

CO₂ chemisorption and cyclability analyses in α -Li₅AlO₄: effects of Na₂CO₃ and K₂CO₃ addition

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Abstract: Lithium aluminate (α -Li₅AlO₄) was synthesized and mixed with potassium carbonate or sodium carbonate. The addition of these alkaline carbonates was produced during or after the synthesis process. The CO₂ chemisorption was evaluated using dynamic, isothermal, and cyclic thermogravimetric analyses. The presence of the K or Na in α -Li₅AlO₄ changes the sorption properties in a wide temperature range. K- and Na-Li₅AlO₄ samples, when the alkaline carbonates were added 10 wt% presented better CO₂ capture properties, capturing 37–39 wt% at 660 °C and ~50 wt% at 710 °C, for doped samples prepared mechanically or synthetically, respectively. The results revealed that the weight gained on α -Li₅AlO₄ mixed with K- or Na-carbonates was attributed to the formation of the eutectic phases. These materials would be suitable for CO₂ capture over a wide temperature range depending on the application process. Nevertheless, the cyclic experiments showed important variations in their respective efficiencies, depending on the temperature. © 2015 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: chemisorption; CO₂ capture; thermal analysis

Introduction

t is well known that human activities contribute significantly to the increase in the atmospheric concentration of carbon dioxide (CO_2) and other greenhouse gases (GHGs), which contributes to further global warming.¹⁻⁴ In this way, there are different alternatives such as energy efficiency improvements, substitution of low or non-carbon fuels.² Most efforts are focused mainly on reducing the amount of CO_2 emitted to the atmosphere.⁴⁻⁶ The success of these issues depends on the design and development of new materials with good CO_2 capture properties. In general, a large sorption capacity, adequate kinetics, cyclability, stability, and a wide thermal operation range could define the ideal perfect capture material.⁷ Thus, it different kinds of materials as potential CO₂ captors had been proposed, such as membranes,^{8,9} zeolites,^{10,11} activated carbons,^{9,11-13} hydrotalcites,^{14,15} metal–organic frameworks (MOFs),⁹ amine-based adsorbents,^{9,13} alkaline oxides and earth alkaline oxides,^{16,17} among others. However, CO₂ capture capacity in these materials is not good enough, and several of these materials cannot be regenerated.

Among alkaline ceramics, Nakagawa and Ohashi¹⁸ showed that lithium metazirconate (Li₂ZrO₃) was able

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to trap CO₂ at high temperatures (400 °C–600 °C), presenting a great advantage because the combustion gas flow does not have to be cooled, and that CO₂ can be removed thermally or chemically regenerating the lithium ceramic. Since then, other lithium and sodium ceramics have been tested as CO₂ captors.^{16–50} However, the ceramics most extensively studied are the lithium zirconates,^{18,21–29} the lithium silicates^{20,28,30–40} and the sodium zirconate.^{26,27} Other lithium ceramics tested as possible CO₂ captors are lithium cuprate,^{41,42} lithium ferrite,^{43,44} lithium titanate,^{45,46} and lithium aluminates (LiAlO₂ and Li₅AlO₄).^{47,48}

Li₅AlO₄ seems to be able to trap CO₂ chemically, in the temperature range from 200 to 700 °C.⁴⁷ Li₅AlO₄ has two polymorphs, at low and high temperatures, α -Li₅AlO₄ and β -Li₅AlO₄, and the $\alpha \rightarrow \beta$ structural transition occurs at around 780 °C. Although, Li₅AlO₄ has a CO₂ theoretical chemisorption of 15.9 mmol/g, experimentally it has been reported chemisorptions of 15.3 and 12.1 mmol/g for the β -Li₅AlO₄ and α -Li₅AlO₄ phases, respectively.⁴⁸ Furthermore, when Li₅AlO₄ reacts with CO₂, LiAlO₂ is produced. This secondary phase does not react with CO₂ due to thermodynamic factors. However, when LiAlO₂ is contained in the external shell, it promotes the lithium diffusion into the Li₂CO₃-LiAlO₂ external shell at temperatures higher than 600 °C.⁵¹

Some of the lithium ceramics, previously mentioned, have been doped adding different carbonates such as K_2CO_3 , Na_2CO_3 ,^{2,52} MgCO_3 and CaCO_3.⁵² The addition of these carbonates favors the formation of eutectic phases on the carbonate external shell, improving the CO₂ chemisorption kinetics and efficiencies, compared with their respective alkali pure ceramics.^{2,19,21,27,45–55} Thus, the aim of the present work was to produce K- or Na-doped Li₅AlO₄ samples, as these mixtures would improve the CO₂ chemisorption rates due to the Li₂CO₃-K₂CO₃ or Li₂CO₃-Na₂CO₃ eutectic phase formations, resulting in a partial molten shell that facilitates the CO₂ diffusion throughout the external shell.

