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Thermochemical Capture of Carbon Dioxide on Lithium Aluminates ($LiAlO_2$ and Li_5AlO_4): A New Option for the CO_2 Absorption

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Lithium aluminates ($LiAlO_2$ and Li_5AlO_4) were synthesized, characterized, and tested as possible CO_2 captors. $LiAlO_2$ did not seem to have good qualities for the CO_2 absorption. On the contrary, Li_5AlO_4 showed excellent behavior as a possible CO_2 captor. Li_5AlO_4 was thermally analyzed under a CO_2 flux dynamically and isothermically at different temperatures. These results clearly showed that Li_5AlO_4 is able to absorb CO_2 in a wide temperature range (200−700 °C). Nevertheless, an important sintering effect was observed during the thermal treatment of the samples, which produced an atypical behavior during the CO_2 absorption at low temperatures. However, at high temperatures, once the lithium diffusion is activated, the sintering effect did not interfere with the CO_2 absorption. Eyring's model was used to determine the activation enthalpies of the CO_2 absorption (15.6 kJ/mol) and lithium diffusion (52.1 kJ/mol); the last one is the limiting process.

1. Introduction

In the last 10 years different lithium and sodium ceramics have been tested as possible carbon dioxide (CO_2) captors. These ceramics present a chemisorption reaction with CO_2, producing the respective alkaline carbonate and a residual metal oxide. For example, lithium metazirconate (Li_2ZrO_3) produces Li_2CO_3 and ZrO_2 because of the CO_2 absorption.[1−3] Into this field, the lithium ceramics most studied until to now are: lithium zirconates (Li_2ZrO_3 and $Li_6Zr_2O_7$), lithium silicates (Li_4SiO_4 and Li_2SiO_3), and, more recently, lithium cuprate (Li_2CuO_2), lithium titanate (Li_4TiO_4), and lithium ferrite ($LiFeO_2$).[1−13]

Among these materials, two of the most promising lithium ceramics are Li_4SiO_4 and Li_4TiO_4. These ceramics present good kinetic behaviors, and their theoretical CO_2 absorption capacities are the best, 0.73 (Li_4SiO_4) and 0.63 (Li_4TiO_4) g_{CO_2}/g_{ceram}.[7,10] As can be deduced from previous data, CO_2 absorption capacity depends on the molecular weight of each ceramic. Consequently, the lighter the ceramic is, the higher the CO_2 absorption capacity would be. On the basis of this idea, lithium aluminates would present advantages over other lithium ceramics, even silicates, which were the lighter ceramics tested until now.

Lithium aluminates ($LiAlO_2$ and Li_5AlO_4) have been used for different applications. $LiAlO_2$ has been proposed as a breeder ceramic into the fusion reactors, a solid electrolyte for lithium batteries, and ceramic carrier material in the fabrication process of electrolyte tiles for molten carbonate fuel cells, among other applications.[14−18] However, there is almost no information about Li_5AlO_4. There are only a few papers in which Li_5AlO_4 has been synthesized and tested for some electrical applications.[19−21] Li_5AlO_4 ceramic presents two different crystal polymorphs α-Li_5AlO_4 and β-Li_5AlO_4, where both polymorphs have orthorhombic crystal structures.[22,23]

If lithium aluminates were able to absorb CO_2, then following reactions may occur

$$2LiAlO_2 + CO_2 \rightarrow Li_2CO_3 + Al_2O_3 \qquad (1)$$

$$2Li_5AlO_4 + 5CO_2 \rightarrow 5Li_2CO_3 + Al_2O_3 \qquad (2)$$

The reactions proposed above are presented assuming that CO_2 is absorbed through the same mechanism observed for other lithium ceramics[24−26] in which lithium aluminates react to produce lithium carbonate in addition to a residual oxide, Al_2O_3. The theoretical CO_2 absorption capacities for $LiAlO_2$ and Li_5AlO_4 are 0.33 and 0.87 $g_{CO_2}/g_{ceramic}$, respectively. Li_5AlO_4 has a very high theoretical CO_2 absorption capacity in comparison with that of the other lithium ceramics (Figure 1). In fact, only lithium oxide (Li_2O) possesses a higher theoretical capacity (1.46 g_{CO_2}/g_{Li_2O}) with the disadvantages of its high reactivity and corrosive characteristics.

