Effect of Oxygen Addition on the Thermokinetic Properties of CO_2 Chemisorption on Li_2ZrO_3

Lorena Martínez-dlCruz and Heriberto Pfeiffer*,†

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito exterior s/n, Cd. Universitaria, Del. Coyoacán, CP 04510, México D.F., Mexico

Lithium zirconate doped with potassium (K-Li_2ZrO_3) was synthesized by solid-state reaction and then its CO_2 chemisorption capacity was evaluated using different CO_2-O_2 gas mixtures. These experiments were performed in order to evaluate the effect produced by the O_2 on the kinetic parameters and on the CO_2 absorption reaction mechanism. Although the CO_2 capture dynamic experiments did not show significant variations as a function of the O_2 content, isothermal experiments and their fitting to the Eyring's model did. Different enthalpy activation ($\Delta H^{\ddagger}$) values were estimated for the CO_2 chemisorption process, as CO_2 capture is produced by two processes: Initially, the CO_2 chemisorption occurs directly over the K-Li_2ZrO_3 surface. Then, once a $Li_2CO_3-ZrO_2$ external shell is produced, CO_2 chemisorption is kinetically controlled by diffusion processes, which must imply the lithium and oxygen diffusion. The $\Delta H^{\ddagger}$ values, of the CO_2 direct chemisorption, increased as a function of the O_2 content. It was explained in terms of a CO_2-O_2 competition to occupy the Li_2ZrO_3 surface. On the other hand, the $\Delta H^{\ddagger}$ values, of the CO_2 chemisorption kinetically controlled by diffusion processes, decreased as a function of the O_2 content. This result confirmed the oxygen diffusion dependency of the CO_2 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*-Li_2ZrO_3) was able to trap carbon dioxide (CO_2), several works have been focused on this ceramic,[2–9] or other lithium ceramics[10–16] as CO_2 captors.

m-Li_2ZrO_3 captures CO_2, chemically, at high temperatures (reaction 1), producing lithium carbonate (Li_2CO_3) and zirconium oxide (ZrO_2). An advantage of this system is the fact that reaction is reversible; in other words, Li_2ZrO_3 can be regenerated.

$$Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2 \quad (1)$$

After the initial publication mentioned above, the same and other authors showed that the CO_2 chemisorption process can be importantly improved if the ceramic is doped with potassium (K-doped Li_2ZrO_3).[2–5,9] All the papers explained this behavior due to CO_2 diffusion through a molten lithium−potassium carbonate. Later, it was shown a different way to increase the CO_2 chemisorption on the Li_2ZrO_3. Ochoa-Fernández et al. showed that the tetragonal phase, *t*-Li_2ZrO_3, is much more reactive than the monoclinic phase, as a CO_2 captor.[6–8]

In both cases, as in other lithium ceramics where CO_2 capture occurs chemically, the reaction mechanism proposed is described as follows. Initially, the Li_2ZrO_3 particles react with CO_2 only at the surface. This superficial reaction involves the formation of a $Li_2CO_3-ZrO_2$ external shell. Then, in order to continue the CO_2 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 CO_2 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 CO_2 chemisorption reaction on Li_2ZrO_3. Into a saturated CO_2 atmosphere, lithium carbonate formation implies that one of each three oxygen atoms, present originally in the Li_2ZrO_3 ceramic, must become part of the Li_2CO_3. Consequently, oxygen diffusion must be involved as well on the reaction mechanism, and not only lithium and/or CO_2 diffuse.

Therefore, the aim of this work was to elucidate if oxygen addition to the gas flow modifies the thermokinetic properties of the CO_2 capture process on Li_2ZrO_3. Li_2ZrO_3 was chosen as a case of study because this ceramic is one of the most studied ceramics as a CO_2 captor.

Experimental Section

K-doped lithium zirconate, labeled as K-Li_2ZrO_3, was synthesized by solid-state reaction, using zirconium oxide (ZrO_2, Aldrich with 99% purity), lithium carbonate (Li_2CO_3, Aldrich with 99+% purity) and potassium carbonate (K_2CO_3, Aldrich with 99% purity). The Li_2CO_3:ZrO_2:K_2CO_3 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-Li_2ZrO_3 sample was heat-treated dynamically, with a heating rate of 5 °C/min from room temperature to 670 °C with different gas-mixtures; CO_2 (100 vol %) and three different CO_2-O_2 mixtures (98−2, 95−5, and 90−10 vol %), using in all the cases a total flow rate of

* To whom correspondence should be addressed. Tel.: +52 (55) 5622 4627. Fax: +52 (55) 5616 1371. E-mail: pfeiffer@iim.unam.mx.
† Member of the American Chemical Society.

