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Effect of Oxygen Addition on the Thermokinetic Properties of CO₂ Chemisorption on Li₂ZrO₃

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Lithium zirconate doped with potassium (K-Li₂ZrO₃) was synthesized by solid-state reaction and then its CO₂ chemisorption capacity was evaluated using different CO₂–O₂ gas mixtures. These experiments were performed in order to evaluate the effect produced by the O₂ on the kinetic parameters and on the CO₂ absorption reaction mechanism. Although the CO₂ capture dynamic experiments did not show significant variations as a function of the O₂ content, isothermal experiments and their fitting to the Eyring's model did. Different enthalpy activation (ΔH^\ddagger) values were estimated for the CO₂ chemisorption process, as CO₂ capture is produced by two processes: Initially, the CO₂ chemisorption occurs directly over the K-Li₂ZrO₃ surface. Then, once a Li₂CO₃–ZrO₂ external shell is produced, CO₂ chemisorption is kinetically controlled by diffusion processes, which must imply the lithium and oxygen diffusion. The ΔH^\ddagger values, of the CO₂ direct chemisorption, increased as a function of the O₂ content. It was explained in terms of a CO₂–O₂ competition to occupy the Li₂ZrO₃ surface. On the other hand, the ΔH^\ddagger values, of the CO₂ chemisorption kinetically controlled by diffusion processes, decreased as a function of the O₂ content. This result confirmed the oxygen diffusion dependency of the CO₂ chemisorption on lithium zirconate.

Introduction

Since 1998, when Nakagawa and Ohashi published a paper,¹ in which it was shown that monoclinic lithium metazirconate (*m*-Li₂ZrO₃) was able to trap carbon dioxide (CO₂), several works have been focused on this ceramic,^{2–9} or other lithium ceramics^{10–16} as CO₂ captors.

m-Li₂ZrO₃ captures CO₂, chemically, at high temperatures (reaction 1), producing lithium carbonate (Li₂CO₃) and zirconium oxide (ZrO₂). An advantage of this system is the fact that reaction is reversible; in other words, Li₂ZrO₃ can be regenerated.



After the initial publication mentioned above, the same and other authors showed that the CO₂ chemisorption process can be importantly improved if the ceramic is doped with potassium (K-doped Li₂ZrO₃).^{2–5,9} All the papers explained this behavior due to CO₂ diffusion through a molten lithium–potassium carbonate. Later, it was shown a different way to increase the CO₂ chemisorption on the Li₂ZrO₃. Ochoa-Fernández et al. showed that the tetragonal phase, *t*-Li₂ZrO₃, is much more reactive than the monoclinic phase, as a CO₂ captor.^{6–8}

In both cases, as in other lithium ceramics where CO₂ capture occurs chemically, the reaction mechanism proposed is described as follows. Initially, the Li₂ZrO₃ particles react with CO₂ only at the surface. This superficial reaction involves the formation of a Li₂CO₃–ZrO₂ external shell. Then, in order to continue the CO₂ chemisorption on the ceramic, bulk diffusion processes must be activated.^{3,4,10,16} From this specific step, the diffusion process, there are several points that have not been totally clarified and understood. Some authors propose that CO₂ diffuse into the ceramic material, while other authors propose a lithium diffusion mechanism. However, none of these theories have been totally proved. Additionally, something else has to be pointed

out from the CO₂ chemisorption reaction on Li₂ZrO₃. Into a saturated CO₂ atmosphere, lithium carbonate formation implies that one of each three oxygen atoms, present originally in the Li₂ZrO₃ ceramic, must become part of the Li₂CO₃. Consequently, oxygen diffusion must be involved as well on the reaction mechanism, and not only lithium and/or CO₂ diffuse.

Therefore, the aim of this work was to elucidate if oxygen addition to the gas flow modifies the thermokinetic properties of the CO₂ capture process on Li₂ZrO₃. Li₂ZrO₃ was chosen as a case of study because this ceramic is one of the most studied ceramics as a CO₂ captor.

