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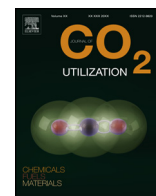


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Thermokinetic and microstructural analyses of the CO₂ chemisorption on K₂CO₃–Na₂ZrO₃

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ABSTRACT

Sodium zirconate (Na₂ZrO₃) was synthesized via a solid-state reaction. Subsequently, a portion of the prepared Na₂ZrO₃ was mechanically mixed with 5 wt.% potassium carbonate (K₂CO₃). The Na₂ZrO₃ and K–Na₂ZrO₃ samples were characterized, and the CO₂ capture processes were evaluated. The potassium addition did not modify the structural or microstructural characteristics of the Na₂ZrO₃. However, during CO₂ chemisorption, the material presented some important variations that depended on the potassium addition. The maximum CO₂ capture of the Na₂ZrO₃ sample was observed at $T \geq 550$ °C, while the CO₂ capture of the K–Na₂ZrO₃ sample was significantly favored at 400 °C. According to DSC analysis, the CO₂ capture increase observed at lower temperatures was due to the formation of a K–Na carbonate eutectic phase. Additionally, for the samples demonstrating effective CO₂ capture at relatively low temperatures, SEM microstructural analysis demonstrated the formation of a Na₂CO₃–ZrO₂ mesoporous external shell. Moreover, some kinetic parameters were determined. The isothermal data were fitted to a double exponential model related to the direct CO₂ chemisorption (k_1) and diffusion processes (k_2). The K–Na₂ZrO₃ sample presented higher k_1 and k_2 values than Na₂ZrO₃ at all temperatures investigated, confirming that the potassium addition improved the CO₂ capture process. Further, the potassium in Na₂ZrO₃ significantly enhanced the CO₂ capture at approximately 400 °C, in comparison to the Na₂ZrO₃ sample. Finally, it was observed that potassium negatively compromised the chemisorption of CO₂ after several cycles, due to potassium segregation and sublimation.

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1. Introduction

In recent decades, the increase in greenhouse gas (GHG) levels in the atmosphere has focused international attention on global warming. Among the various GHGs, CO₂ is the largest contributor with respect to its present content in the atmosphere [1,2].

There are three options for reducing the total CO₂ emitted into the atmosphere, including the use of renewable energy, reductions in CO₂ emissions and enhanced CO₂ sequestration. The first option requires a decrease in the amount of energy consumed, for example, by using energy more efficiently. The second option requires switching to the use of renewable energy sources and non-fossil fuels, such as hydrogen. The third option involves the development of technologies to capture and sequester CO₂ at high concentrations [1,2]. In the case of the third option, several materials have been proposed and analyzed as possible CO₂ captors. The materials proposed include zeolites, activated carbons, hydrotalcites, supported amines and different alkaline and earth alkaline ceramics as promising CO₂ captors due to their favorable sorption behaviors [3–7].

Among the proposed alkaline ceramics, lithium and sodium zirconates (Li₂ZrO₃ [8–13] and Na₂ZrO₃ [14–19]) have attracted the attention of researchers due to their adequate thermal stability and sorption capacity, as well as the ease of fabrication of these materials. This behavior is attributed to their excellent thermal stability, kinetics and CO₂ capture capacity. Specifically, Na₂ZrO₃ exhibits some of the most promising characteristics as a possible CO₂ captor. For example, Na₂ZrO₃ presents better CO₂ capture efficiencies in comparison to lithium-based absorbents [10,14–17,20–22]. Despite the importance of this application, this material has not been deeply analyzed.

However, it has been demonstrated that the CO₂ chemisorption process can be significantly improved in lithium ceramics following the addition of sodium or potassium carbonates [23–26]. The process of CO₂ chemisorption on this mixed alkaline ceramic-carbonate produces a molten carbonate phase, decreasing the partial fusion temperature and increasing the various diffusion processes involved in the CO₂ capture reaction mechanism as a result [17,27]. Therefore, the aim of the present work is to evaluate the CO₂ chemisorption process in the K₂CO₃–Na₂ZrO₃ system at different temperatures. In particular, the microstructural, kinetic and regeneration changes produced in the ceramic are analyzed.

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2. Experimental

Sodium zirconate (Na_2ZrO_3) was prepared via a solid-state reaction. Zirconium oxide (ZrO_2 , Aldrich) and sodium carbonate (Na_2CO_3 , Aldrich) were mechanically mixed and heat treated at 850 °C for 12 h. For the Na_2CO_3 case, an excess of 10 wt.% was used to compensate the sublimation of sodium during the reaction time [15]. After Na_2ZrO_3 synthesis, part of this sample was mechanically mixed with 5 wt.% potassium carbonate (K_2CO_3 , Aldrich). The samples were labeled as follows: the pure sodium zirconate was named Na_2ZrO_3 , and the potassium containing sample was labeled $\text{K-Na}_2\text{ZrO}_3$.