Therefore, the aim of this work was to study and demonstrate whether $LiAlO_2$ and Li_5AlO_4 are able to capture CO_2 by a mechanism similar to that reported previously for other lithium ceramics. Special attention was given to Li_5AlO_4 because of its high theoretical CO_2 absorption capacity, which is mainly caused by its high Li/Al molar ratio equal to 5, and the fact that aluminum is a lighter atom than any other element tested, such as zirconium, copper, or even silicon.

2. Experimental Section

$LiAlO_2$ and Li_5AlO_4 were synthesized by solid state reaction using, in both cases, lithium oxide (Li_2O, Aldrich) and aluminum oxide (Al_2O_3, Aldrich). Initially, reagents were mixed mechanically and then heat-treated under different conditions. Whereas $LiAlO_2$ powders were thermally treated at 900 °C for 6 h, Li_5AlO_4 powders were heated at 900 °C for 24 h with two intermediate milling processes. To improve the synthesis of both lithium aluminates, 10 wt % of lithium excess was used because of the high tendency of lithium to sublimate.[24]

X-ray diffraction (XRD) patterns were obtained from a diffractometer (Bruker AXS, D8 Advance) coupled to a copper anode X-ray tube. Compounds were identified conventionally

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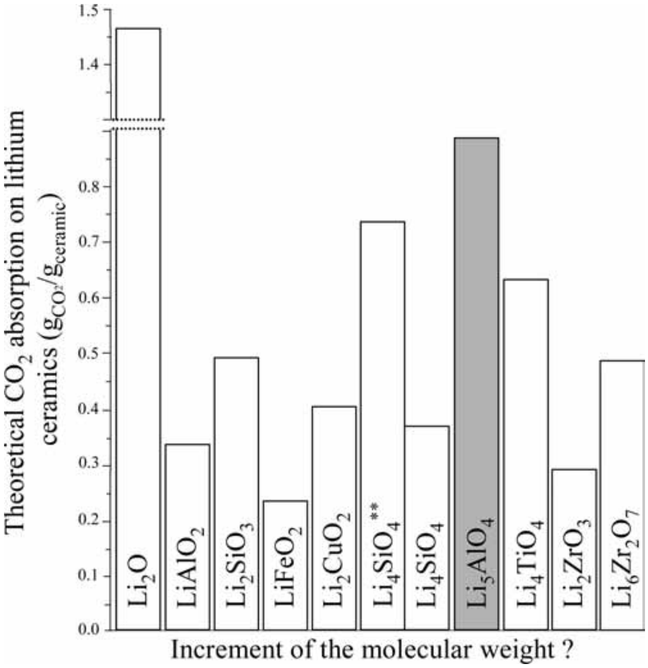

Figure 1. Comparison of the maximum theoretical CO_2 absorption capacities of different lithium ceramics. Li_4SiO_4** and Li_4SiO_4 represent the CO_2 absorption capacities, assuming a total and half lithium conversion to Li_2CO_3, respectively.

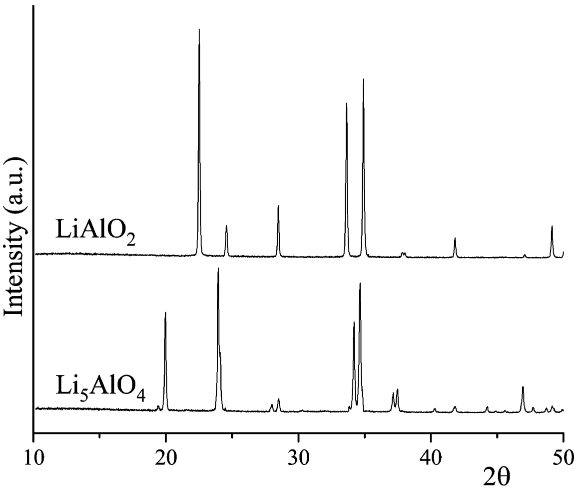

Figure 2. XRD patterns of the $LiAlO_2$ and Li_5AlO_4 powder samples.

by the corresponding Joint Committee Powder Diffraction Standards (JCPDS) files. We determined the particle size and morphology by scanning electron microscopy using a Stereoscan 440, Leica-Cambridge microscope. The samples were covered with gold to avoid the lack of electrical conductivity, and the particle size was determined using standard procedures. Finally, different thermal analyses were performed in a Q500HR equipment from TA Instruments. Initially, a set of samples was heat-dynamically treated with a heating rate of 5 °C/min from room temperature to 850 °C in a CO_2 flux (Praxair, grade 3.0). Then, Li_5AlO_4 sample was tested isothermically at different temperatures in the same CO_2 flux.