Experimental

The α -Li₅AlO₄ phase was synthesized using a solidstate reaction that employs lithium oxide (Li₂O, Aldrich, St. Louis, MO, USA) and gamma alumina (γ -Al₂O₃). Powders were mechanically mixed, pressed into pellets (2.5 tons/cm²) and heated under different thermal conditions. The α -Li₅AlO₄ pellets were heated to 500 °C for 24 h and slowly cooled down to room temperature. After the thermal treatment the α -Li-₅AlO₄ pellets were pulverized.⁴⁸ To obtain pure α -Li₅AlO₄, 30 mol% excess of lithium was used, as lithium tends to sublimate.⁵⁶ The formation of α -Li-₅AlO₄ phase was confirmed by powder X-ray diffraction (XRD, data not shown). However, very small peaks corresponding to lithium carbonate were found in the α -Li₅AlO₄ sample. After the α -Li₅AlO₄ synthesis, powder was mechanically mixed with 10 wt% of potassium (K₂CO₃, Aldrich) or sodium (Na₂CO₃, Aldrich, St. Louis, MO, USA). These samples were labeled as m-K- α -Li₅AlO₄ and m-Na- α -Li₅AlO₄. Additionally, Na- and K-doped α -Li₅AlO₄ samples were synthesized by a solid-state reaction, adding 10 wt% of potassium or sodium carbonates during the synthesis process mentioned above. In these cases, the samples were labeled with an initial *s*- instead of *m*-. Again, the XRD patterns fitted to the α -Li₅AlO₄ phase (data not shown).

After the synthesis and structural characterization all the samples were analyzed by N_2 adsorption-desorption analysis and different thermal analyses. N_2 isotherms were performed using a Minisorp II instrument (BEL-Japan, Osaka, Japan) at 77 K. Samples were previously degassed at room temperature for 24 h in a vacuum. The BET model was used to determine the sample's surface area.^{57–59}

Different thermal analyses were performed using TGA and DSC equipments. The thermobalance used was a Q500HR instrument, from TA Instruments. Initially, a set of samples was dynamically heated from room temperature to 900 °C at 5 °C/min, using a saturated CO₂ flow (60 mL/min, Praxair, grade 3.0). Subsequently, the samples were tested isothermically at different temperatures (from 400 to 700 °C) in presence of the same CO_2 flow. For the isothermal experiments, each sample was heated to the corresponding temperature into a N_2 flux (Praxair, grade 4.8). Then, once the temperature was reached, the gas was switched from N_2 to CO_2 . Regenerability tests were conducted under the uptake conditions in a CO₂ atmosphere (700 °C for 20 min, 60 mL/min) and the desorption conditions in a N_2 atmosphere (750 °C for 20 min, 60 mL/min).

Differential scanning calorimetry (DSC) experiments were performed using a DSC equipment from Instruments Specialists Incorporated (Twin Lakes, WI, USA). Different Li-K and Li-Na carbonate mixtures were heated from room temperature to 600 °C at 20 °C/min, into a N_2 atmosphere. Then, the mixture were cooled down to 200 °C and reheated from 200 °C to 600 °C at the same rate, in order to elucidate the fusion temperature of each eutectic mixture.

Results and discussion

CO₂ capture preliminary experiments were performed by adding different quantities of potassium or sodium carbonates (3, 10 or 20 wt%). The addition was produced during or after the α -Li₅AlO₄ synthesis processes. Then, theses samples were analyzed thermogravimetrically in the presence of a CO₂ flux (data not shown). The dynamic thermograms showed that the best conditions were presented when 10 wt% of the corresponding carbonate was added, in the temperature range of 400 to 700 °C. Based in these results, only the Na- and K-doped α -Li₅AlO₄ results are presented here.

The surface area of the pristine α -Li₅AlO₄ sample was determined using the BET model. The obtained value was 0.8 m²/g. Furthermore, in the K- and Nadoped lithium aluminates synthesized cases, the surface areas were 0.8 and 0.6 m²/g, respectively. As it can be seen, the surface area of the ceramic tended to decrease by the K and Na addition. It must be mentioned that, in any case, the surface area is considerably low (>1 m²/g), so it should not influence the CO₂ capture.