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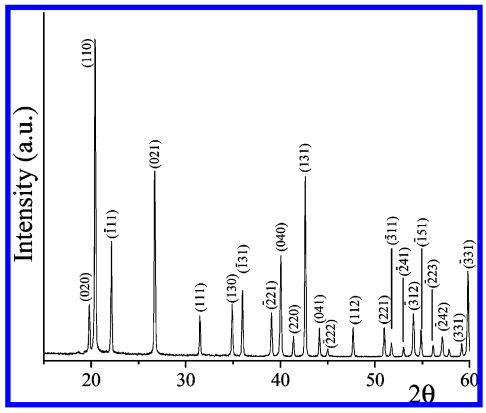

Figure 1. XRD pattern of the K-Li_2ZrO_3 sample.

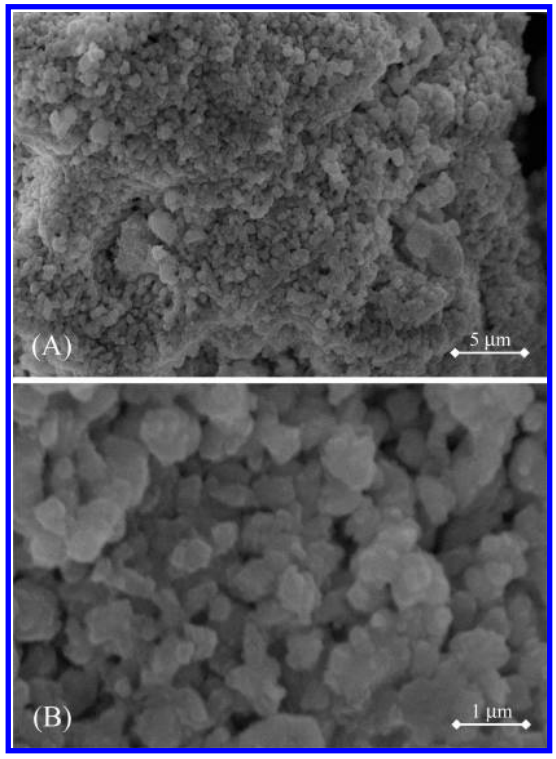

Figure 2. Secondary electron images of the K-Li_2ZrO_3 sample at two different magnifications.

150 mL/min. Both gases, CO_2 and O_2, were provided by Praxair with the following grades of purity: 4.0 and 4.8, respectively. Then, the K-Li_2ZrO_3 sample was tested isothermically at different temperatures, under the same CO_2 and CO_2-O_2 flows. All the gas mixtures were digitally prepared into a Chem-flow gas mixer from Bel-Japan.

Results and Discussion

Initially, a K-Li_2ZrO_3 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 Li_2ZrO_3 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-Li_2ZrO_3 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

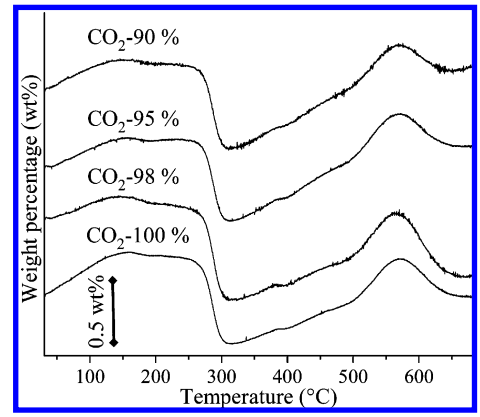

Figure 3. Dynamic thermograms of the K-Li_2ZrO_3 sample, varying the CO_2-O_2 gas mixtures from 100 vol % of CO_2 up to 90−10 vol % of CO_2-O_2.