The Na_2ZrO_3 and $\text{K-Na}_2\text{ZrO}_3$ samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption. To obtain X-ray diffraction patterns, a diffractometer (Bruker AXS, D8 Advance) coupled to a copper anode X-ray tube was used. The compounds were identified by the corresponding JCPDS files (Joint Committee Powder Diffraction Standards). The microstructural characteristics of Na_2ZrO_3 and $\text{K-Na}_2\text{ZrO}_3$ before and after the CO_2 capture process were determined using N_2 adsorption/desorption and SEM. For the N_2 adsorption/desorption experiments, the isotherms were acquired in a Bel-Japan Minisorp II at 77 K using a multipoint technique. The samples were degassed at room temperature for 24 h under vacuum prior to analysis. Then, the SEM images were taken on a JEOL JMS-7600F microscope.

Different CO_2 chemisorption experiments (dynamic and isothermal) were performed using a Q500HR instrument from TA Instruments. Initially, the sodium zirconate samples were dynamically heated from room temperature to 850 °C under a CO_2 atmosphere at 5 °C/min. Then, isothermal experiments were performed to evaluate the effect of potassium on the Na_2ZrO_3 - CO_2 reaction mechanism. For isothermal analysis, the samples were initially heated to 850 °C at 50 °C/min with a subsequent isothermal treatment of 15 min under N_2 flow. This procedure was conducted to ensure that all of the samples received an equivalent sintering process prior to performing the CO_2 chemisorption isotherms. Additionally, this heating process desorbed all of the water and CO_2 previously trapped in the samples as a result of the handling processes. After this heating process, each sample was cooled to the respective isothermal temperature to perform an independent CO_2 chemisorption process. Once the sample reached the corresponding temperature, the gas flow was switched from N_2 to CO_2 , and the isothermal experiments were performed using a gas flow rate of 60 mL/min. Some of the Na_2ZrO_3 - CO_2 isothermal products were re-characterized microstructurally using SEM. Finally, Na_2ZrO_3 and $\text{K-Na}_2\text{ZrO}_3$ samples, as well as some of the Na_2ZrO_3 - CO_2 and $\text{K-Na}_2\text{ZrO}_3$ - CO_2 isothermal products, were characterized by thermogravimetric (TGA and DTG) and differential

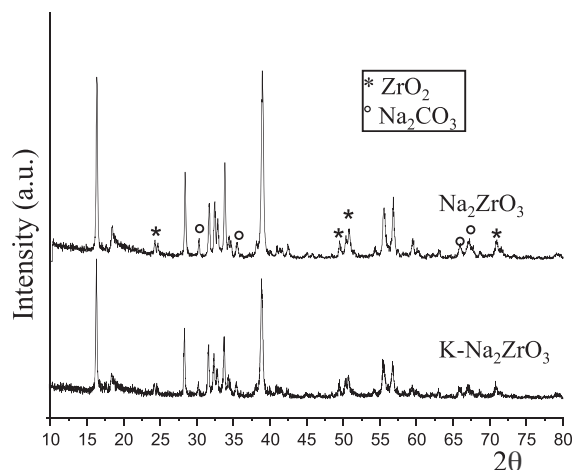


Fig. 1. XRD patterns of the Na_2ZrO_3 and $\text{K-Na}_2\text{ZrO}_3$ samples prepared via a solid-state reaction. The secondary phases were labeled with different symbols.

scanning calorimetry (DSC). These experiments were carried out using a previously described thermogravimetric set-up (using N_2 as carrier gas) with DSC equipment from Instrument Specialists Inc. For the DSC experiments, the samples were heated from room temperature to 600 °C at 20 °C/min under an inert argon atmosphere. Finally, different multicycle CO_2 chemisorption-desorption experiments were performed at 400 and 700 °C (chemisorption) and 850 °C (desorption) to elucidate the thermal stability and cyclic performance of both samples.

3. Results and discussion

To establish the structural and microstructural characteristics of both sodium zirconates (Na_2ZrO_3 and $\text{K-Na}_2\text{ZrO}_3$), the samples were analyzed by XRD, SEM and N_2 adsorption. Fig. 1 shows the XRD patterns of the Na_2ZrO_3 and $\text{K-Na}_2\text{ZrO}_3$ samples after thermal treatment at 850 °C and the corresponding potassium addition. The diffraction patterns fitted to JCPDS file 35-0770 corresponds to monoclinic Na_2ZrO_3 , although the presence of ZrO_2 and Na_2CO_3 was also observed. The presence of these secondary phases can be attributed to the CO_2 chemisorption process, producing these phases during sample handling, or to an incomplete solid-state reaction process. Additionally, the $\text{K-Na}_2\text{ZrO}_3$ diffraction pattern showed was very similar to that of Na_2ZrO_3 , as the K_2CO_3 concentration was insufficient for quantification by this technique.