After the textural characterization, the CO_2 capture was evaluated in all these samples. It has been reported that Li_5AIO_4 chemisorbs CO_2 according to the following reaction, which is independent of the Li_5AIO_4 crystalline phase:

$$Li_{5}AlO_{4(s)} + 2CO_{2(g)} \rightarrow 2Li_{2}CO_{3(s)} + LiAlO_{2(s)}$$
(1)

Initially the CO₂ chemisorption capacities of both Na- and K-doped α -Li₅AlO₄ samples (prepared mechanically or synthetically) were analyzed in the presence of a CO₂ flux. Figure 1 shows the dynamic thermograms of these samples and their comparison with the pristine α -Li₅AlO₄. In the pure α -Li₅AlO₄ case, the dynamic thermogram clearly shows two different processes. First, between 180 and 407 °C, there is an initial weight increment of 8.5 wt%, which corresponds to the superficial CO₂ chemisorption process. Then, at higher temperatures (510–798 °C) occurred the second processes, where the weight increment was equal to 39.8 wt% and it corresponds to CO₂ chemisorption process through the ceramic bulk, which is produced once different diffusion



Figure 1. Comparative dynamic thermogravimetric analyses of Na- and K-containing α -Li₅AlO₄ samples with pure α -Li₅AlO₄ sample into a CO₂ flux.

processes are thermally activated. So, the total weight increase was 54.6 wt%. Similar thermal trends have already been observed for other lithium ceramics.^{40,41,45,47,49,60,61}

Then, all the Na- and K-doped α -Li₅AlO₄ samples lost some weight between 30 and 200 °C, which can be associated to dehydration and dehydroxylation processes, induced by the sodium or potassium carbonates presence. However, in the *s*-K- α -Li₅AlO₄ and *s*-Na- α -Li₅AlO₄ samples, the weight loss is almost imperceptible, while it is more pronounced in the sample where the K and Na were added mechanically. It should be simply explained as a consequence of the K and Na surface availabilities, as in the synthesis cases these two elements may be located into the Li₅AlO₄ material.

After the dehydroxylation process, doped samples presented similar CO_2 chemisorption trends with slight temperature variations. Initially, there were superficial CO_2 chemisorption reactions, which were continued at higher temperatures once the diffusion processes were thermally induced. Nevertheless, most of the doped samples presented slight increases at moderate temperatures (380–425 °C, between the superficial and bulk CO_2 chemisorptions). All the temperature variations and the third weight increase at moderate temperatures must be associated to the K- or Na-doping processes. In addition, something else must be pointed out. While the *s*-Li₅AlO₄ samples presented similar final weight increments than Li₅AlO₄ (~50 wt%), the *m*-Li₅AlO₄ samples did not



Figure 2. CO_2 isotherms of *s*-K- α -Li₅AIO₄, *m*-K- α -Li₅AIO₄, *s*-Na- α -Li₅AIO₄ and *m*-Na- α -Li₅AIO₄ samples at different temperatures.

reach those weight increments. In those samples, the final weight increased only around 37–39 wt%. It seems that K_2CO_3 and Na_2CO_3 , at the Li_5AlO_4 surface, reduce the CO_2 chemisorption at high temperatures.

To further analyze and understand the K- and Na-doping effects, mechanically or synthesized, in α -Li₅AlO₄, different and independent kinetic experiments were performed. Figure 2 shows the CO₂ isotherms at different temperatures. *s*-K- α -Li₅AlO₄ thermally treated at 400 °C showed an exponential weight increase of 34.2 wt%. In this case, the isotherm reached equilibrium after 30 min. However, a totally different behavior was observed t higher temperatures. At 450 °C, *s*-K- α -Li₅AlO₄ seemed to stay non-reactive during the first 20 minutes, and only after that time, the isotherm showed a slight weight increment of 10.6

wt% after 180 min, without reaching equilibrium. Similar but shorter lag-periods were observed at 500 and 550 °C. At these temperatures, the final weight increases were 11.2 and 11.5 wt%, respectively. A similar isothermal behavior had been already reported on the K-doped Li₈SiO₆ in the same temperature range.⁵⁵ In that case, the explanation given to the isotherms was as follows. At low temperatures, the CO_2 chemisorption must be mainly limited to the lithium ceramic surface (Li₅AlO₄ in the present case), as the diffusion processes have not been activated. Then, between 400 and 550 °C, the Li₂CO₃ and K_2CO_3 surface (products of the CO_2 chemisorption) must produce eutectic phases which fusing partially. This liquid phase in addition to the possible presence of mesoporous in the external shell microstructure, as it has been seen for other lithium ceramics in a

similar temperature range,⁶² may modify the CO₂ diffusion. At temperatures higher than 550 °C, these isotherms (600, 650, and 700 °C) presented a fast weight increment in the first minutes, which may be associated to the activation of diffusion processes enhanced by the eutectic phase formation.

Conversely, if the potassium was added mechanically, after the Li_5AlO_4 synthesis, the isotherms presented a different thermal trend. Between 400 and 550 °C all the isotherms presented exponential growths, which increased as a function of temperature from 7 to 42.2 wt%. Here, it was not evidenced the double increment weight observed on the previous samples. Latter, the isotherm preformed at 600 °C slightly decreased the final weight increment (38.7 wt%), although the kinetic behavior shows to be faster than that produced at 550 °C. The decrement observed at this temperature may be related to a sintering ceramic process.⁴⁷ Finally, the weight increases at higher temperatures increased to 43.7 and 46.0 wt%, at 650 and 700 °C, respectively.