of potassium in the K-Li_2ZrO_3 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-Li_2ZrO_3 sample was characterized, different dynamic and isothermal analyses were performed, for the CO_2 chemisorption process. These experiments were carried out varying the CO_2-O_2 volume percentage from 100 vol % of CO_2 to 98−2, 95−5, and 90−10 vol % of CO_2-O_2. Dynamic thermogravimetric analyses, varying the CO_2-O_2 vol %, are presented in Figure 3. As it can be seen, between room temperature and 150 °C, K-Li_2ZrO_3 gained weight (∼0.3−0.4 wt %), independently of the CO_2-O_2 flow, which may be attributed to a CO_2 capture at the surface of the material. However, it is evident that a sample treated with 100% of CO_2 was the sample that trapped more CO_2. Once, oxygen was added to the gas flow, the amounts of weight gained decreased. These results suggest a CO_2-O_2 competition for being initially sorbed over the K-Li_2ZrO_3 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 CO_2-O_2 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 CO_2-O_2 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 CO_2 molecules in order to be sorbed over the K-Li_2ZrO_3 particles. Therefore, it could be proposed that O_2 presence on the gas flow contribute positively to the CO_2 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-Li_2ZrO_3 sample (Figure 4). Isotherms with

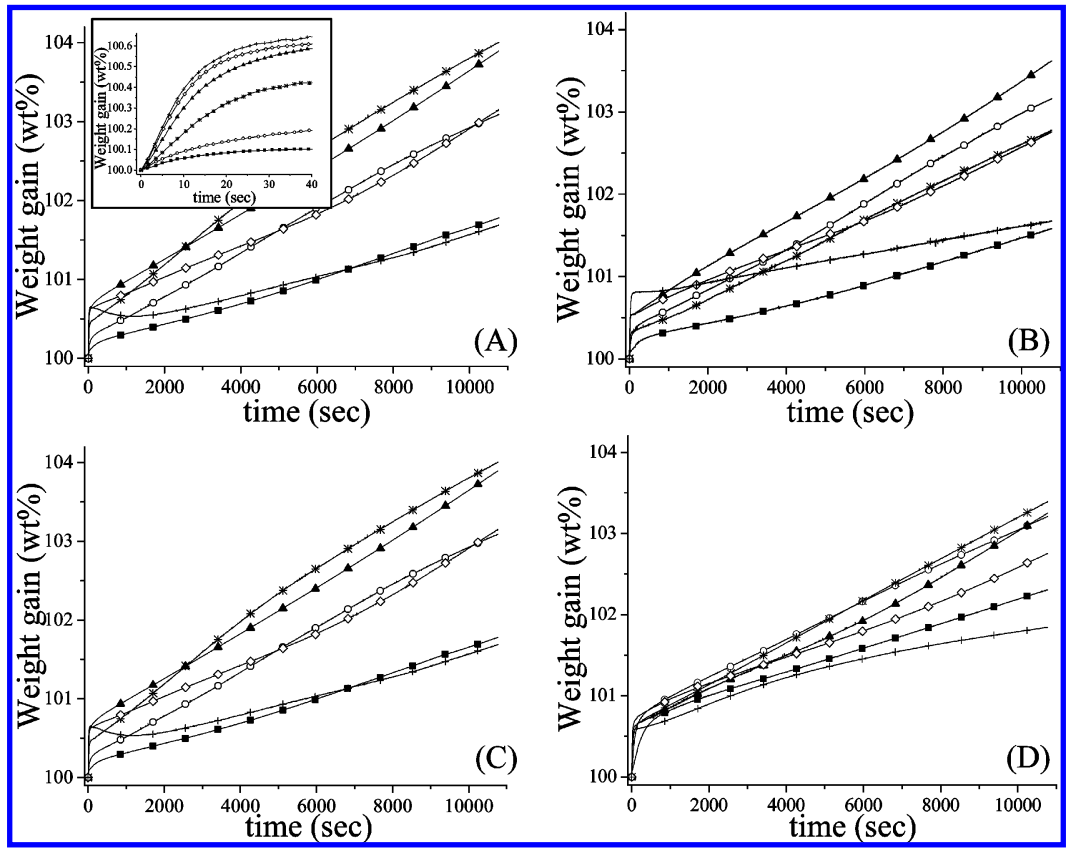

Figure 4. Isotherms of the K-Li_2ZrO_3 sample at different temperatures, varying the CO_2-O_2 gas mixtures: (A) 100 vol % of CO_2, (B) 98−2 vol % of CO_2-O_2, (C) 95−5 vol % of CO_2-O_2, and (D) 90−10 vol % of CO_2-O_2. Each temperature was labeled as follows: (■) 420, (○) 440, (∗) 460, (▲) 480, (◇) 500, and (+) 520 °C. The inset in part A corresponds to the first seconds of the same isotherms.

