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Experimental and Modeling Studies on High-Temperature Capture of CO_2 Using Lithium Zirconate Based Sorbents

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Lithium zirconate (Li_2ZrO_3) is one of the most promising materials for CO_2 separation from flue gas at high temperature. This material is known to be able to adsorb a large amount of CO_2 around 500−600 °C. It was also reported that the addition of lithium/potassium carbonate to Li_2ZrO_3 increased the CO_2 sorption rate when compared to pure Li_2ZrO_3. In this study, we examine the CO_2 sorption mechanism on Li_2ZrO_3 by analyzing phase and microstructure changes of Li_2ZrO_3 during the CO_2 sorption process with the help of thermogravimetric analysis, scanning electron microscopy, and X-ray diffraction analyses. We report on CO_2 sorption experiments for different Li_2ZrO_3 based sorbents at different operating conditions in order to identify the most appropriate sorbent and experimental conditions. We also propose a kinetic model that is a variant of a double-shell model proposed in the literature by introducing additional dynamics to obtain a consistent response of the CO_2 uptake curve during the initial part of the sorption process. The proposed model, which has two temperature-dependent parameters that can be adjusted by regression on experimental data, shows excellent capabilities for describing the CO_2 uptake on a Li_2ZrO_3 based sorbent.

1. Introduction

Carbon dioxide (CO_2) is a greenhouse gas that is customarily released to the environment during the use of fossil fuels, including electric power generation. With the projected increase in consumption and demand for fossil fuels, CO_2 emissions will correspondingly increase in the absence of any capture/sequestration strategy. Given that CO_2 is a greenhouse gas with the potential to contribute to global climate warming, existing and improved technologies to mitigate the release of CO_2 to the environment are being considered as a prudent precaution against global warming. Therefore, the removal and recovery of carbon dioxide from power plant fuel gases is considered to be one of the effective approaches for reducing CO_2 emissions.

A number of techniques can be used for the separation of carbon dioxide from fuel gas streams. Physical absorption using amine solution is the only technology that is currently deployed commercially for CO_2 capture. However, there is a significant energy penalty associated with this technology, which operates at low temperature.

Recently, selective adsorption technology (using membrane or solid sorbents) has been identified as one of the ways to capture CO_2 at high temperature, without cooling the flue gas to ambient or even lower temperature. For the separation of carbon dioxide from hot gas stream, the adsorbent must have high selectivity for CO_2 over N_2 at elevated temperatures and high adsorption capacity for carbon dioxide at the operating temperature.

The development of inorganic membranes for CO_2 separation, such as zeolite, sol−gel derived zirconia, and sol−gel derived silica membranes, has received increasing attention in the past few years.[1] However, these inorganic membranes do not offer sufficiently high permselectivity for separation of CO_2 over N_2 at temperatures greater than 350 °C.[2]

Among the various solid sorbents that have been studied, carbon-based adsorbents, metal oxide sorbents,[3] and hydrotalcite-like compounds[4,5] can be used as adsorbents for the removal of carbon dioxide from hot flue gas. However, the sorption capacity of these materials is low and the adsorption capacity of CO_2 decreases during adsorption/desorption cycles.[6,7]

Lithium zirconate (Li_2ZrO_3) is another material for CO_2 separation from flue gas at high temperature that has received increasing attention in the past few years. This material is known to be able to adsorb a large amount of CO_2 around 500−600 °C. The main advantages of this material are its lower regeneration temperature (750 °C) compared to current mineral origin based sorbents, which tend to sinter at high temperatures, and its stability that allows operation over a significant number of cycles without losing its sorption capacity. Li_2ZrO_3 can adsorb CO_2 through its sorption mechanism based on the following reaction:

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

From a kinetic point of view, the reaction occurs in two steps. First, Li_2ZrO_3 decomposes according to the following reaction:

$$Li_2ZrO_3 \rightarrow 2Li^+ + O^{2-} + ZrO_2 \quad (2)$$

Then, CO_2 reacts with lithium and oxygen ions to produce Li_2CO_3:

$$CO_2 + 2Li^+ + O^{2-} \rightarrow Li_2CO_3 \quad (3)$$

Lithium zirconate does not react with N_2 at all; thus, it could give an infinitely large CO_2/N_2 selectivity.

