



Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem
<http://www.journals.elsevier.com/journal-of-energy-chemistry/>

Thermokinetic and conductivity analyzes of the high CO₂ chemisorption on Li₅AlO₄ and alkaline carbonate impregnated Li₅AlO₄ samples: Effects produced by the use of CO₂ partial pressures and oxygen addition

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ARTICLE INFO

Article history:

Received 22 March 2017

Revised 11 May 2017

Accepted 22 May 2017

Available online xxx

Keywords:

CO₂ capture

Thermogravimetric analysis

Partial pressure

Ionic conduction

ABSTRACT

The effect of CO₂ partial pressure was evaluated during the CO₂ chemisorption in penta lithium aluminate (Li₅AlO₄), using different CO₂ and O₂ partial pressures in the presence or absence of alkaline carbonates. Results showed that using low P_{O₂} (0.1) did not affect the kinetic and final CO₂ chemisorption process. Moreover, small additions of oxygen (P_{O₂} = 0.05) into the mixture flue gas, seemed to increase the CO₂ chemisorption. Additionally, the presence of alkaline carbonates modified the CO₂ capture temperature range. CO₂ chemisorption kinetic parameters were determined assuming a double exponential model where direct CO₂ chemisorption and CO₂ chemisorption controlled by diffusion processes are considered. Finally, ionic diffusion was analyzed by ionic conduction analysis, where all the gravimetric and ionic measurements were in good agreement showing different diffusion processes depending on temperature. Finally, the oxygen and alkaline carbonate additions have positive effects during the CO₂ chemisorption process in Li₅AlO₄, and a possible reaction mechanism is presented.

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1. Introduction

Carbon dioxide (CO₂) is considered to be the main contributor of the global warming, and due to this problem it is necessary to reduce the amounts of these emissions. Moreover, it is important to separate it from exhaust gases, developing effective CO₂ separation techniques and CO₂ sorbents [1]. Therefore, CO₂ capture and storage (CCS) technologies have attracted interest to reduce the increasing amount of CO₂ released into the atmosphere. CCS involves capturing the CO₂ emitted by power plants and other industrial operations and permanently storing it deep underground [2].

On the other hand, the removal of CO₂ has also been used to improve the hydrogen production in a steam methane reforming (SMR) system, called sorption enhanced steam methane reforming (SE-SMR), which is operated at temperatures between 500 and 700 °C. In this process, a CO₂ captor is installed together with the catalyst in the reactor bed for removal of CO₂ from the gas phase, showing several advantages compared to conventional steam methane reforming, among them, high-purity H₂ production

(>95%). High-temperature sorption, using solid sorbents, is a good choice in the application fields mentioned above, compared with current low-temperature methods, such as amine-based absorption, because these processes work at high operation temperatures, where the flue gas does not need to be cooled prior to chemisorbing CO₂ [3–7].

Among the various high-temperature solid sorbents that have been studied, different lithium-containing ceramics have been proposed as possible CO₂ captors. Li₄SiO₄ [8–12], Li₂CuO₂ [1,13,14], Li₂ZrO₃ [15–18], Li₅AlO₄ [19,20] and Li₈SiO₆ [12,21–23], among others, are all examples of ceramic sorbents with interesting capture properties from the point of view of high CO₂ capture capacities, high carbonation reaction rates at elevated temperatures and in some cases, good stabilities and cyclic properties.

Among all these lithium-based materials, lithium aluminate (Li₅AlO₄) has attracted increasing attention in different research fields for its high lithium density [19,20,24]. Li₅AlO₄ ceramic presents two different crystal polymorphs α-Li₅AlO₄ and β-Li₅AlO₄, where both polymorphs have orthorhombic crystal structures. As CO₂ captor, both phases have been tested by Pfeiffer and coworkers [19,20], demonstrating that β-Li₅AlO₄ crystal phase presents better chemisorption properties, being able to trap CO₂

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chemically in the temperature range from 200 to 700 °C (reaction 1) and have good cyclability characteristics.



The sorption process consists of a rapid superficial CO_2 chemisorption stage and a much slower ion-diffusion-controlled stage, meaning that once CO_2 reacts with Li_5AlO_4 on the solid surface to completely form an external shell composed of Li_2CO_3 and LiAlO_2 , the Li^+ and O^{2-} ions should diffuse through the product layer to the surface to continue reacting with CO_2 [8,25]. The secondary phase, LiAlO_2 , does not react with CO_2 due to thermodynamic factors. However, when LiAlO_2 is contained in the external shell, it promotes the lithium ionic diffusion into the Li_2CO_3 - LiAlO_2 external shell at temperatures higher than 600 °C. Moreover, the lithium carbonate formation implies that one of each four oxygen atoms, present originally in the Li_5AlO_4 ceramic, must become part of the Li_2CO_3 . Consequently, these oxygen atoms must diffuse as well. So, the presence of this gas in the whole reactive atmosphere would modify the reaction kinetics [26].

The reaction stage of CO_2 chemisorption in Li_5AlO_4 is a gas-surface reaction, and the sorption kinetics determined in other lithium-based materials as Li_4SiO_4 [5], Na_2ZrO_3 [27,28] or Li_2ZrO_3 [3,29] are relatively poor at low CO_2 partial pressure ($P_{\text{CO}_2} < 0.5$), owing to less molecular collision and taking more time to attain satisfactory sorption conversions. Iwan et al. [3] concluded that there is a linear relationship between the apparent reaction rate and the carbon dioxide partial pressure. Because the CO_2 concentration of flue gases in power plants or SE-SMR is only 4–20 vol%, and gas cannot remain in reactors for a long time because of the high flowrate; there is an urgent need to obtain sorbents with fast and stable cyclic kinetics of sorption/desorption at low CO_2 partial pressure.