Identical experiments were performed for the Na-doped Li_5AlO_4 . The results produced were very similar to those previously described for the K-doped samples. On the contrary, samples, in which sodium or potassium were added mechanically as carbonates, seem to diminish the CO_2 as in the K systems. Figure 3 summarizes the maximum weight increase obtained in the isotherms.



Figure 3. Comparison of maximum weight increment obtained at isotherm analysis of Na- and K-containing α -Li₅AlO₄ samples with the α -Li₅AlO₄.pure sample.

After the qualitative analysis, the resulted curves were fitted to different kinetic models, as previously reported for the other alkaline ceramics.^{20,61,62} In general, for this kind alkaline ceramics, isotherms have been fitted to a double o triple exponential models. But, it was not the case for the Na- and K-doped α -Li₅AlO₄ samples. Thus, the kinetic data had to be analyzed by a different kind of approximation,^{40,60,61} a first-order reaction model with respect to Li₅AlO₄ (Eqn (2)),

$$ln[Li_5AlO_4] = -kt \tag{2}$$

Where *k* is the reaction rate constant, *t* is the time, and $[\text{Li}_5\text{AlO}_4]$ is the molar concentration of the ceramic. $\ln[\text{Li}_5\text{AlO}_4]$ *versus* time were plotted in order to fit to the first-order reaction model and obtain *k* values (data not shown). The data only followed a straight line at short times, before the external shell was completed. The corresponding *k* values *versus* temperature are plotted in Fig. 4 for all Na- and K-containing α -Li₅AlO₄ samples.

Once the external shell was completed, diverse diffusion processes must be activated. Thus, it was necessary to employ a diffusion model.⁶⁰ If the reaction is controlled by the interface movement from the surface inwards it can be described as:

$$1 - (1 - \alpha)^{1/3} = k_D t \tag{3}$$



Figure 4. Comparison of plots of k *versus* Temperature, for the data obtained at kinetic analysis of Na- and K-containing α -Li₅AlO₄ samples and the α -Li₅AlO₄ pure sample, assuming a first-order reaction of α -Li₅AlO₄ for short times.

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Figure 5. Comparison of plots of k *versus* Temperature, for the data obtained at kinetic analysis of Na- and K-containing α -Li₅AlO₄ samples and the α -Li₅AlO₄ pure sample, assuming a diffusion mechanism controlled by the interface movement from the surface inward for long times.

where α is the molar fraction of Li₂CO₃ produced (Eqn (1)), *t* is time and k_D is a constant which depends on the diffusion coefficient, particle size, and temperature. Assuming a diffusion mechanism controlled by the interface movement from the surface inwards (1-(1- α)^{1/3}) *versus* time were plotted in order to obtain k_D values (data not shown). The data only followed a straight line at long times, when the diffusion behavior has started. The corresponding k_D values *versus* temperature are plotted in Fig. 5 for all Na- and K-containing α -Li₅AlO₄ samples. Eyring's model (Eqn (4)), is typically used on heterogeneous reactions and solid–gas system to describe this kind of temperature dependence diffusion processes, then *k* and k_D were to Eyring's model.

$$n(k_{i}/T) = -(\Delta H^{\ddagger}/R)(1/T) + \ln E + \Delta S^{\ddagger}/R$$
(4)

where k_i is the rate constant value of the process *i*; E is the pre-exponential factor, which in Eyring's formulation is equal to the ratio between the Boltzmann and Planck constants; R ideal gas constant; and ΔH^{\ddagger} and ΔS^{\ddagger} are the activation is the enthalpy and entropy, respectively. Data demonstrate that $\ln(k_i / T)$ versus 1/T plots cannot be described by a linear trend when using Eyring's model (data not shown). Thus, by means of fit the data obtained to a linear model, the activation enthalpies (ΔH^{\ddagger}) were calculated for both different processes (Tables 1 and 2), for at least two temperature ranges. ΔH^{\ddagger} values for CO₂ direct

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Table 1. The activation enthalpies (Δ H [‡]) for the CO ₂ direct chemisorption in the temperature range from 500 to 700 °C.	
Sample	ΔH^{\ddagger} (kJ/mol)
α−Li ₅ AlO ₄	75.324
<i>m</i> -K- <i>α</i> -Li ₅ AlO ₄	42.440
<i>m</i> -Na- <i>α</i> -Li ₅ AlO ₄	31.451
s-K- <i>a</i> -Li ₅ AlO ₄	45.323
s-Na-α–Li ₅ AlO ₄	38.131

chemisorption are lower in K- and Na-containing samples compared to the α -Li₅AlO₄ pure sample. However, these values are higher for the kinetically controlled chemisorption processes. It means that the direct chemisorptions process is less dependent of temperature for doped samples than without doping. In the kinetically controlled chemisorption case it could be observed the opposite behavior. This implies that the direct chemisorption process is more temperature dependent than the chemisorption process kinetically controlled by diffusion processes.