Experimental Section

K-doped lithium zirconate, labeled as K-Li₂ZrO₃, was synthesized by solid-state reaction, using zirconium oxide (ZrO₂, Aldrich with 99% purity), lithium carbonate (Li₂CO₃, Aldrich with 99+% purity) and potassium carbonate (K₂CO₃, Aldrich with 99% purity). The Li₂CO₃:ZrO₂:K₂CO₃ molar ratio was 1.1:1.0:0.2. Powders were mechanically mixed and then fired at 850 °C for 12 h. The sample was characterized by different techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and dynamic and isothermal thermogravimetric analyses (TGA). For the XRD experiments, a diffractometer Bruker AXS D8 Advance was used coupled to a copper anode X-ray tube. The composition of the sample was identified conventionally by the Joint Committee Powder Diffraction Standard (JCPDS) files. SEM micrographs and elemental analyses (energy dispersive X-ray (EDX)) were obtained in a Cambridge Leica Stereoscan 440 microscope. Before the microscope electronic analysis, powders were coated with gold to avoid the lack of conductivity. Finally, different thermal analyses were performed in the Q500HR equipment from TA Instruments, with an autosampler. The K-Li₂ZrO₃ sample was heat-treated dynamically, with a heating rate of 5 °C/min from room temperature to 670 °C with different gas-mixtures; CO₂ (100 vol %) and three different CO₂–O₂ mixtures (98–2, 95–5, and 90–10 vol %), using in all the cases a total flow rate of

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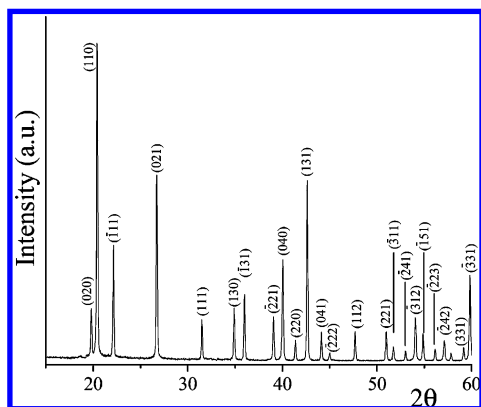


Figure 1. XRD pattern of the K-Li₂ZrO₃ sample.

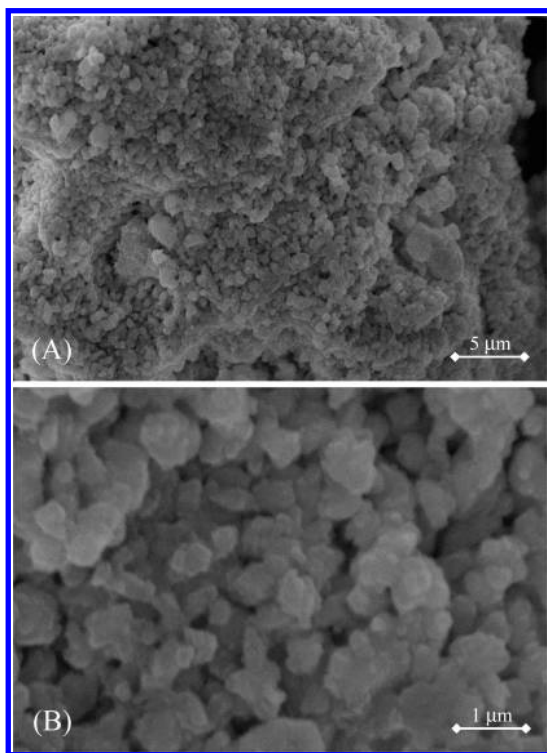


Figure 2. Secondary electron images of the K-Li₂ZrO₃ sample at two different magnifications.

150 mL/min. Both gases, CO₂ and O₂, were provided by Praxair with the following grades of purity: 4.0 and 4.8, respectively. Then, the K-Li₂ZrO₃ sample was tested isothermally at different temperatures, under the same CO₂ and CO₂-O₂ flows. All the gas mixtures were digitally prepared into a Chem-flow gas mixer from Bel-Japan.