100 vol % of CO_2 are presented in Figure 4A. At short times, the CO_2 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-Li_2ZrO_3 surface reactivity when the temperature increases. However, at long times the CO_2 chemisorption behavior varied. Between 420 to 460 °C, the CO_2 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 CO_2 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 suggests that CO_2 desorption is being produced at high temperatures (480−520 °C). Then, at these thermal conditions, K-Li_2ZrO_3 is chemisorbing CO_2, but at the same time, the Li_2CO_3 produced during the CO_2 capture on the first moments of the reaction must decompose and desorbs CO_2. In fact, the desorption process must be slower than the chemisorption process, kinetically, as the isotherm did not reached the equilibrium and their trend is to continue increasing weight.

Similar behaviors were observed on the isotherms performed varying the CO_2-O_2 vol % as follows: 98−2, 95−5, and 90−10 vol % (Figure 4B−D). In all these cases, the CO_2 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 CO_2 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 CO_2-O_2 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. CO_2 chemisorption is produced under two different conditions: Initially, CO_2 is chemisorbed directly on the K-Li_2ZrO_3 surface particles (process 1). Then, once the carbonate−oxide external shell is produced, CO_2 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 CO_2 desorption process is presented, the triple exponential model was utilized (process 3).[10,16–18]

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

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

where, y represents the weight percentage of CO_2 chemisorbed, t is the time, k_1 is the kinetic constant for the CO_2 direct chemisorption over the Li_2ZrO_3 particles, k_2 is the kinetic constant for the CO_2 chemisorption kinetically controlled by diffusion processes, and k_3 is the kinetic constant for the CO_2 desorption. Additionally, the pre-exponential factors A, B, and C indicate the intervals in which each process controls the whole CO_2 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 CO_2 direct chemisorption constants values (k_1) are at least 2 orders of magnitude larger than CO_2 chemisorption kinetically controlled by diffusion processes (k_2), in agreement to previous reports.[10,16–18] It means that the second CO_2 chemisorption process is the limiting step. Additionally,

Table 1. Kinetic Constant Values for the CO_2 Chemisorption Processes and Desorption on K-Li_2ZrO_3, Varying Temperature and Using Different CO_2-O_2 Mixture Gases

	100 vol % of CO_2				98 vol % of CO_2			
temp (°C)	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			
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 CO_2 desorption constant values (k_3) are always smaller than direct CO_2 chemisorption (k_1). It confirms the qualitative description given above about the difference on the CO_2 chemisorption and desorption processes. It has to be pointed out that isotherms performed with a CO_2 flow of 100 vol % presented the largest k_2 temperature dependence (Table 1). It may be explained as follows. At this CO_2-O_2 flow condition, there is not competition between CO_2 and O_2 for being initially sorbed over the K-Li_2ZrO_3 surface, so CO_2 seemed to be chemisorbed more rapidly; for example, at 420 °C k_1 is at least two times faster with 100 vol % of CO_2 than in any other CO_2-O_2 flow. Therefore, the results should contribute to a faster activation of the chemisorption kinetically controlled by diffusion processes (k_2). In other words, once O_2 was added to the gas flow, CO_2 absorption became slower, even at the K-Li_2ZrO_3 surface, decreasing the CO_2 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.

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

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 $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activation enthalpy and entropy, respectively.

The effect of temperature on the rate constants of CO_2 direct chemisorption and CO_2 chemisorption kinetically controlled by diffusion processes, varying the CO_2-O_2 volume ratio, are illustrated in Figure 5A and B. Fitting these data to linear plots gave the activation enthalpies ($\Delta H^{\ddagger}$) for the different processes, which are plotted, as well, in the Figure 5C. Initially, when CO_2 chemisorption on K-Li_2ZrO_3 was performed in a saturated CO_2 atmosphere (CO_2 100 vol %), the $\Delta H^{\ddagger}$ values obtained were 5.8 and 43 kJ/mol for the CO_2 direct chemisorption reaction and CO_2 chemisorption controlled by diffusion processes, respectively. These results clearly show that CO_2 chemisorption controlled by diffusion processes is more dependent on temperature than CO_2 direct chemisorption. However, when oxygen was added to the CO_2 flow, these tendencies changed notably. For a CO_2-O_2 flow of 98−2 vol %, the two $\Delta H^{\ddagger}$ values became similar: 16.9 and 19.9 kJ/mol for the CO_2 direct chemisorption reaction and the CO_2 chemisorption controlled by diffusion processes, respectively. Here, two different effects were produced, a significant increment of the temperature dependency of the CO_2 direct chemisorption, and perhaps the most important, a decrement of the temperature dependency of the CO_2 chemisorption kinetically controlled by diffusion processes. The increment of the temperature dependency of the CO_2 direct chemisorption may be explained in terms of CO_2 saturation over the K-Li_2ZrO_3 surface particles. As there are O_2 molecules present on the gas, they must compete