The morphologies and particle sizes of the samples were analyzed by SEM (Fig. 2). Na_2ZrO_3 and $\text{K-Na}_2\text{ZrO}_3$ presented similar morphologies and particle sizes. The particles presented dense

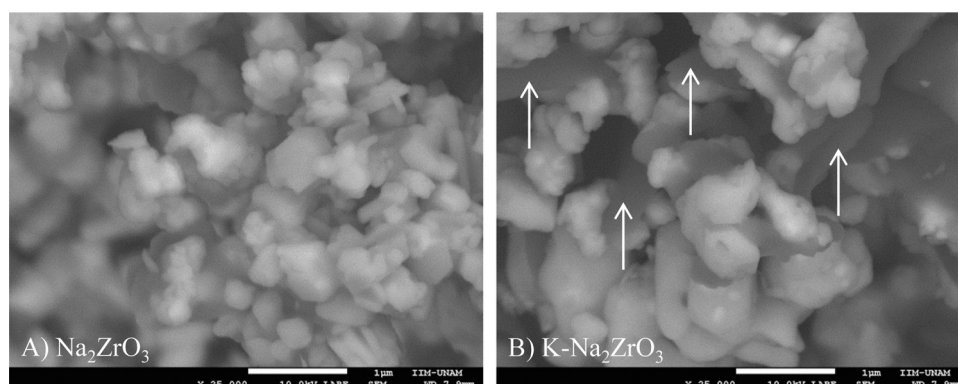


Fig. 2. Backscattered electron images of the Na_2ZrO_3 (A) and $\text{K-Na}_2\text{ZrO}_3$ (B) samples. The arrows indicates the presence of flat dark particles associated to the K_2CO_3 .

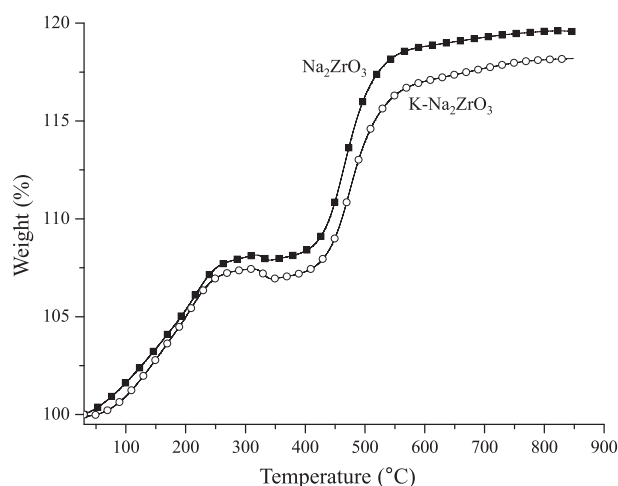


Fig. 3. Dynamic thermogravimetric curves of Na₂ZrO₃ and K-Na₂ZrO₃ samples, between 30 and 850 °C into a CO₂ flux.

polyhedral morphologies with an average particle size of approximately 500–800 nm. These particles produced agglomerates measuring approximately 5 μm. In the K-Na₂ZrO₃ sample, some flat dark particles were observed, which were associated with the presence of K₂CO₃. The surface morphology was analyzed via N₂ adsorption. The Na₂ZrO₃ and K-Na₂ZrO₃ samples presented surface areas of 1.5 and 1.1 m²/g, respectively, according to the BET model [28,29].

After characterizing the structures and microstructures of Na₂ZrO₃ and K-Na₂ZrO₃, both materials were thermally analyzed under CO₂ flow (Fig. 3). Na₂ZrO₃ and K-Na₂ZrO₃ presented typical and similar CO₂ dynamic chemisorption behaviors. The thermograms show two different weight increases. The first weight increase was produced between 30 and 290 °C, while the second was produced at temperatures higher than 400 °C. The first process was associated with the chemisorption of CO₂ on the particle surface. At this point, a thin Na₂CO₃ external shell, mixed with ZrO₂, is likely produced over the Na₂ZrO₃ particle surface. In contrast, the second weight increase was produced at $T > 400$ °C, as a result of the activation of diffusion processes [27]. Although the potassium addition did not appear to significantly modify the dynamic CO₂ chemisorption, nonetheless, between 290 and 400 °C, an interesting difference in the thermograms can be observed. While the Na₂ZrO₃ sample lost 0.29 wt.% in this temperature range, the K-Na₂ZrO₃ sample lost 0.82 wt.%, which is approximately three times the weight loss. This result may be associated with a partial CO₂ desorption process produced over the particle surface, which indicates a different CO₂ absorption–desorption equilibrium than that observed for the Na₂ZrO₃ sample. A similar effect was previously observed in the Na₂ZrO₃ and Na₂(Zr–Al)O₃ systems [30].