Results and Discussion

Initially, a K-Li₂ZrO₃ sample was characterized by different techniques. Figure 1 shows the XRD pattern of the sample. As it can be seen, the XRD pattern fit the 33-0843 JCPDS file, corresponding to the Li₂ZrO₃ monoclinic phase. Therefore, the presence of potassium in the sample did not produce any kind of structural variation, at least at the XRD detection limits. A second characterization analysis was performed by SEM (Figure 2). The K-Li₂ZrO₃ sample seemed to be conformed by dense agglomerates of about 20–30 μm, produced by tiny sintered polygonal particles of around 0.5–1 μm (Figure 2A and B). An EDX analysis was performed, in order to verify the presence

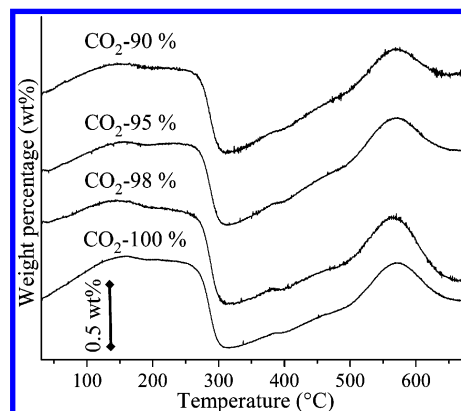


Figure 3. Dynamic thermograms of the K-Li₂ZrO₃ sample, varying the CO₂-O₂ gas mixtures from 100 vol % of CO₂ up to 90–10 vol % of CO₂-O₂.

of potassium in the K-Li₂ZrO₃ sample. It has to be taken into account that this analysis is not able to determine lithium and the fact that it is a punctual analysis. Thus, the average Zr and K abundances, on the particle surface, were 15.9 and 0.6 at %, respectively. Although, this result can not be considered as a global elemental analysis, it confirmed the presence of potassium, at least over the surface of the sample. Additionally, SEM morphological results are in total agreement with the synthesis method and heat-treatment utilized.

Once the K-Li₂ZrO₃ sample was characterized, different dynamic and isothermal analyses were performed, for the CO₂ chemisorption process. These experiments were carried out varying the CO₂-O₂ volume percentage from 100 vol % of CO₂ to 98–2, 95–5, and 90–10 vol % of CO₂-O₂. Dynamic thermogravimetric analyses, varying the CO₂-O₂ vol %, are presented in Figure 3. As it can be seen, between room temperature and 150 °C, K-Li₂ZrO₃ gained weight (~0.3–0.4 wt %), independently of the CO₂-O₂ flow, which may be attributed to a CO₂ capture at the surface of the material. However, it is evident that a sample treated with 100% of CO₂ was the sample that trapped more CO₂. Once, oxygen was added to the gas flow, the amounts of weight gained decreased. These results suggest a CO₂-O₂ competition for being initially sorbed over the K-Li₂ZrO₃ surface. Then, between 150 and 250 °C samples did not present variations on weight. At 250 °C, all the thermograms show a lost of weight, between 0.6 and 0.8 wt % depending on the CO₂-O₂ molar ratio. These results can be explained by the presence of hydroxyls, as potassium is a highly hygroscopic element, where the superficial hydroxyls formation must be produced during the sample exposition to environment, as an autosampler was used.

The carbonation process was evidenced between 320 and 570 °C. From this part of the thermograms, there is a point that should be mentioned. The weight gained seemed to increase as a function of the oxygen content, as follows: 0.66, 0.66, 0.83, and 0.80 wt % for CO₂-O₂ volume percentages of 100–0, 98–2, 95–5, and 90–10 vol %, respectively. This result is important as there is a higher absorption even though the oxygen seems to compete with the CO₂ molecules in order to be sorbed over the K-Li₂ZrO₃ particles. Therefore, it could be proposed that O₂ presence on the gas flow contribute positively to the CO₂ chemisorption. Finally, at higher temperatures than 570 °C all the thermograms showed a lost of weight attributed to the decarbonation process.

In order to further analyze the effect of the oxygen presence on the gas flow, different isothermal experiments were performed on the K-Li₂ZrO₃ sample (Figure 4). Isotherms with