3. Results and Discussion

Figure 2 shows the XRD patterns of both lithium aluminates, Li_5AlO_4 and $LiAlO_2$. In both cases, the diffraction patterns fitted to their respective JCPDS files: 70-0432 for Li_5AlO_4 and 18-0714 for $LiAlO_2$. Therefore, both ceramics could be considered to be pure materials, at least at the XRD detection level. Then, particle size and morphology of the samples were obtained by SEM. Figure 3 shows the micrographs of Li_5AlO_4 and $LiAlO_2$. Li_5AlO_4 presented a particle size average of 60 μm, where the particle size was determined by standard procedures (inset of Figure 3A). These particles seemed to be highly sintered dense agglomerates, where their surface did not present any kind of texture (Figure 3A). This morphology can be merely explained by the high and long thermal treatment, in addition to the high lithium mobility, which tends to propitiate high sintering levels. A similar effect could be established for the $LiAlO_2$ sample in which the average particle size was equal to 50 μm. Perhaps the only difference observed on $LiAlO_2$ is that these particles seemed to be slightly less sintered (Figure 3B). Again, it can be explained by the shorter thermal-treatment time and lower lithium quantities present in the sample.

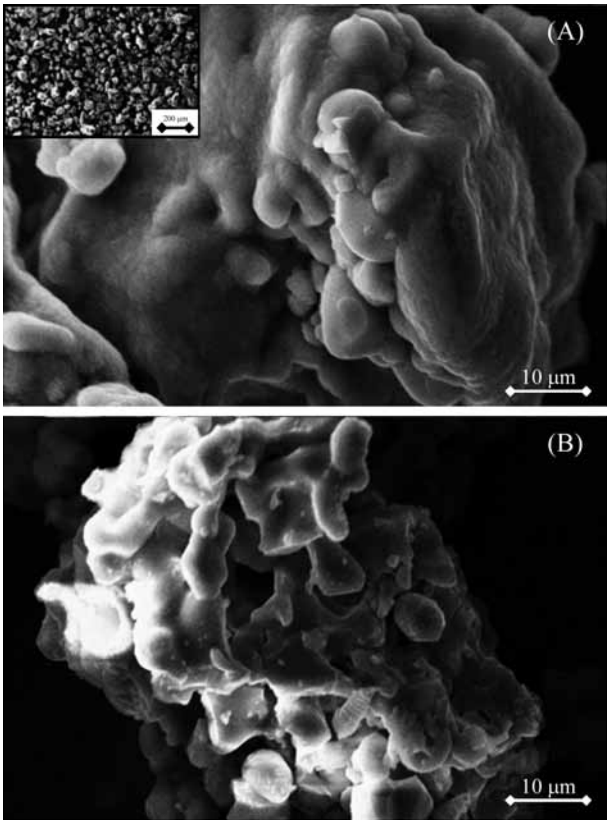

Figure 3. Scanning electron micrographs of the (A) Li_5AlO_4 and (B) $LiAlO_2$ samples. The rectangle inset shows a general view of the sample powders.

Once Li_5AlO_4 and $LiAlO_2$ were characterized, these materials were thermally treated under a CO_2 flux to analyze whether they were able to act as CO_2 captors. Figure 4 presents the dynamic thermograms of $LiAlO_2$ and Li_5AlO_4 into a CO_2 flux. It is more than evident that both ceramics presented very different behaviors. $LiAlO_2$ practically did not absorb CO_2. This ceramic was able to increase its weight percentage by only 0.13 wt % between 540 and 830 °C. This may be explained by its high thermal stability and its high dense structure.