To analyze the influence of the potassium addition on the CO₂ capture process in Na₂ZrO₃, different isothermal experiments were performed between 300 and 700 °C (Fig. 4). For the Na₂ZrO₃ case (Fig. 4A), all of the isothermal experiments followed a typical exponential behavior, where the CO₂ chemisorption increased as a function of temperature. At 300 and 400 °C, the isotherms did not reach equilibrium after 3 h, and the weight increments were 2.0 and 14.3 wt.%, respectively. Later, a more rapidly increasing exponential behavior was obtained for the sample treated at 500 °C, which significantly increased the CO₂ chemisorption behavior (18.5 wt.%). Treating the sample isothermally at 600 °C resulted in a partial decrease in the CO₂ chemisorption. This atypical phenomenon has recently been associated with a Na₂CO₃–ZrO₂ external shell densification process, as the external shell presents a degree of mesoporosity at $T \leq 550$ °C, which allows for

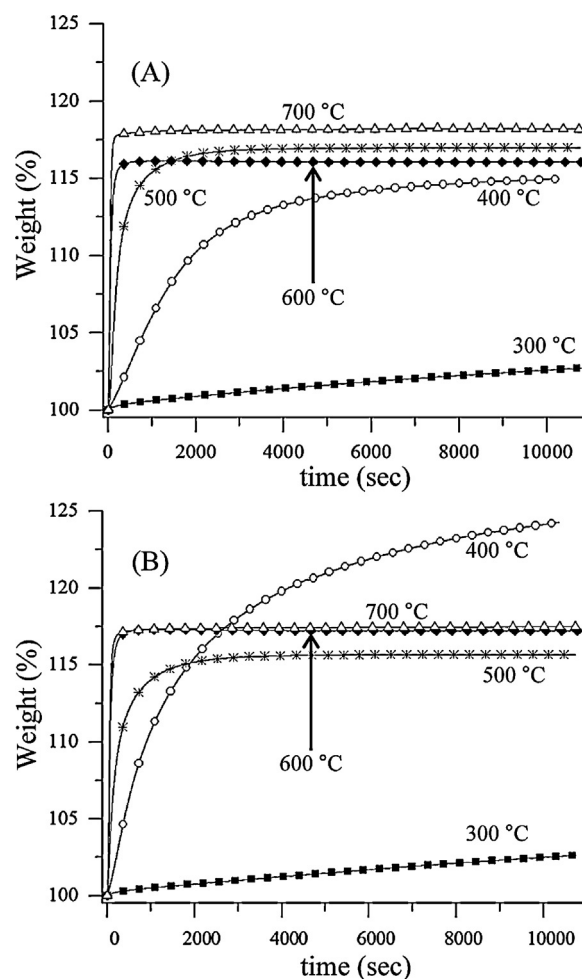


Fig. 4. Isothermal analyses at different temperatures (300–700 °C) of the Na₂ZrO₃ (A) and K-Na₂ZrO₃ (B) samples.

higher CO₂ chemisorption [17,31]. Finally, at 700 °C, the inter-crystalline diffusion processes are activated, recovering the CO₂ chemisorption behavior, which increases as a function of temperature.

However, although the K-Na₂ZrO₃ sample (Fig. 4B) presented a similar exponential behavior, some significant variations were also observed. At 300 °C, the amount of CO₂ chemisorbed was very poor (2.6 wt.%), as in the Na₂ZrO₃ case. Nevertheless, the K-Na₂ZrO₃ sample presented the highest CO₂ chemisorption at 400 °C, with a value of 24.2 wt.%. Later, between 500 and 700 °C, the CO₂ chemisorption values decreased, although the CO₂ chemisorption process occurred faster during the initial minutes of the test than the behavior observed at 400 °C. It has been reported that the process of CO₂ absorption in Na- or K-containing lithium ceramics produces a molten lithium–sodium or lithium–potassium carbonate phase [23–26,31]. The K and Na additions usually do not exceed 5–10 wt.% because the main intention of adding these elements is to improve the diffusion processes due to partial melt processes. Therefore, to demonstrate that the partial melting process of the Na₂CO₃–K₂CO₃ eutectic phase is present in the Na₂ZrO₃ external shell, different DSC experiments were carried out. Additionally, the potassium addition produced more rapid densification of the porosity in the Na₂CO₃–ZrO₂ external shell because the isothermal capture of CO₂ in the K-Na₂ZrO₃ sample decreased at 500 °C and not at 600 °C, as in the Na₂ZrO₃ case.

