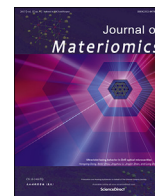




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Structural evolution and reaction mechanism of lithium nickelate (LiNiO₂) during the carbonation reaction

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ABSTRACT

Lithium nickelate (LiNiO₂) was synthesized using the lithium excess method, and then characterized by X-ray diffraction, scanning electron microscopy and N₂ adsorption-desorption. Finally, differential thermal and thermogravimetric analyses were performed in CO₂ presence, at high temperatures. Results show that LiNiO₂ is able to react with CO₂ through a complex structural evolution process, where lithium atoms are released to produce Li₂CO₃, while some nickel atoms are rearranged on different Li_{1-x}Ni_{1+x}O₂ crystalline phases. LiNiO₂-CO₂ reaction kinetic parameters were determined assuming a first-order reaction, where kinetic constants tended to increase as a function of temperature. However, kinetic constant values did not follow a linear trend. This atypical behavior was attributed to LiNiO₂ sintering and crystalline evolution performed as a function of temperature.

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1. Introduction

High temperature carbon dioxide (CO₂) sorbents have recently drawn significant interest, as direct CO₂ capture (in this temperature range, T > 400 °C) can improve energy efficiency by overcoming the gas cooling process to ambient temperature [1]. In this context, lithium-based ceramics such as Li₂ZrO₃ [2–5], Li₆Zr₂O₇ [6], Li₈SiO₆ [7,8], Li₅AlO₄ [9,10], Li₄SiO₄ [11–17] and Li₂CuO₂ [18–21] have been extensively studied as possible high temperature CO₂ captors, among other applications [22–26]. Moreover, some researchers have tried to improve their CO₂ capture properties developing different synthesis methods, modifying structural or microstructural characteristics and identifying the most appropriate operation conditions [7,13,25–32].

Other important applications of the high-temperature CO₂ sorbents are the sorption enhanced steam reforming (SESR) and the oxidation-capture of carbon monoxide in H₂-rich gas flows (eliminating CO from the reformed fuels) [1,33–38]. In the first case, very few theoretical and experimental studies have documented the application of alkaline ceramics such as Li₂ZrO₃, Li₄SiO₄, and

Na₂ZrO₃ in the SESR of methane and ethanol, where in most of these cases the addition of another catalytic material is needed [1,33–38]. Also, some alkaline ceramics have been used cyclically in the carbonation and subsequent methane reforming processes [39] and last but not least, some of these ceramics have shown high CO₂ chemisorption even at low CO₂ partial pressures (P_{CO₂} values between 0.2 and 0.05) [12,14,20], which is a closer CO₂ concentration than those present in real combustion gases.

On the contrary, CO oxidation process has been widely studied using different catalysts, such as noble or transition metals (Fe, Ni, Cu, Co) [40]. However, in the last year, some alkaline ceramics, as Na₂ZrO₃, NaCoO₂ and Li₂CuO₂, have been tested as bifunctional materials (CO oxidant catalyst and CO₂ captors), showing interesting CO conversions in wide temperature ranges [21,41,42].

Contrariwise, lithium nickelate (LiNiO₂) is widely used as attractive cathode material for rechargeable lithium batteries [43–45]. LiNiO₂ has a rhombohedral structure with trigonal symmetry (space group: *R-3m*), with two interpenetrating close-packed FCC sub-lattices: One sub-lattice containing oxygen ions, while the other contains Li and Ni cations, both alternating (111) planes [43]. LiNiO₂ synthesis has been developed using different techniques, such as hydrothermal decomposition, melt-impregnation, Pechini method, solid-state and sol-gel, among others [43,45].

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LiNiO₂ has interesting structural and diffusion characteristics. Thus, CO₂ chemisorption would be produced on LiNiO₂, as this crystalline structure might facilitate lithium diffusion and release processes towards CO₂ reactivity. Therefore, in the present work, the excess lithium method was used to synthesize lithium nickelate and its CO₂ capture properties were investigated by thermogravimetric analysis at different temperatures.

2. Experimental section

Lithium nickelate (LiNiO₂) was synthesized by lithium excess method. Initially, lithium hydroxide (LiOH•H₂O, Caledon) and nickel nitrate (Ni(NO₃)₂•6H₂O, Meyer) were dissolved in water, using a Li/Ni molar ratio equal to 4. This solution was mechanically mixed and heated to 80 °C till water was totally evaporated (~20 h). Resulting powder was calcined at 700 °C for 5 h in air [44].

Lithium nickelate was analyzed structural and microstructurally by X-ray diffraction (XRD), N₂ adsorption-desorption, scanning electron microscopy (SEM), thermogravimetric (TGA) and differential thermal (TDA) analyses. XRD patterns were obtained with a BRUKER AXS D8-Advance diffractometer coupled to a Cu anode X-ray tube. The K_α wavelength was selected with a diffracted beam monochromator, and compounds were identified conventionally using the PDF database. N₂ adsorption-desorption isotherm of the LiNiO₂ sample was obtained on a Bel-Japan Minisorp II instrument at 77 K, using a multipoint technique (N₂ from Praxair, grade 4.8). Prior to analysis, the sample was degassed at room temperature for 24 h. The surface area was determined using the Brunauer-Emmett-Teller (BET) method. Then, LiNiO₂ morphological characteristics were determined by SEM, using a JEOL JMS-7600F equipment. Finally, simultaneous thermogravimetric and differential thermal analyses were performed in SDT-Q600 TA Instruments equipment, from TA Instruments. LiNiO₂ was heat-treated, using a heating rate of 5 °C min⁻¹ and a gas flow of 60 ml min⁻¹, from room temperature to 850 °C. These analyses were carried out on two different atmospheres: N₂ (Praxair, grade 4.8) and CO₂ (Praxair, grade 3.0).