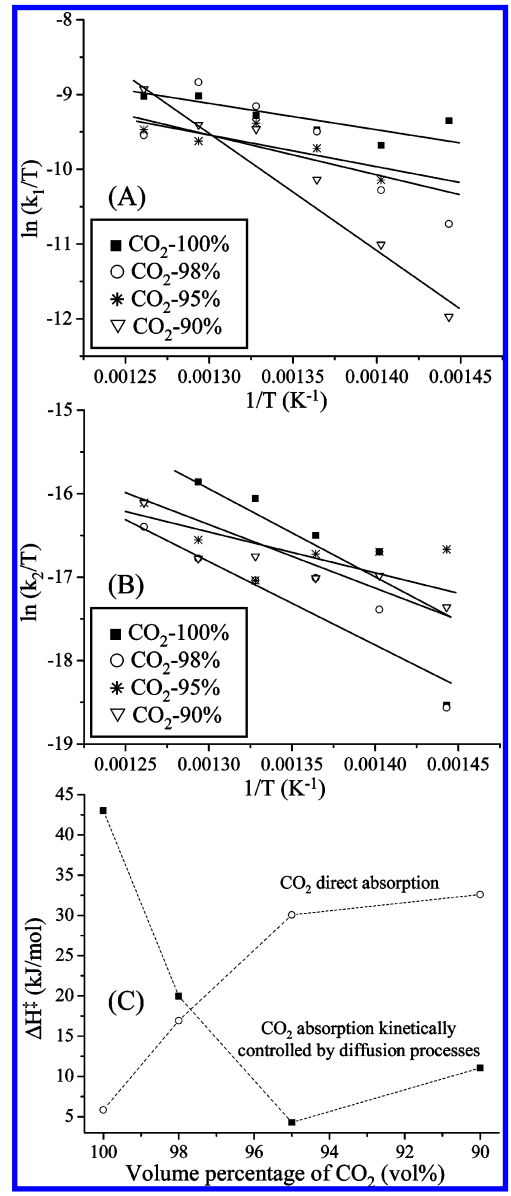

Figure 5. Eyring's plots for the rate constant values of the two CO_2 chemisorption processes: direct (A) and kinetically controlled by diffusion processes (B). Plot of the $\Delta H^{\ddagger}$ values of both processes as a function of the oxygen content (C).

with the CO_2 molecules for some places on the particle surface. Nevertheless, the most important feature corresponds to the decrement of the temperature dependency of the CO_2 chemisorption kinetically controlled by diffusion processes. In this case, as CO_2 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 CO_2 chemisorption process. The carbonation process implies that two lithium atoms and one oxygen atom, from the Li_2ZrO_3 crystal, react with CO_2 to produce Li_2CO_3. 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 CO_2 chemisorption, there are lithium and oxygen atoms on the Li_2ZrO_3 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 CO_2 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 CO_2−O_2 vol %, respectively. In those cases, while the $\Delta H^{\ddagger}$ values of the CO_2 direct chemisorption reaction continued increasing (30.1 and 32.6 kJ/mol for CO_2−O_2 volume ratios of 95−5 and 90−10 vol %), $\Delta H^{\ddagger}$ values of the CO_2 chemisorption controlled by diffusion processes decreased to 4.3 and 11.0 kJ/mol. As it can be seen, in these conditions, the CO_2 direct chemisorption reaction is more dependent on temperature than CO_2 kinetically controlled by diffusion processes.

Conclusions

CO_2 absorption kinetics, of K-Li_2ZrO_3 under different CO_2−O_2 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 CO_2 capture process on different CO_2−O_2 gas flows, suggested that O_2 addition into the gas mixtures improve the CO_2 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 CO_2 chemisorption on K-Li_2ZrO_3. It was identified measuring the $\Delta H^{\ddagger}$ values. The presence of oxygen produced a reduction of the temperature dependency of the CO_2 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-Li_2ZrO_3 particles partially inhibits the CO_2 chemisorption process, due to a CO_2−O_2 competition to occupy the Li_2ZrO_3 surface, so the CO_2 chemisorption reaction becomes more dependent on temperature.

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