Fig. 5 shows different DSC analyses of the Na₂ZrO₃ and K-Na₂ZrO₃ samples. In the K-Na₂ZrO₃ case, the sample was analyzed

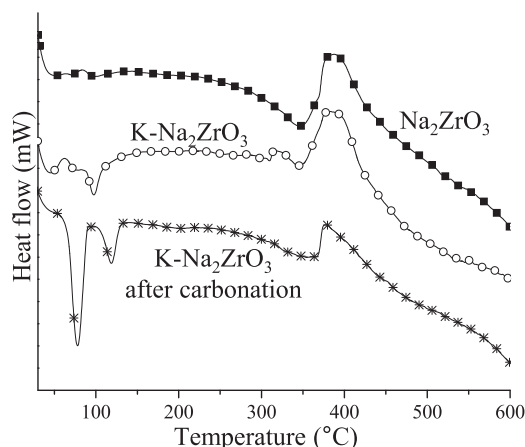


Fig. 5. DSC analysis of the Na₂ZrO₃ and K-Na₂ZrO₃ samples and the K-Na₂ZrO₃ sample previously treated at 400 °C into a CO₂ flux.

before and after the CO₂ capture processes. Initially ($T < 150$ °C), the three samples presented calorimetric behaviors that fit very well with the thermogravimetric experiments. The different peaks observed in this temperature range correspond to superficial or crystalline dehydration processes. After the carbonation process, the K-Na₂ZrO₃ sample presented the highest endothermic dehydration peaks, which are associated with the water affinity presented by the Na₂CO₃ produced over the highly hygroscopic Na₂ZrO₃ particle surface. However, additional information that can be obtained from the decarbonation peaks is observed below 300 °C. The Na₂ZrO₃ sample presented a single well-defined endothermic peak with an onset temperature of 255 °C and an

enthalpy (ΔH) value of 179.3 kJ/mol. However, the K-Na₂ZrO₃ sample presented a double peak, which corresponds with the superficial Na₂CO₃ presence because the Na₂ZrO₃ sample had added K₂CO₃. These two peaks could not be separated for parameter determination, so the onset temperature and ΔH values obtained were 247 °C and 125.2 kJ/mol. It is clear that both the onset temperature and ΔH were reduced by the K₂CO₃ addition, which is in agreement with the formation of the carbonate solid solution [33]. In the third case (K-Na₂ZrO₃ sample isothermally treated at 400 °C in a CO₂ atmosphere), the corresponding ΔH value was 100.5 kJ/mol. Thus, the ΔH value continued to decrease, as the Na₂CO₃–K₂CO₃ eutectic phase was completely formed during previous carbonations.

To complete the analysis of sample characterization, Figs. 6 and 7 present SEM images of the Na₂ZrO₃ and K-Na₂ZrO₃ samples following isothermal treatment at 500 °C in a CO₂ atmosphere. The backscattered electron image (BSEI) confirms the presence of two phases in the surface region, due to the different contrasts observed in the particles. These two phases are identified as ZrO₂ and Na₂CO₃ or K-containing Na₂CO₃ (the eutectic carbonate phase), as they are the Na₂ZrO₃ carbonation products. In this case, the Na₂ZrO₃ phase is not identifiable in the image because the remaining Na₂ZrO₃ must be located within the particle's core, as it has been reported in other micrometric CO₂-alkaline ceramic reaction models [4,27]. The difference in observed contrast arises from the difference in the mean atomic number, \bar{Z} , of ZrO₂ ($\bar{Z} = 18.666$) relative to the mixed carbonate phase (for the Na₂CO₃ $\bar{Z} = 8.666$, which is the majority phase). The \bar{Z} difference produces changes in the backscattered electron coefficient, η , of the two phases [33,34]. Thus, the dark phase corresponds to the mixed carbonate phase, while the lighter phase is ZrO₂. Although the K-Na₂ZrO₃ particle size did not change significantly after the

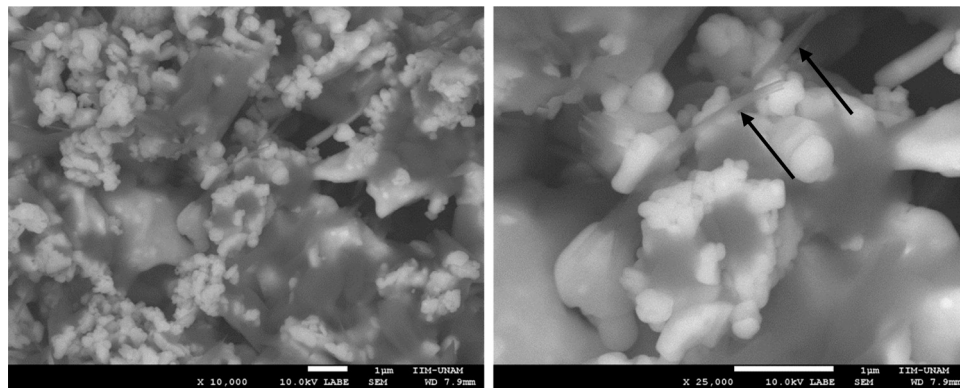


Fig. 6. Backscattered electron images of the Na₂ZrO₃ sample isothermally treated at 500 °C into a CO₂ atmosphere. The arrows indicate the filament-like particle formations.