It is also possible to observe that in CO_2 direct chemisorption processes, K_2CO_3 -doped samples have less temperature dependence than the Na_2CO_3 -containing samples. In contrast, the chemisorption controlled by diffusion processes, Na_2CO_3 -doped samples present higher temperature dependence than that of K_2CO_3 -containing samples.

Based on the obtained results and previous papers,⁵¹ it is proposed the following explanation: At temperatures lower than 500 °C the direct chemisorption is limited by the surface of the ceramic, due to the formation of external shell containing an LiAlO₂ secondary phase and Li₂CO₃, product of direct reaction between the CO₂ and Li₅AlO₄ (Eqn (1)).⁵¹ At around 500 °C it should appear the molten points caused by the eutectic phases of potassium or sodium

Table 2. The activation enthalpies (ΔH^{\ddagger}) for diffusion mechanism controlled by the interface movement from the surface inward in the temperature range from 400 to 550 °C.	
Sample	∆H‡ (kJ/mol)
α -Li ₅ AlO ₄	27.676
<i>m</i> -K-α-Li ₅ AlO ₄	65.193
<i>m</i> -Na-α-Li ₅ AlO ₄	102.939
s-K- <i>a</i> -Li ₅ AlO ₄	65.447
s-Na- <i>a</i> -Li ₅ AlO ₄	62.965



Figure 6. Comparison of temperatures (dotted lines) and enthalpies of fusion (solid lines) of different Li-K (squares) and Li-Na (triangles) carbonate mixtures. They were heated from room temperature to 600 °C at the rate of 20 °C/min, into a N₂ atmosphere. Then, the mixtures were cooled down to 200°C and again heated from 200°C to 600 °C at the rate of 20 °C/min.

carbonate added before exposure to CO_2 with lithium carbonate produced. At this temperature range the partial molten generated by eutectic phases should promote diffusion processes. Then, at temperatures higher 500 °C CO_2 chemisorption is controlled by the interphase diffusion mechanism from the surface inwards. Finally, the chemisorption process kinetically controlled by diffusion processes is completely activated at 700 °C.

In order to understand the formation of the partial molten phases due to the presence of Li-Na or Li-K carbonate eutectic phases, different DSC experiments were performed. Initially, the samples were heated from room temperature to 600 °C, and then cooled down to 200 °C. After that, the samples were reheated to 600 °C. Figure 6 shows the different temperatures and enthalpies of fusion for different the mixtures of Li_2CO_3 -K₂CO₃ and Li_2CO_3 -Na₂CO₃. From these data, it is clear that both systems melt at around 500 °C, so it may be possible to find partial molten phases in the ceramics.

Finally, to test the regeneration properties and the thermal stability after several cycles of CO₂ chemisorption/desorption in Na- and K-containing α -Li- $_5$ AlO₄ samples, the samples were analyzed using a multicycle method (data not shown). The result for the *s*-K- α -Li₅AlO₄ sample indicates that the CO₂

chemisorption capacity reaches approximately 37.7 wt% for the first cycle, for the second cycle, the CO₂ chemisorption capacity decreases to 9.8 wt% and after 20 cycles, it is observed 17.1 wt%. For the m-K- α -Li₅AlO₄ sample, the CO₂ chemisorption in the first cycle was 45.9 wt%, but for the second cycle, its capacity decreased dramatically to only 12.5 wt% and after 20 cycles it was stabilized in 18.2 wt%. The result, for the *s*-Na- α -Li₅AlO₄ sample, shows that the CO₂ chemisorption capacity reaches around 43.6 wt% for the first cycle, but its capacity was stabilized in 19.9 wt% after 20 cycles. For the *m*-Na- α -Li₅AlO₄ sample, the CO₂ chemisorption in the first cycle was 39.4 wt%, but for the second cycle the CO_2 chemisorption capacity decreases to 11.6 wt%, and after 20 cycles, its capacity is 15.5 wt%.

Making a comparison of the regeneration behavior during each cycle of chemisorption/desorption of CO₂, it is observed that α -Li₅AlO₄ pure sample presented a CO_2 chemisorption capacity of 9.4 mmol/g, similar capacity Na- and K-containing α -Li₅AlO₄ samples, and 4.4 mmol/g for the second cycle, much higher than that obtained for the Na- and K-doped samples. However, from the second cycle the CO₂ chemisorption capacity begins to increase gradually for the Na- and K-containing samples, so when the last cycle is analyzed, the obtained values are similar than those observed by the pure sample (3.6-3.9 mmol/g). The different tendencies observed may be related to the different eutectic phases produced, which increase the diffusion processes enhancing the CO₂ chemisorption, but these eutectic phases must decrease the carbonate decomposition processes, enabling the cyclability.