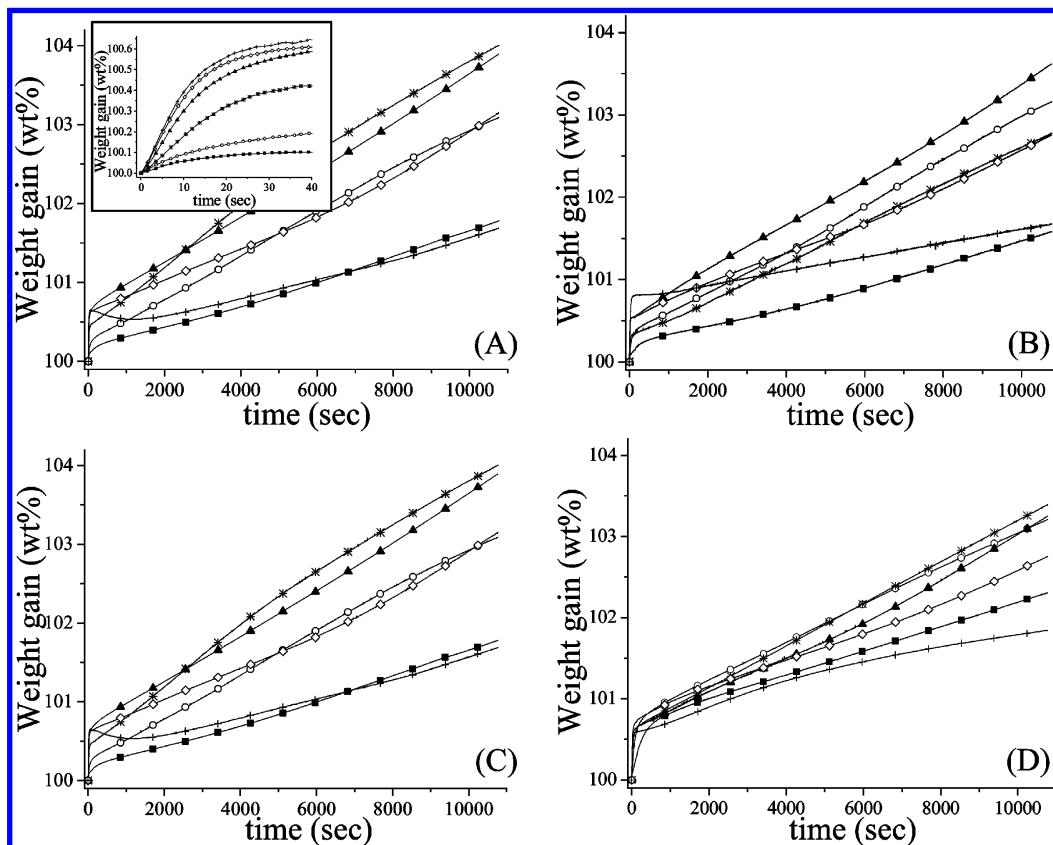


Figure 4. Isotherms of the K-Li₂ZrO₃ sample at different temperatures, varying the CO₂–O₂ gas mixtures: (A) 100 vol % of CO₂, (B) 98–2 vol % of CO₂–O₂, (C) 95–5 vol % of CO₂–O₂, and (D) 90–10 vol % of CO₂–O₂. Each temperature was labeled as follows: (■) 420, (○) 440, (*) 460, (▲) 480, (◇) 500, and (+) 520 °C. The inset in part A corresponds to the first seconds of the same isotherms.

100 vol % of CO₂ are presented in Figure 4A. At short times, the CO₂ chemisorption increased as a function of the isothermal temperature (see inset of Figure 4A), as it could be expected. These results indicate a faster K-Li₂ZrO₃ surface reactivity when the temperature increases. However, at long times the CO₂ chemisorption behavior varied. Between 420 to 460 °C, the CO₂ chemisorption increased as a function of the temperature, chemisorbing up to 4.0 wt % after 11 000 s at 460 °C. After that, the total CO₂ chemisorption decreased as a function of the temperature. While the sample treated at 480 °C chemisorbed 3.9 wt %, the sample treated at 520 °C only chemisorbed 1.7 wt %. These results suggest that CO₂ desorption is being produced at high temperatures (480–520 °C). Then, at these thermal conditions, K-Li₂ZrO₃ is chemisorbing CO₂, but at the same time, the Li₂CO₃ produced during the CO₂ capture on the first moments of the reaction must decompose and desorb CO₂. In fact, the desorption process must be slower than the chemisorption process, kinetically, as the isotherm did not reach the equilibrium and their trend is to continue increasing weight.