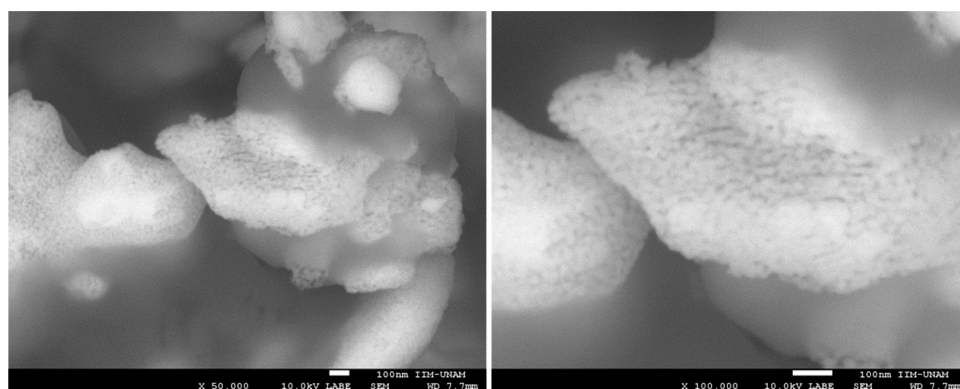


Fig. 7. Backscattered electron images of the K-Na₂ZrO₃ sample isothermally treated at 500 °C into a CO₂ atmosphere.

Table 1

Kinetic parameters obtained from the isothermal fitting to the double exponential model.

T (°C)	k_1 (s ⁻¹)	k_2 (s ⁻¹)	R^2
Na ₂ ZrO ₃			
300	0.00045	0.00012	0.99876
400	0.00043	0.00026	0.99908
500	0.00271	0.00056	0.99688
600	0.00953	0.00184	0.99153
700	0.01496	0.0001	0.94342
K-Na ₂ ZrO ₃			
300	0.00832	0.00005	0.9997
400	0.00113	0.00021	0.99992
500	0.00659	0.00127	0.9998
600	0.01495	0.00132	0.99233
700	0.01904	0.00025	0.98244

carbonation process, the mixed carbonate phase (dark phase) produced layered-like and filamentous structures, and the presence of mesoporosity was evidenced (see Fig. 7). These results are in good agreement with a previous report in which the presence of an external mesoporous phase was reported in Na₂ZrO₃ as a result of carbonation at $T \leq 550$ °C [17].

To analyze whether the potassium addition affects the CO₂ capture process of Na₂ZrO₃, the isothermal data were fitted to a double exponential model, as a result of the two different processes taking place: (1) CO₂ chemisorption occurs over the Na₂ZrO₃ particle surface (k_1), which induces the formation of an external shell of alkaline carbonate and ZrO₂, and (2) the CO₂ chemisorption is kinetically controlled by diffusion processes (k_2) [35–39]:

$$y = A \exp^{k_1 t} + B \exp^{k_2 t} + C$$

where y represents the weight percentage of chemisorbed CO₂, t is the time, and k_1 and k_2 are the exponential constants for the CO₂ chemisorption over the Na₂ZrO₃ particle surface and the chemisorption of CO₂ kinetically controlled by diffusion processes, respectively. Additionally, the pre-exponential factors A and B indicate the intervals over which each process controls the whole CO₂ capture process, and the constant C denotes the y -intercept. All of the exponential constant parameters are presented in Table 1. It can be observed that, independently of the potassium addition, the direct CO₂ chemisorption constant values (k_1) are higher than that

of the CO₂ chemisorption kinetically controlled by diffusion processes (k_2). This result is in good agreement with previous reports [35,36,39] and indicates that the rate limiting step is the CO₂ chemisorption, which is kinetically controlled by diffusion processes. However, at 400 °C, the k_1 values decreased independently of the potassium addition. This effect is attributed to the partial superficial desorption of CO₂ observed during dynamic thermogram analysis in the same temperature range. Additionally, it should be noted that the k_1 and k_2 constants were different for the Na₂ZrO₃ and K-Na₂ZrO₃ samples. K-Na₂ZrO₃ presented higher k_1 and k_2 values than Na₂ZrO₃ throughout the entire temperature range, confirming that potassium addition improves the CO₂ capture process. It should be noted that the potassium addition enhances the initial reaction process upon melting because the liquid phase promotes the superficial CO₂ reaction and the porous diffusion processes.