Conclusions

Na- and K-doped α -Li₅AlO₄ samples were synthesized using a solid-state reaction and then characterized by XRD and N₂ adsorption. At the same time, pure α -Li₅AlO₄ was mixed mechanically with potassium or sodium carbonates. During the dynamic thermal analyses, the different α -Li₅AlO₄ samples showed similar trends, exhibiting higher CO₂ chemisorptions than that of α -Li₅AlO₄, at specific temperatures each. Thus, the possible application of each sample may depend on temperature. Isotherms were fitted to the first-order surface chemisorption and diffusional mechanism controlled by the movement of an interface moving from the surface inward. The kinetic constant values were fitted to Eyring's model. ΔH^{\ddagger} values obtained showed that the CO₂ direct chemisorption process is more dependent of temperature for α -Li₅AlO₄ pure sample than for Na- and K-doped α -Li₅AlO₄ samples. On the contrary, in the kinetically controlled chemisorption processes the opposite behavior was observed.

Finally, the cyclic analysis showed that Na- and K-doped α -Li₅AlO₄ samples exhibit a dramatic decrease, after one cycle. Then, the CO₂ chemisorption tended to increase gradually, until stability was reached after ten cycles. It is evident that the CO₂ chemisorption capacities in the doped samples are more stable than α -Li₅AlO₄ after 20 cycles. Thus, these materials might be good considered as possible candidates for multicycle CO₂ chemisorption processes.

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References

- D'Alessandro DM, Smit B and Long JR, Carbon dioxide capture: prospects for new materials. *Angew Chem Int Ed* 49:2–27 (2010).
- Olivares-Marín M and Maroto-Valer M, Development of adsorbents for CO₂ capture from waste materials: a review. *Greenhouse Gas Sci Tech* 2:20–35 (2012).
- Wang J, Huang L, Yang R, Zhang Z, Wu J, Gao Y, Wang Q, O'Hareb D and Zhong Z, Recent advances in solid sorbents for CO₂ capture and new development trends. *Energy Environ Sci* 7:3478–3518 (2014).
- Wang Q, Luo J, Zhong Z and Borgna A, CO₂ capture by solid adsorbents and their applications: current status and new trends. *Energy Environ Sc* 4:42–55 (2011).
- Boot-Handford ME, Abanades JC, Anthony EJ, Blunt MJ, Brandani S, Mac Dowell N *et al.*, Carbon capture and storage update. *Energy Environ Sci* 7:130–189 (2014).
- Leung DYC, Caramanna G and Maroto-Valer MM, An overview of current status of carbon dioxide capture and storage technologies. *Renew Sust Energ Rev* 39:426–443 (2014).
- Choi S, Drese JH and Jones CW, Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* 2:796–854 (2009).
- Wilcox J, Haghpanah R, Rupp EC, He J and Lee K, Advancing adsorption and membrane separation processes for the gigaton carbon capture challenge. *Annu Rev Chem Biomol Eng* 5:479–505 (2014).
- Spigarelli BP and Kawatra SK, Opportunities and challenges in carbon dioxide capture. J CO2 Util 1:69–87 (2013).
- Siriwardane RV, Shen MS and Fisher EP, Adsorption of CO₂ on zeolites at moderate temperatures. *Energ Fuel* 19:1153–1159 (2005).