Similar behaviors were observed on the isotherms performed varying the CO₂–O₂ vol % as follows: 98–2, 95–5, and 90–10 vol % (Figure 4B–D). In all these cases, the CO₂ chemisorption decrement was detected at 480 °C, as in the previous sample. However, there is an important difference which has to be pointed out: Although the maximum CO₂ chemisorption is always performed at around 460–480 °C, it decreased as a function of the oxygen content, from 4.01 to 3.39 wt %, varying the CO₂–O₂ flow from 100 to 0 to 90–10 vol %.

For this kind of process, isothermal plots have been usually fitted to double (eq 2) or triple (eq 3) exponential models, as there are two or three different processes taking place. CO₂

chemisorption is produced under two different conditions: Initially, CO₂ is chemisorbed directly on the K-Li₂ZrO₃ surface particles (process 1). Then, once the carbonate–oxide external shell is produced, CO₂ chemisorption is kinetically controlled by diffusion processes (process 2). It has to be mentioned that diffusion processes have been usually associated to lithium diffusion from the bulk to the surface of the particles, without taking into account the oxygen requirements. Finally, in those cases where CO₂ desorption process is presented, the triple exponential model was utilized (process 3).^{10,16–18}

$$y = A \exp^{-k_1 t} + B \exp^{-k_2 t} + D \quad (2)$$

$$y = A \exp^{-k_1 t} + B \exp^{-k_2 t} - C \exp^{-k_3 t} + D \quad (3)$$

where, y represents the weight percentage of CO₂ chemisorbed, t is the time, k_1 is the kinetic constant for the CO₂ direct chemisorption over the Li₂ZrO₃ particles, k_2 is the kinetic constant for the CO₂ chemisorption kinetically controlled by diffusion processes, and k_3 is the kinetic constant for the CO₂ desorption. Additionally, the pre-exponential factors A , B , and C indicate the intervals in which each process controls the whole CO₂ chemisorption–desorption process, and the D constant indicates the y -intercept.

As it was described qualitatively, all these isothermal experiments fitted to one of these two exponential models and the different constants obtained are presented in the Table 1. From this table, it is evident that CO₂ direct chemisorption constants values (k_1) are at least 2 orders of magnitude larger than CO₂ chemisorption kinetically controlled by diffusion processes (k_2), in agreement to previous reports.^{10,16–18} It means that the second CO₂ chemisorption process is the limiting step. Additionally,

Table 1. Kinetic Constant Values for the CO₂ Chemisorption Processes and Desorption on K-Li₂ZrO₃, Varying Temperature and Using Different CO₂–O₂ Mixture Gases

temp (°C)	100 vol % of CO ₂				98 vol % of CO ₂			
	k_1 (1/s)	k_2 (1/s)	k_3 (1/s)	R^2	k_1 (1/s)	k_2 (1/s)	k_3 (1/s)	R^2
420	6.0×10^{-2}	6.2×10^{-6}		0.9154	1.5×10^{-2}	6.0×10^{-6}		0.9004
440	4.4×10^{-2}	4.4×10^{-5}		0.9531	2.4×10^{-2}	2.2×10^{-5}		0.94751
460	5.6×10^{-2}	5.3×10^{-5}		0.9016	5.5×10^{-2}	3.0×10^{-5}		0.9356
480	7.0×10^{-2}	8.1×10^{-5}	7.2×10^{-5}	0.9724	7.9×10^{-2}	2.7×10^{-5}		0.9551
500	9.3×10^{-2}	1.1×10^{-4}	1.2×10^{-4}	0.9822	11.2×10^{-2}	4.2×10^{-5}	2.6×10^{-4}	0.9412
520	9.5×10^{-2}	9.8×10^{-4}	6.3×10^{-5}	0.8421	5.6×10^{-2}	6.1×10^{-5}	1.1×10^{-4}	0.8942
	95 vol % of CO ₂				90 vol % of CO ₂			
	k_1 (1/s)	k_2 (1/s)	k_3 (1/s)	R^2	k_1 (1/s)	k_2 (1/s)	k_3 (1/s)	R^2
420	1.8×10^{-3}	4.2×10^{-5}		0.9451	4.3×10^{-3}	2.4×10^{-5}		0.8512
440	2.8×10^{-2}	4.5×10^{-5}		0.9941	1.2×10^{-2}	3.1×10^{-5}		0.9014
460	4.4×10^{-2}	4.4×10^{-5}		0.9415	2.9×10^{-2}	3.3×10^{-5}		0.9412
480	6.3×10^{-2}	3.2×10^{-5}		0.9321	5.8×10^{-2}	4.3×10^{-5}		0.9114
500	5.1×10^{-2}	5.4×10^{-5}		0.9005	6.3×10^{-2}	4.4×10^{-5}	1.7×10^{-4}	0.8873
520	6.1×10^{-2}	8.7×10^{-5}	8.1×10^{-3}	0.8745	10.5×10^{-2}	7.8×10^{-5}	4.4×10^{-5}	0.9123