Once the high-temperature isotherms were analyzed more thoroughly, a third process was identified, i.e., CO₂ desorption. This process was evidenced by a slight decrease in the weight ($T \geq 600$ °C, see Fig. 8). The chemisorption/desorption equilibrium was not present at lower temperatures because there may not have been a desorption process. Therefore, this isotherm showed three different trends. At short times, the increase in weight was equal to that observed for the other isotherms, after fitting these data to a double exponential model. The k_1 and k_2 values obtained fitted the previous analysis very well. Then, the curve showed a lag period, in which the absorption did not increase. At long times, the desorption process became evident, although it was minimal. The samples only lost between 0.03 and 0.05 wt.%, due to the considerably low value of k_3 (0.00041 s⁻¹). Thus, using the entire data range, a different fitting was performed with a triple exponential model. This model considers three processes, including (1) the CO₂ chemisorption over the sample particle surface, (2) the CO₂ chemisorption that is kinetically controlled by diffusion processes and (3) the CO₂ desorption.

Finally, multicyclic experiments were performed with the K-Na₂ZrO₃ sample. The CO₂ chemisorption process was performed at 400 and 700 °C, but it was necessary to perform the desorption process at 850 °C because at lower temperatures, the desorption of CO₂ was not produced. Fig. 9A shows the cyclic performance of the K-Na₂ZrO₃ sample. It can be observed that the CO₂ capture efficiency decreased significantly after each chemisorption–desorption cycle at 400 °C. This effect is associated with the potassium and sodium segregations and the sublimation of potassium that occurred during the desorption processes performed at 850 °C. Previous multicyclic reports on alkaline ceramics, specifically, lithium ceramics such as K-Li₄SiO₄ and K-Li₂ZrO₃, have demonstrated better cycling stabilities [4,10,18,24,32,36,40–44]. However, in such cases, the desorption temperatures were always equal to the chemisorption temperatures ($T \leq 630$ °C). At this temperature, the influence of the potassium–lithium segregation and sublimation processes must be reduced. Nevertheless, it is not possible to use the same conditions for Na₂ZrO₃–CO₂ because the Na₂CO₃ decomposition temperature is approximately 850 °C.

When Na₂ZrO₃ and K-Na₂ZrO₃ were tested at 700 °C, the cycling stability appeared to be sufficient (Fig. 9B). However, the CO₂ capture decreased in both cases as a function of the cycle number; the CO₂ desorption capacity of the K-Na₂ZrO₃ sample decreased, while the Na₂ZrO₃ sample appeared to partially decompose. The CO₂ capture of Na₂ZrO₃ decreased from 4.76 to 4.2 mmol/g, while that of K-Na₂ZrO₃ decreased from 4.48 to 4.01 mmol/g (Fig. 9C). This effect may be associated with different effects, such as the particle sintering process and the Na and K sublimation processes. Hence, the potassium addition does not seem to produce any significant change, as the CO₂ capture behavior is mainly produced

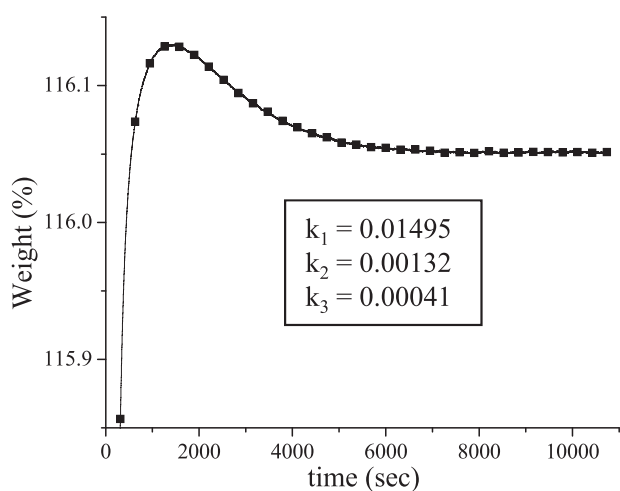


Fig. 8. Isotherm of the K-Na₂ZrO₃ sample treated at 600 °C into a CO₂ flux. The sample was fitted to a triple exponential model, as it was evidenced in the presence of an additional process; the CO₂ desorption.