However, Li_5AlO_4 presented a very high CO_2 absorption. It is clear that two different sorption processes took place; the first one between 200 and 380 °C and a second one between 590 and 750 °C. Although this kind of thermal trend has already been observed for other lithium ceramic, for example Li_2CuO_2,[9,27] it is not the most common behavior among the lithium ceramics,

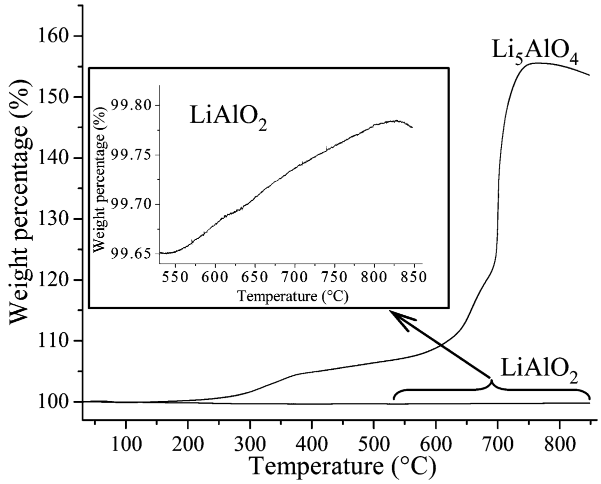

Figure 4. Dynamic thermogravimetric curves of Li_5AlO_4 and $LiAlO_2$ in a CO_2 flux. The rectangular inset shows an enlargement of the $LiAlO_2$ thermogram, 530−880 °C.

where the absorption is produced in just one step.[4,11] In other words, the superficial and bulk absorption processes are not distinguishable on lithium ceramics. Nevertheless, in the Li_2CuO_2 case, the whole absorption process was divided into two thermal steps: Initially, at low temperatures, a superficial reaction is produced. At this moment, an external lithium carbonate and residual oxide shell are formed over the surface of the ceramic particles, inhibiting the CO_2 absorption process. Then, when the temperature is increased and the lithium diffusion is activated, the reaction continues through the bulk of the ceramic, completing the CO_2 chemisorption.[9,27] For Li_5AlO_4, a similar behavior could be described. The superficial reaction takes place between 200 and 380 °C, where the sample increased its weight by 4.5 wt %. Then, an increment of weight, equal to 3.8 wt % (8.3 wt % in total), was observed between 380 and 590 °C. In this temperature range, CO_2 absorption is highly controlled by the diffusion process, considering that the Li_2CO_3 external shell has already been formed during the first process. Finally, between 580 and 750 °C, the lithium diffusion is activated, and the process is completed through the bulk of the particles. In this case, the weight increased by 47.2 wt % (55.5 wt % in total). In addition, it can be observed in Figure 4 that at temperatures higher than 780 °C, the CO_2 desorption process began.

To analyze the CO_2 absorption process on Li_5AlO_4 further, different isothermal experiments were performed (Figure 5). At the lowest temperature (250 °C), the isothermal showed an exponential behavior, which had not reached the plateau after 4 h, and it absorbed 3.35 wt %. Then, samples treated at 300 and 350 °C presented the same exponential behavior, increasing their weights by 3.7 and 4.22 wt %. Then, the sample treated at 400 °C presented an atypical behavior. Although this sample showed a fast CO_2 absorption at short times (in comparison with the previous isotherms), the final absorption was smaller than that observed for the samples heat treated at 300 and 350 °C. The same effect, but more dramatically, was observed for the sample heat treated at 450 °C, where the sample increased its weight by only 0.65 wt %. This atypical behavior has been reported for the CO_2 absorption on other alkaline ceramics such as Na_2ZrO_3 and Li_2CuO_2.[27,28] This behavior has been associated with a sintering process produced during the heating of the samples, which produces an important decrement of the surface area. This phenomenon is usually observed at low temperatures because once the diffusion process is activated, sintering and surface area are not preponderant factors on the CO_2 absorption. Therefore, in the isothermal analyses at 500, 550, 600, and 650 °C, the weight gained increased again, absorbing more CO_2 as a function of the temperature (Figure 5B). This means that although the sintering effect must be produced in those samples, the lithium diffusion was activated. Finally, the behavior presented at 700 °C should be pointed out, where the quantity and rate of the CO_2 absorption were very high and fast, presenting a totally different isothermal shape. In the first 3 min, the sample absorbed 35.7 wt %. Then, the absorption rate, between 3 and 30 min, decreased, getting a CO_2 maximum total absorption of 47.8 wt %. After that time, the isotherm reached the plateau. This means that in the first few minutes, the CO_2 absorption efficiency reached 53.7%, and after 30 min, the maximum efficiency under these thermal conditions, 68.5%, was obtained.