- Cheung O and Hedin N, Zeolites and related sorbents with narrow pores for CO₂ separation from flue gas. *RSC Adv* 4:14480–14494 (2014).
- Sircar S, Golden TC and Rao MB, Activated carbon for gas separation and storage. *Carbon* 34:1–12 (1996).
- Chen Z, Deng S, Wei H, Wang B, Huang J and Yu G, Activated carbons and amine-modified materials for carbon dioxide capture – a review. *Front Environ Sci Eng* 7:326–340 (2013).
- Ding Y and Alpay E, Equilibria and kinetics of CO₂ adsorption on hydrotalcite adsorbent. *Chem Engi Sci* 55:3461–3474 (2000).
- Sharma BK, Sharma MP, Kumar S, Roy SK, Badrinarayanan S, Sainkar SR *et al.*, Studies on cobalt-based Fischer–Tropsch catalyst and characterization using SEM and XPS techniques. *Appl Catal A* **211**:203–211 (2001).
- Yong Z, Mata V and Rodrigues AE, Adsorption of carbon dioxide at high temperature–a review. *Sep Purif Technol* 26:195–205 (2002).
- Kumar S and Saxena SK, A comparative study of CO₂ sorption properties for different oxides. *Mater Renew Sustain Energy* 3:30 (2014).
- Nakagawa K and Ohashi T, A novel method of CO₂ capture from high temperature gases. *J Electrochem Soc* 145:1344–1346 (1998).
- Pfeiffer H, Advances in CO₂ conversion and utilization, in ACS Symposium Series, ed by HuYH. American Chemical Society, Washington, DC. **1056**:233–253 (2010).
- 20. Venegas MJ, Fregoso-Israel E, Escamilla R and Pfeiffer H, Kinetic and reaction mechanism of CO_2 sorption on Li₄SiO₄: Study of the particle size effect. *Ind Eng Chem Res* **46**:2407–2412 (2007).
- Xiong R, Ida J and Lin YS, Kinetics of carbon dioxide sorption on potassium-doped lithium zirconate. *Chem Eng Sci* 58:4377–4385 (2003).
- 22. Nakagawa K and Ohashi T, Reversible change between lithium zirconate and zirconia in molten carbonate. *Electro-chem* **67**:618–621 (1999).
- Fauth DJ, Frommell A, Hoffman JS, Reasbeck RP and Pennline HW, Eutectic salt promoted lithium zirconate: Novel high temperature sorbent for CO₂ capture. *Fuel Processing Tech* 86:1503–1521 (2005).
- Nair BN, Yamaguchi T, Kawamura H and Nakagawa K, Processing of lithium zirconate for applications in carbon dioxide separation: structure and properties of the powders. *J Am Ceram Soc* 87:68–74 (2004).
- Yi KB and Eriksen DØ, Low temperature liquid state synthesis of lithium zirconate and its characteristics as a CO₂ sorbent. *Separ Sci Tech* **41**:283–296 (2006).
- Ochoa-Fernández E, Rønning M, Grande T and Chen D, Synthesis and CO₂ capture properties of nanocrystalline lithium zirconate. *Chem Mater* **18**:6037–6046 (2006).
- Ochoa-Fernández E, Rønning M, Yu X, Grande T and Chen D, Compositional effects of nanocrystalline lithium zirconate on its CO₂ capture properties. *Ind Eng Chem Res* 47:434–442 (2008).
- Nair BN, Burwood RP, Goh VJ, Nakagawa K and Yamaguchi T, Lithium based ceramic materials and membranes for high temperature CO₂ separation. *Prog Mater Sci* 54:511–541 (2009).
- 29. Yin XS, Zhang QH and Yu JG, Three-step calcination synthesis of high-purity Li₈ZrO₆ with CO₂ absorption properties. *Inorg Chem* **50**:2844–2850 (2011).

- Okumura T, Enomoto K, Togashi N and Oh-Ishi K, CO₂ Absorption reaction of Li₄SiO₄ studied by the rate theory using thermogravimetry. *J Ceram Soc Japan* **115**:491–497 (2007).
- Essaki K, Nakagawa K, Kato M and Uemoto H, CO₂ absorption by lithium silicate at room temperature. *J Chem Eng Japan* 37:772–777 (2004).
- 32. Khomane RB, Sharma B, Saha S and Kulkarni BD, Reverse microemulsion mediated sol–gel synthesis of lithium silicate nanoparticles under ambient conditions: Scope for CO₂ sequestration. *Chem Eng Sci* 61:3415–3418 (2006).
- Kato M and Nakagawa K, New series of lithium containing complex oxides, lithium silicates, for application as a high temperature CO₂ absorbent. *J Ceram Soc Japan* **109**:911–914 (2001).
- 34. Kato M, Yoshikawa S and Nakagawa K, Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations. *J Mater Sci Lett* **21**:485–487 (2002).
- Tsumura N, Kuramoto A, Shimamoto Y, Aono H and Sadaoka Y, Thermal stability of sodium aluminum silicates with and without alkali carbonates. *J Ceram Soc Japan* 113:269–274 (2005).
- Rodriguez MT and Pfeiffer H, Sodium metasilicate (Na₂SiO₃): A thermo-kinetic analysis of its CO₂ chemical sorption. *Thermochimica Acta* 473:92–95 (2008).
- Yamaguchi T, Niitsuma T, Nair BN and Nakagawa K, Lithium silicate based membranes for high temperature CO₂ separation. *J Mem Sci* **294**:16–21 (2007).
- Mejía-Trejo VL, Fregoso-Israel E and Pfeiffer H, Textural, structural, and CO₂ chemisorption effects produced on the lithium orthosilicate by its doping with sodium (Li_{4-x}Na_xSiO₄). *Chem Mater* **20**:7171–7176 (2008).
- Qi Z, Daying H, Yang L, Qian Y and Zibin Z, Analysis of CO₂ sorption/desorption kinetic behaviors and reaction mechanisms on Li₄SiO₄. *AIChE Journal* **59**:901–911 (2013).
- Durán-Muñoz F, Romero-Ibarra IC and Pfeiffer H, Analysis of the CO₂ chemisorption reaction mechanism in lithium oxosilicate (Li₈SiO₆): a new option for high temperature CO₂ capture. *J Mater Chem A* 1:3919–3925 (2013).
- Palacios-Romero LM and Pfeifer H, Lithium Cuprate (Li₂CuO₂): A new possible ceramic material for CO₂ chemisorption. *Chem Lett* **37**:862–863 (2008).
- Matsukura Y, Okumura T, Kobayashi R and Oh-ish K, Synthesis and CO₂ absorption properties of single-phase Li₂CuO₂ as a CO₂ absorbent. *Chem Lett* **39**:966–967 (2010).
- Kato M, Essaki K, Nakagawa K, Suyama Y and Terasaka K, CO₂ absorption properties of lithium ferrite for application as a high-temperature CO₂ absorbent. *J Ceram Soc Japan* **113**:684–686 (2005).
- 44. Yanase I, Kameyama A, and Kobayashi H, CO₂ absorption and structural phase transition of α -LiFeO₂. *J Ceram Soc Japan* **118**:48–51 (2010).
- Togashi N, Okumura T and Oh-ishi K, Synthesis and CO₂ absorption property of Li₄TiO₄ as a novel CO₂ absorbent. *J Ceram Soc Japan* **115**:324–328 (2007).
- Ueda S, Inoue R, Sasaki K, Wakuta K and Ariyama T, CO₂ Absorption and desorption abilities of Li₂O–TiO₂ compounds. *ISIJ Inter* **51**:530–537 (2011).