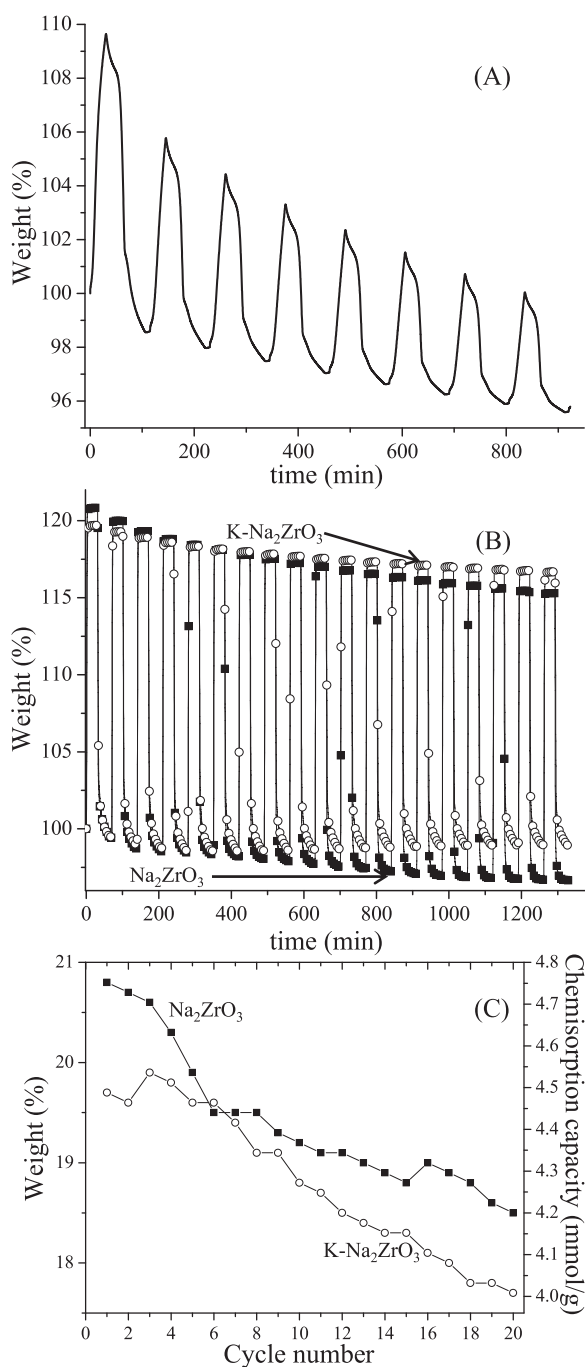


Fig. 9. Multicycle performance of CO₂ chemisorption/desorption in K-Na₂ZrO₃, in which the consecutive CO₂ chemisorptions were performed at 400 °C for 30 min, while the desorption processes were performed at 850 °C over 30 min into a N₂ flux (A and B). Na₂ZrO₃ and K-Na₂ZrO₃ multicycle experiments, in which the CO₂ chemisorption were performed at 700 °C (C).

by intercrystalline diffusion processes at this temperature range [17].

4. Conclusions

Na₂ZrO₃ was synthesized via a solid-state reaction. Further, part of the Na₂ZrO₃ sample was also mechanically mixed with K₂CO₃ (5 wt.%). Then, both samples were characterized structurally and microstructurally, and the CO₂ capture process was evaluated. Although the CO₂ dynamic experiments did not show significant differences following the addition of potassium, the isothermal

analysis did. The K-Na₂ZrO₃ sample treated at 400 °C captured more CO₂ than the Na₂ZrO₃ original sample over all of the analyzed temperature range. Na₂ZrO₃ usually presents the best CO₂ capture behavior at $T \geq 550$ °C. Under these conditions, the CO₂ capture of the samples in this work was very close to 100% efficiency (specifically, 98%). Independent of the potassium addition, the direct CO₂ chemisorption constant values (k_1) were found to be higher than that of the CO₂ chemisorption that was kinetically controlled by diffusion processes (k_2). The increased CO₂ chemisorption was attributed to the formation of a K–Na carbonate eutectic phase, which can produce a partial liquid phase, favoring the diffusion of CO₂ through the mesoporous external shell. This possibility was supported by various DSC and isothermal analyses and SEM observations.

Conversely, the potassium addition produced a CO₂ desorption process at T 600 °C, which was not observed in the Na₂ZrO₃ sample. Finally, multicycle experiments were performed at 400 and 700 °C to elucidate the thermal stability and CO₂ capture efficiency through different cycles in both ceramics. In this case, it was observed that the addition of potassium did not stabilize the CO₂ chemisorption behavior after several cycles, due to potassium segregation, and sublimation developed during CO₂ desorption at 850 °C. Therefore, the addition of K to Na₂ZrO₃ significantly enhances the CO₂ capture behavior of the material at approximately 400 °C, relative to that of the Na₂ZrO₃ sample, although the thermal and cyclic stability of this sample were compromised.

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