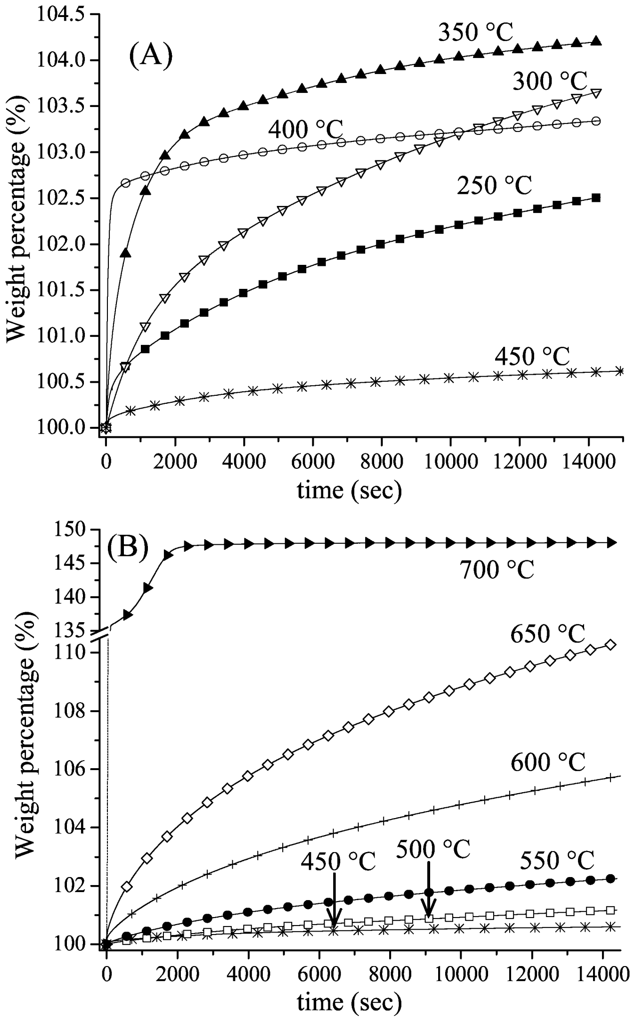

Figure 5. Isotherms of CO_2 absorption on Li_5AlO_4 at different temperatures into a flux of CO_2. (A) Isotherms obtained between 250 and 450 °C. (B) Isotherms obtained between 450 and 700 °C.

These results clearly show that the sintering process affects CO_2 absorption on Li_5AlO_4. Therefore, to corroborate and eliminate the presence of this effect, a second set of isotherms was performed. In this case, all of the Li_5AlO_4 samples were initially heated to 675 °C at 100 °C/min with a subsequent isothermal treatment of 60 min. Then, each sample was cooled to its respective isothermal temperature for the CO_2 absorption. All of these procedures were carried out under an inert atmosphere (N_2). Once the sample reached the corresponding temperature, the flux gas was switched from N_2 to CO_2 and the

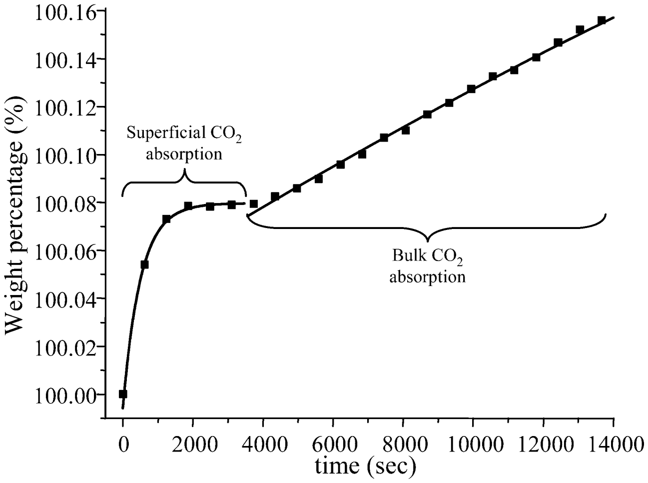

Figure 6. CO_2 absorption isotherm of Li_5AlO_4 at 350 °C after a sintering process at 675 °C.