- Ávalos-Rendón T, Casa-Madrid J and Pfeiffer H, Thermochemical capture of carbon dioxide on lithium aluminates (LiAlO₂ and Li₅AlO₄): A new option for the CO₂ absorption. *J Phys Chem A* **113**:6919–6923 (2009).
- 48. Ávalos-Rendón T, Lara VH and Pfeiffer H, CO₂ chemisorption and cyclability analyses of lithium aluminate polymorphs (α - and β -Li₅AlO₄). *Ind Eng Chem Res* **51**:2622–2630 (2012).
- Ávalos-Rendón TL and Pfeiffer H, Evidence of CO₂ chemisorption at high temperature in lithium gallate (Li₅GaO₄). *Chem Lett* **40**:504–505 (2011).
- Roman-Tejeda A and Pfeiffer H, α→ γLithium borate phase transition produced during the CO₂ chemisorption process. J Therm Anal Calorim 110:807–811 (2012).
- Ortiz-Landeros J, Ávalos-Rendón TL, Gómez-Yáñez C and Pfeiffer H, Analysis and perspectives concerning CO₂ chemisorption on lithium ceramics using thermal analysis. *J Therm Anal Calorim* **108**:647–655 (2012).
- 52. Seggiani M, Puccini M and Vitolo S, High-temperature and low concentration CO₂ sorption on Li₄SiO₄ based sorbents: Study of the used silica and doping method effects. *Int J Greenhouse Gas Control* **5**:741–748 (2011).
- 53. Pannocchia G, Puccini M, Seggiani M and Vitolo S, Experimental and modeling studies on high-temperature capture of CO₂ using lithium zirconate based sorbents. *Ind Eng Chem Res* 46:6696–6706 (2007).
- Olivares-Marín M, Drage T and Maroto-Valer M, Novel lithium-based sorbents from fly ashes for CO₂ capture at high temperatures. *Int J Greenhouse Gas Control* **4**:623–629 (2010).
- Romero-Ibarra IC, Durán-Muñoz F and Pfeiffer H, Influence of the K-, Na- and K-Na-carbonate additions during the CO₂ chemisorption on lithium oxosilicate (Li₈SiO₆). *Greenhouse Gas Sci Tech* **4**:145–154 (2014).
- Pfeiffer H and Knowles KM, Reaction mechanisms and kinetics of the synthesis and decomposition of lithium metazirconate through solid-state reaction. *J Eur Ceram Soc* 24:2433–2443 (2004).
- 57. McCash EM, *Surface Chemistry*. Oxford University Press, Great Britain, pp.77–79 (2002).
- Lowell S, Shields JE, Thomas MA and Thommes M, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density. Kluwer Academic Publishers, Netherlands, pp.11–14 (2004).
- 59. Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J and Siemieniewska T, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure & Appl Chem*, **57**:603–619 (1985).
- Mosqueda HA, Vazquez C, Bosch P and Pfeiffer H, Chemical sorption of carbon dioxide (CO₂) on lithium oxide (Li₂O). *Chem Mater* 18:2307–2310 (2006).
- Alcérreca-Corte I, Fregoso-Israel E and Pfeiffer H, CO₂ Absorption on Na₂ZrO₃: A kinetic analysis of the chemisorption and diffusion processes. *J Phys Chem C* **112**:6520–6525 (2008).
- Martínez-dlCruz L and Pfeiffer H, microstructural thermal evolution of the Na₂CO₃ phase produced during a Na₂ZrO₃– CO₂ chemisorption process. *J Phys Chem C* **116**:9675–9680 (2012).



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