the CO₂ desorption constant values (k_3) are always smaller than direct CO₂ chemisorption (k_1). It confirms the qualitative description given above about the difference on the CO₂ chemisorption and desorption processes. It has to be pointed out that isotherms performed with a CO₂ flow of 100 vol % presented the largest k_2 temperature dependence (Table 1). It may be explained as follows. At this CO₂–O₂ flow condition, there is not competition between CO₂ and O₂ for being initially sorbed over the K-Li₂ZrO₃ surface, so CO₂ seemed to be chemisorbed more rapidly; for example, at 420 °C k_1 is at least two times faster with 100 vol % of CO₂ than in any other CO₂–O₂ flow. Therefore, the results should contribute to a faster activation of the chemisorption kinetically controlled by diffusion processes (k_2).

In order to completely analyze these data, k_1 and k_2 constant values were fitted to the Eyring's model (eq 4) to elucidate their temperature dependency.

$$\ln(k/T) = -(\Delta H^\ddagger/R)(1/T) + \ln E + \Delta S^\ddagger/R \quad (4)$$

where k is the rate constant value and E represents a pre-exponential factor, which in Eyring's formulation is equal to the ratio of Boltzmann's constant to Planck's constant and ΔH^\ddagger and ΔS^\ddagger are the activation enthalpy and entropy, respectively.

The effect of temperature on the rate constants of CO₂ direct chemisorption and CO₂ chemisorption kinetically controlled by diffusion processes, varying the CO₂–O₂ volume ratio, are illustrated in Figure 5A and B. Fitting these data to linear plots gave the activation enthalpies (ΔH^\ddagger) for the different processes, which are plotted, as well, in the Figure 5C. Initially, when CO₂ chemisorption on K-Li₂ZrO₃ was performed in a saturated CO₂ atmosphere (CO₂ 100 vol %), the ΔH^\ddagger values obtained were 5.8 and 43 kJ/mol for the CO₂ direct chemisorption reaction and CO₂ chemisorption controlled by diffusion processes, respectively. These results clearly show that CO₂ chemisorption controlled by diffusion processes is more dependent on temperature than CO₂ direct chemisorption. However, when oxygen was added to the CO₂ flow, these tendencies changed notably. For a CO₂–O₂ flow of 98–2 vol %, the two ΔH^\ddagger values became similar: 16.9 and 19.9 kJ/mol for the CO₂ direct chemisorption reaction and the CO₂ chemisorption controlled by diffusion processes, respectively. Here, two different effects were produced, a significant increment of the temperature dependency of the CO₂ direct chemisorption, and perhaps the most important, a decrement of the temperature dependency of the CO₂ chemisorption kinetically controlled by

diffusion processes. The increment of the temperature dependency of the CO₂ direct chemisorption may be explained in terms of CO₂ saturation over the K-Li₂ZrO₃ surface particles. As there are O₂ molecules present on the gas, they must compete

