carbon dioxide, in the absence or presence of oxygen. The present analysis should help to elucidate the use of this material into a more realistic combustion flow gas.

2. Experimental section

Lithium cuprate (Li_2CuO_2) was synthesized *via* solid-state method. Lithium oxide (Li_2O, Aldrich) and copper oxide (CuO, Acros Organics) were mixed mechanically. The mixture was prepared using a lithium excess of 10 wt%, based on the stoichiometric lithium content on Li_2CuO_2. Then, the powders were calcined at 800 °C for 6 h in air. The Lithium cuprate structural and microstructural properties were analyzed as it was described in a previous paper (data not shown) [27].

To evaluate CO_2 chemisorption under different partial pressure of CO_2 and the effect of the oxygen addition in the flow a thermobalance (TA Instruments, model Q500SA) was used, where various dynamic and isothermal experiments were carried out. The experiments were performed using different gas mixtures of CO_2 (Praxair, grade 3), O_2 (Praxair, grade 2.6) and N_2 (Praxair, grade 4.8) as balance and carrier gas with a total flow rate of 60 mL/min. Mixtures were performed into a digital gas mixer (CHEM flow, Microtrac-Bel). Initially, the samples were dynamically heated from 30 to 850 °C at a heating rate of 5 °C/min using different CO_2:N_2 and CO_2:O_2:N_2 gas mixtures, where the P_{CO2} varied between 0.05 and 1, while P_{O2} was varied between 0.03 and 0.2. For the isothermal analysis samples were heated to the desired temperature (between 450 and 750 °C) under a N_2 flow. Then, when each sample reached the corresponding temperature, the gas flow was switched from N_2 to the corresponding gas mixture.

The Li_2CuO_2 cyclability experiments were performed at 700 °C using the following partial pressures; P_{CO2}:P_{O2}:P_{N2} = 0.2:0.05:0.75 for the chemisorption and P_{O2}:P_{N2} = 0.05:0.95 for the desorption processes. As desorption process resulted to be slower than sorption one, the cyclability experiments were evaluated for 1 and 2 h for sorption and desorption processes, respectively. Finally, some cyclic products were analyzed by X-ray diffraction (XRD) using an equipment D8 Advance from Bruker.

3. Results and discussion

Dynamic TG curves of the Li_2CuO_2-CO_2 system, using different P_{CO2} are shown in the Fig. 1. Initially, for the CO_2 saturated atmosphere case ($P_{CO2} = 1.0$), the thermogram presented the typical behavior according to previous Li_2CuO_2 reports and other lithium ceramics [23–29]. First, between 250 and 500 °C the sample weight increased by 6 wt%. Here, a superficial reaction occurs, where an external lithium carbonate and CuO shell is formed over the surface of the Li_2CuO_2 ceramic particles. Then, the thermogram presented a slight weight increase up to 640 °C where a second CO_2

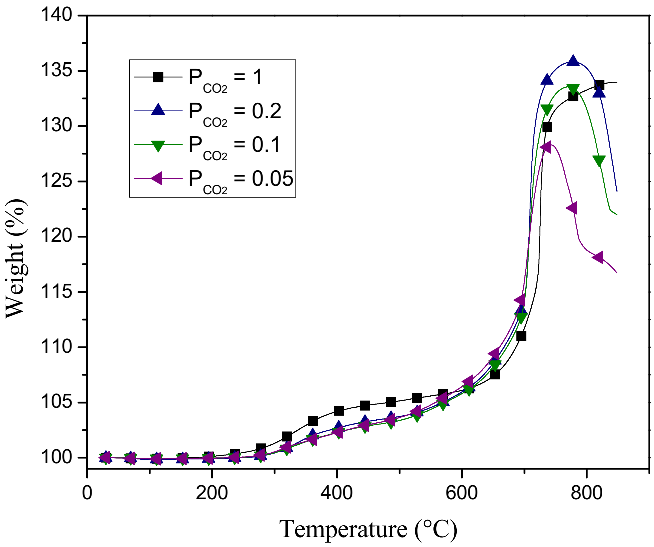

Fig. 1. Dynamic thermogravimetric analysis of the Li_2CuO_2 sample using different P_{CO2} (0.05, 0.1, 0.2 and 1.0).