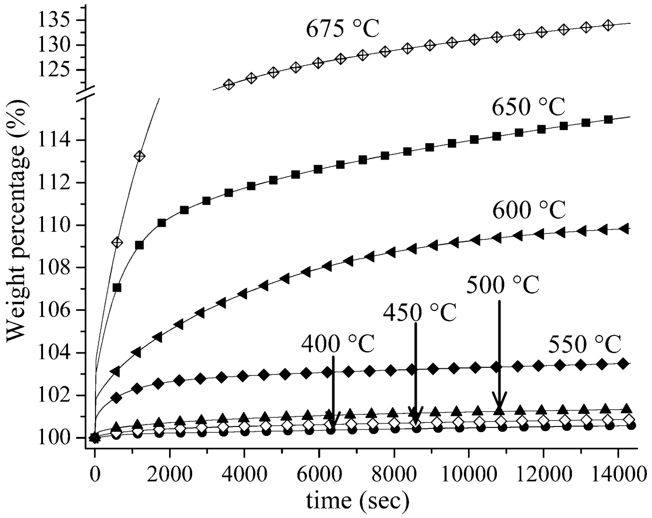

Figure 7. Isotherms of CO_2 absorption on Li_5AlO_4 at different temperatures (400 to 675 °C) in a flux of CO_2 after a sintering process at 675 °C.

TABLE 1: Kinetic Parameters Obtained from Li_5AlO_4 Isotherms Fitted to Exponential Models

temp (°C)	k_1 (1/s)	k_2 (1/s)
300[a]	0.00073	6.7802×10^{-6}
350[a]	0.00097	5.2696×10^{-6}
400[a]	0.00092	1×10^{-5}
450	0.00116	2×10^{-5}
500	0.00175	3×10^{-5}
550	0.00153	8×10^{-5}
600	0.00276	2.7×10^{-4}
650	0.00257	2.7×10^{-4}
675	0.00736	6.8×10^{-4}

[a] Isotherms fragmented and fitted to a simple exponential model. All other isotherms were fitted to a double exponential model.

isothermal experiments were performed. As could be expected, all of the isothermals followed the typical behavior. In other words, the CO_2 absorption on Li_5AlO_4 increased as a function of the temperature.

The isotherms performed at the lowest temperatures (300, 350, and 400 °C) clearly showed the presence of two different processes (Figure 6). Initially, during the first 3000 s, CO_2 is absorbed only over the surface. Then, at larger times, the absorption occurred on the bulk, although the total quantity of CO_2 absorbed over time is very poor. In fact, the only difference among these three samples is that the total CO_2 absorbed slightly increased progressively as a function of the temperature (0.15, 0.16, and 0.57 wt % for 300, 350, and 400 °C, respectively). The behavior and the quantity of CO_2 absorbed are very different than those observed when the samples were not previously sintered. In these cases, as Li_5AlO_4 powders were sintered, their surface area must have dramatically decreased, reducing the possibility of CO_2 reacting with the surface, and because the lithium diffusion is very slow at those temperatures, the final CO_2 absorbed decreased.

However, all other isotherms performed at higher temperatures (450, 500, 550, 600, 650, and 675 °C) presented an exponential typical behavior. In these cases, samples increased their weights from 0.88 (450 °C) to 34.2 wt % (675 °C) after 4 h. These results are presented in Figure 7. Additionally, it is clearly evident that CO_2 absorption at short times was dramatically increased as a function of the temperature. However, the isothermal slopes became almost the same in long time periods. It can be explained as follows: in short time periods, the increase in weight depends on the CO_2 absorption reaction, whereas in long time periods, it depends on the lithium diffusion.

To prove these qualitative observations, we fitted all isotherms to simple (300−400 °C) or double (450−675 °C) exponential models because there are two different processes taking place: the CO_2 absorption and the lithium diffusion. In the first three samples, the isotherms were divided and adjusted to a simple exponential model, whereas in the other cases, a double exponential model was used because the reaction and diffusion processes were undistinguished. From these results, it was possible to obtain two different constant values, k_1 and k_2, which represent the kinetic constant values of the CO_2 absorption and lithium diffusion, respectively. Table 1 shows the different parameters obtained from the isotherms. From these data, it can be seen that CO_2 absorption constants (k_1) are at least one order of magnitude higher than lithium diffusion constants (k_2). In other words, the limiting step of the total process is the lithium diffusion. Additionally, CO_2 absorption and diffusion constant values were enhanced as a function of the temperature, as was already qualitatively described in Figures 6 and 7. In both cases, the processes were improved by one (k_1) or two (k_2) orders of magnitude, increasing the temperature from 300 to 675 °C.