A part from that, the CO_2 capture of some lithium ceramics has been modified by the addition of different alkaline carbonates, which favours the formation of eutectic phases on the carbonate external shell [10]. In fact, Li_5AlO_4 has shown variations on its CO_2 capture temperature range, depending on the alkaline carbonate [10,30]. Moreover, it has been reported in literature the use of alkaline carbonate molten phases for different applications, and it has been reported that the specific Li_2CO_3 : Na_2CO_3 : $\text{K}_2\text{CO}_3 = 42.5:32.5:25$ mol% mixture presents one of the lowest melting points (~ 400 °C) [31].

Therefore, the aim of the present work was to analyze the CO_2 chemisorption process on Li_5AlO_4 varying different physicochemical conditions such as the CO_2 and O_2 partial pressures as well as the alkaline carbonate addition to pristine Li_5AlO_4 . The present work was performed using different techniques for the kinetic analysis and for the sample and diffusion characterization.

2. Experimental

Li_5AlO_4 was synthesized by solid state reaction using lithium oxide (Li_2O , Aldrich) and aluminum oxide (Al_2O_3 , Aldrich). Initially, powders were mechanically mixed and pressed into pellets (10 MPa). Subsequently, the pellets were heated to 900 °C for 12 h and rapidly cooled to room temperature. Lithium was used in excess (10 wt%), due to its tendency to sublimate. In addition, part of the sample was mixed with an eutectic molten carbonate mixture composed of Li_2CO_3 , Na_2CO_3 and K_2CO_3 with a mole percent ratio of 42.5/32.5/25 mol%, which presents a melting point at around 400 °C [31].

X-ray diffraction (XRD) patterns were obtained from a diffractometer (Bruker AXS, D8 Advance) coupled to a copper anode X-ray tube. Li_5AlO_4 and other crystalline phases were identified by their corresponding Joint Committee Powder Diffraction Standards

(JCPDS) files. Nitrogen adsorption–desorption isotherms and BET surface area analyzes were performed using a Minisorp II instrument, from the Bel-Japan. These experiments were performed at 77 K, using a multipoint technique, where samples were previously degassed at room temperature for 24 h in vacuum. The BET model was used to determine the corresponding surface areas.

Different thermal analyzes were performed using a Q500HR instrument from TA Instruments. Initially, a set of samples was dynamically heated from room temperature to 850 at 3 °C/min, using a mixture flow containing different CO_2 concentrations (Praxair, grade 3.0) in N_2 balance atmosphere (Praxair, grade 4.8). Subsequently, other dynamic experiments were performed adding O_2 (Praxair, grade 3.0) to the CO_2/N_2 mixture flow. The partial pressures of CO_2 and O_2 were determined by its fraction of the total feed flow rate and the total pressure. The total feed flow was always set at 60 mL/min. Afterwards, the samples were tested isothermally at different temperatures (between 650 and 750 °C) in presence of the same mixture flows. For the isothermal experiments, each sample was heated to the corresponding temperature into a N_2 flux. Then, once the temperature was reached, the gas was switched from N_2 to the different mixture flows.

Electrical measurements on Li_5AlO_2 and LiAlO_2 samples were performed by impedance spectroscopy with a Precision Impedance Analyzer 6500B Wayne Kerr Electronics, in order to determine the lithium ion diffusion properties. Colloidal platinum (Tanaka Kikin-zoku Kogyo K.K.) was used on samples as electrodes. Those electrodes were annealed at 600 °C for 2 h before the electrical measurements. Impedance spectra were collected in the 40 Hz–10 MHz range at 500 mV. The electrical measurements were accomplished by cooling in the temperature range 800–200 °C in a quartz cell coupled with a vacuum pump, the pressure inner cell was 30 Pa. The temperature inside the cell was monitored with a K-type thermocouple. For each single data point, the equilibrium time was 2 h. Each impedance spectrum was fitted to a single RC circuit using the software Zview®.

3. Results and discussion

Fig. 1(a) shows the powder X-ray diffraction (XRD) measurements of Li_5AlO_4 , which confirmed the purity of the sample. The diffraction pattern fitted to the JCPDS file 70-0432, which corresponds to Li_5AlO_4 with an orthorhombic crystalline structure. In addition to the Li_5AlO_4 structural characterization, some microstructural properties were evaluated by N_2 adsorption-desorption (Fig. 1(b)). According to the IUPAC classification, the Li_5AlO_4 sample showed an adsorption isotherm type II, corresponding to non-porous material [32]. Additionally, this sample presented a very narrow H3 hysteresis loop, which may have produced a few mesoporous due to a partial particle sintering. The BET surface area was found to be equal to 0.8 m²/g.

After the sample characterization, different dynamic TG experiments were performed, varying the CO_2 partial pressure (Fig. 2). The P_{CO_2} was varied from 1 to 0.1, and as it can be seen, all the thermograms presented the same thermal trend and very similar weight increments. Between room temperature and 100 °C all the samples lost around 1 wt%, which can be attributed to water desorption. Then, two different weight increments were evidenced between 300–500 °C and 550–720 °C. As in previous Li_5AlO_4 - CO_2 reports [19], these weight increments are attributed to the superficial and bulk CO_2 chemisorptions on Li_5AlO_4 and other alkaline ceramics. Only small weight differences are observed in these thermograms during the superficial CO_2 chemisorption (see square inset of Fig. 2), where the thermogram corresponding to a $P_{\text{CO}_2} = 1$ gained around 2–3 wt% more CO_2 than $P_{\text{CO}_2} = 0.1$. The other visual difference is observed at temperatures higher than 700 °C, as the final weight increment was slightly better when the P_{CO_2} was

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