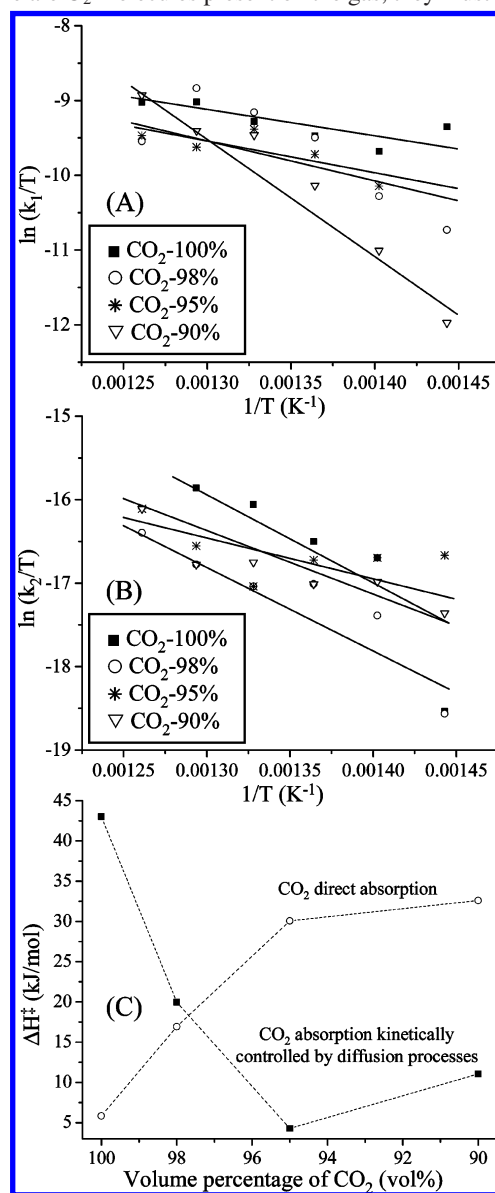


Figure 5. Eyring's plots for the rate constant values of the two CO₂ chemisorption processes: direct (A) and kinetically controlled by diffusion processes (B). Plot of the ΔH^\ddagger values of both processes as a function of the oxygen content (C).

with the CO₂ molecules for some places on the particle surface. Nevertheless, the most important feature corresponds to the decrement of the temperature dependency of the CO₂ chemisorption kinetically controlled by diffusion processes. In this case, as CO₂ chemisorption is controlled through a bulk process (diffusion), it can not be attributed to the same molecule competition. Therefore, the presence of oxygen must be changing the bulk diffusion process in some way, which is directly correlated to this second CO₂ chemisorption process. The carbonation process implies that two lithium atoms and one oxygen atom, from the Li₂ZrO₃ crystal, react with CO₂ to produce Li₂CO₃. In other words, the diffusion process not only corresponds to the lithium atoms, but one-third of the oxygen atoms as well. In the first moments of the CO₂ chemisorption, there are lithium and oxygen atoms on the Li₂ZrO₃ surface, and then reaction occurs directly. However, once the carbonate–oxide shell is formed, lithium and oxygen atoms must diffuse, from the bulk to the surface, in order to continue the CO₂ chemisorption. Hence, if the gas flow contains oxygen, its diffusion might be reduced or even not needed. This may explain why this process is not as dependent on temperature as in the previous system reaction. These interpretations were confirmed increasing the oxygen contents to 95–5 and 90–10 vol % of CO₂–O₂ vol %, respectively. In those cases, while the ΔH^\ddagger values of the CO₂ direct chemisorption reaction continued increasing (30.1 and 32.6 kJ/mol for CO₂–O₂ volume ratios of 95–5 and 90–10 vol %), ΔH^\ddagger values of the CO₂ chemisorption controlled by diffusion processes decreased to 4.3 and 11.0 kJ/mol. As it can be seen, in these conditions, the CO₂ direct chemisorption reaction is more dependent on temperature than CO₂ kinetically controlled by diffusion processes.

Conclusions

CO₂ absorption kinetics, of K–Li₂ZrO₃ under different CO₂–O₂ gas flows, was analyzed in this work. First, the sample was prepared by a solid-state reaction and then characterized to obtain composition and morphological properties. Dynamic thermogravimetric experiments, of the CO₂ capture process on different CO₂–O₂ gas flows, suggested that O₂ addition into the gas mixtures improve the CO₂ chemisorption, when it is kinetically controlled by diffusion processes. Therefore, different isothermal experiments were performed. From the last experiments, it could be said that oxygen addition into the gas flow changes the thermal dependency of the CO₂ chemisorption on K–Li₂ZrO₃. It was identified measuring the ΔH^\ddagger values. The presence of oxygen produced a reduction of the temperature dependency of the CO₂ chemisorption kinetically controlled by diffusion processes, which involves lithium and oxygen diffusion during the lithium carbonate formation. Conversely, the presence of oxygen over the K–Li₂ZrO₃ particles partially inhibits the CO₂ chemisorption process, due to a CO₂–O₂ competition to occupy the Li₂ZrO₃ surface, so the CO₂ chemisorption reaction becomes more dependent on temperature.

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