If both processes, CO_2 absorption (k_1) and lithium diffusion (k_2), follow a linear trend as a function of temperature, then the gradients of these best fit lines should fit the Eyring's model. These results are illustrated in Figure 8. It is clear that plots of $\ln(k/T)$ versus $1/T$ describe linear trends, fitting Eyring's model. Therefore, the activation enthalpies (ΔH) of the two different processes could be determined. The ΔH values obtained were 15.6 kJ/mol for CO_2 absorption and 52.1 kJ/mol for lithium diffusion. Therefore, this result clearly shows that lithium diffusion on Li_5AlO_4 is more dependent on temperature in comparison to the CO_2 absorption. It is very clear that lithium diffusion is the limiting step in the whole temperature range, although it is highly activated as a function of the temperature in comparison with the CO_2 absorption process.

4. Conclusions

Lithium aluminates ($LiAlO_2$ and Li_5AlO_4) were synthesized by solid state reaction and then characterized by XRD and SEM. In both cases, pure materials were obtained, and they presented a considerably large particle size. Then, during the dynamic thermal analyses, both ceramics presented very different behaviors for the CO_2 absorption. Whereas $LiAlO_2$ practically did

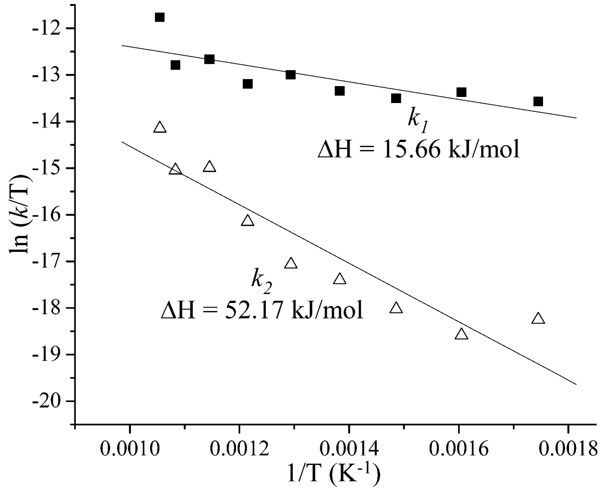

Figure 8. Eyring's plots for the rate constants of CO_2 absorption (k_1) and lithium diffusion (k_2).

not absorb CO_2 at all, Li_5AlO_4 presented a high CO_2 absorption. Li_5AlO_4 absorbed CO_2 in a wide temperature range from 200 to 700 °C, but it sintered as a function of temperature. At low temperatures, the CO_2 absorption decreased because of the sintering effect, which implies a reduction of the surface area. However at high temperatures, this phenomenon was not observed because lithium diffusion was activated.

To avoid the sintering effect and to perform a kinetic analysis, a different set of samples was homogeneously sintered before the isothermal experiments were carried out. All of these isotherms were fitted to exponential models, which described two different processes: the CO_2 absorption reaction and the lithium diffusion from the core of the particles to the surface. It could be determined that the diffusion process is the limiting step of the whole process. Additionally, the ΔH values obtained for the CO_2 absorption and lithium diffusion processes were 15.6 and 52.1 kJ/mol, respectively. This means that lithium diffusion is more dependent on the temperature.

Last but not least, it has to be mentioned that aluminum is a lighter element in comparison with the other elements used as structural ceramics for this application, for example silicates (Li_4SiO_4 and Li_2SiO_3), cuprates (Li_2CuO_2), zirconates (Li_2ZrO_3 and $Li_6Zr_2O_7$), or titanates (Li_4TiO_4). Therefore, because Li_5AlO_4 has the best theoretical CO_2 chemisorption capacity per gram of ceramic among the lithium ceramics and because of the results obtained, Li_5AlO_4 may become an important case of study as a CO_2 captor.

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