The CO₂ chemisorption processes were evaluated in a thermobalance (TA Instruments, model Q500HR), using dynamic and isothermal conditions. Initially, LiNiO₂ was dynamically heated from 30 to 850 °C using a heating rate of 5 °C min⁻¹. LiNiO₂ isothermal experiments were performed by heating the sample to desired temperature (between 400 and 800 °C), under a N₂ flux. Then, the gas flow was switched from N₂ to CO₂. All these experiments were performed using a CO₂ flow of 60 ml min⁻¹ (CO₂-Praxair, grade 3.0). Finally, isothermal products were re-characterized by XRD in order to identify CO₂ chemisorption mechanism on LiNiO₂.

3. Results and discussion

The XRD pattern, of LiNiO₂ synthesized using the lithium excess method, is shown in Fig. 1. As it can be seen, XRD pattern fitted to the 00-089-3601 PDF file, which corresponds to LiNiO₂. In addition, small amounts of Li₂CO₃ were detected (00-022-1141 PDF file). The formation of this secondary phase is in good agreement with synthesis method; lithium excess.

After the structural characterization, some microstructural characteristics of LiNiO₂ were analyzed by SEM and N₂ adsorption-desorption. Fig. 2 shows a backscattered electron image of LiNiO₂ particles. The morphology corresponded to agglomerates composed by irregular polyhedral particles of around 400–600 nm. This image shows the presence of two different compounds, by contrast, which must correspond to LiNiO₂ (bright and main phase) and very small amounts of Li₂CO₃ (dark phase), according to their differences in the mean atomic numbers (\bar{Z}) and backscattered

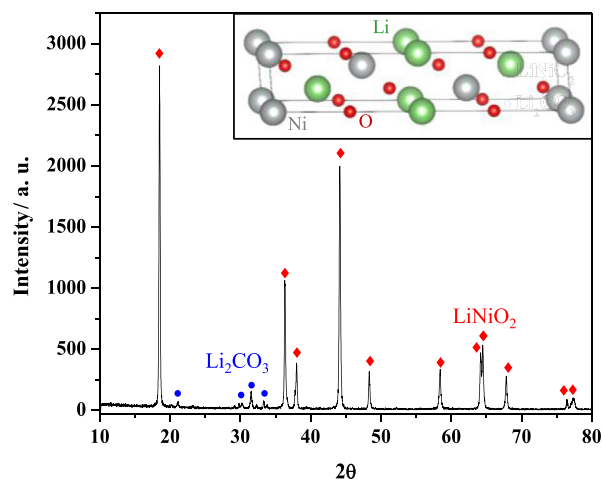


Fig. 1. XRD pattern and crystal structure of LiNiO₂ synthesized using the lithium excess method.

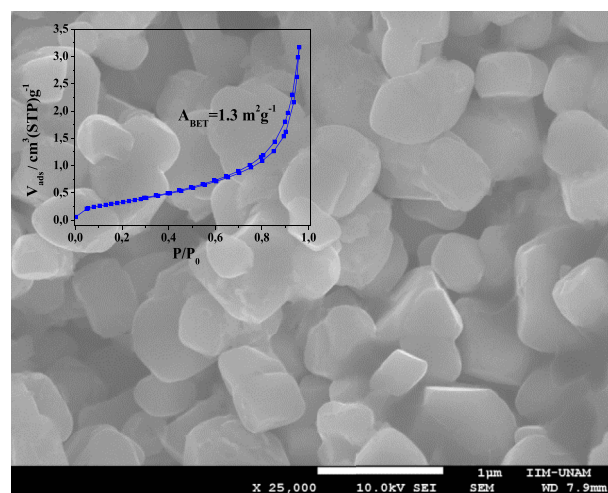


Fig. 2. Backscattered electron image of LiNiO₂ particles and N₂ adsorption-desorption isotherm (square inset).

electron coefficients (η); LiNiO₂ ($\bar{Z} = 11.75$ and $\eta = 0.138$) and Li₂CO₃ ($\bar{Z} = 6$ and $\eta = 0.064$). Additionally, N₂ adsorption-desorption analysis (square inset of Fig. 2) fits to type II isotherm without hysteresis, according to IUPAC classification, which corresponds to non-porous materials [46]. The LiNiO₂ surface area, calculated using BET model [46], was equal to 1.3 m² g⁻¹. All these microstructural features are in good agreement with the final heating process performed during LiNiO₂ synthesis, which must induce a ceramic sintering process, producing polyhedral particles with low surface area.

Different nickel compounds have been used as catalysts. Then, combination of this transition metal and lithium may propitiate some interesting physicochemical properties, such as its possible application on sorption enhance processes or bifunctional components, as it was described in the introduction section. Here, as an initial case of study, the CO₂ capture process was analyzed. It has to be pointed out that lithium availability on LiNiO₂ (Li/Ni_{molar ratio} = 1) is not as high as in other alkaline ceramics, where Li/M (M = Si, Zr, Al or Cu, among others) molar ratio is equal or higher than two [7–11,16,21,32,47–50]. In this case, lithium nickelate may react with carbon dioxide according to the following reaction:

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