A double-shell model to describe the sorption mechanism of CO_2 on Li_2ZrO_3 was proposed by Ida and Lin.[2] According to this model, which is schematically shown in Figure 1, the CO_2 sorption mechanism can be described as follows. During the sorption process carbon dioxide diffuses to the surface of Li_2ZrO_3 and reacts with Li^+ and O^{2-} on the surface to form ZrO_2 and Li_2CO_3. Zirconium oxide forms a solid shell that covers unreacted Li_2ZrO_3, and similarly, Li_2CO_3 forms another shell outside the ZrO_2 shell. Therefore, during the carbonation process the sorption rate begins to decrease because Li^+ and O^{2-}

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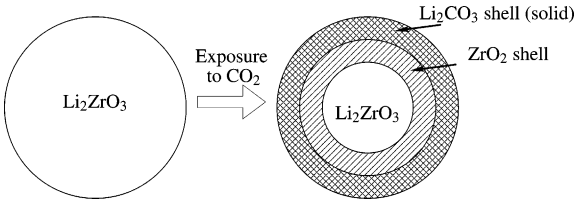

Figure 1. Schematic illustration of double-shell model for CO_2 sorption on Li_2ZrO_3.

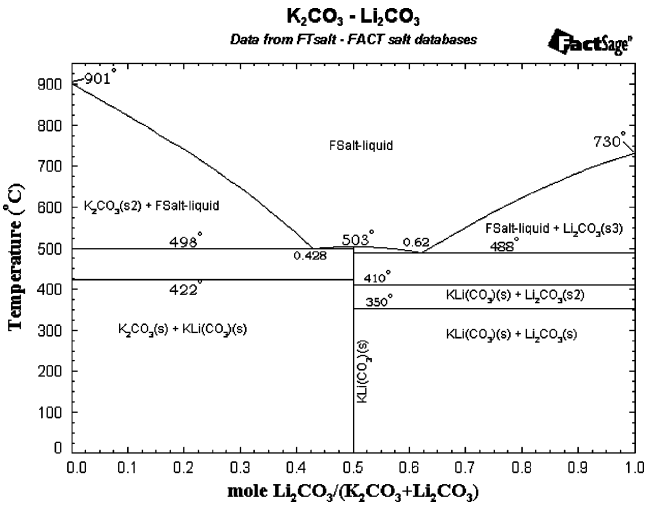

Figure 2. Phase diagram of Li_2CO_3/K_2CO_3.

have to diffuse through this ZrO_2 shell to react with CO_2 and carbon dioxide molecules have to diffuse through the Li_2CO_3 shell for reaction. It was found that pure Li_2ZrO_3 has a very slow CO_2 sorption rate. However, doping Li_2CO_3/K_2CO_3 into Li_2ZrO_3 can substantially increase the sorption rate because Li_2CO_3/K_2CO_3 dopant can form eutectic molten carbonate at high temperature (e.g., 500 °C). This molten carbonate "shell" can greatly reduce CO_2 diffusion resistance compared to the solid Li_2CO_3 shell in the pure Li_2ZrO_3 case. Moreover, the oxygen ion diffusion through the ZrO_2 shell can be improved by doping lithium zirconate with yttrium oxide, Y_2O_3.[8,9]

In this study, we synthesized several lithium zirconate based sorbents, pure and modified with carbonates and/or yttrium, and we characterized them using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. We also conducted CO_2 sorption experiments at different operating conditions with the help of thermogravimetric analysis (TGA). Furthermore, in this paper we describe the sorption process of CO_2 on a proposed Li_2ZrO_3 based sorbent with a mathematical model that is similar to the double-shell model present in the literature,[2,6,8] but contains a number of modifications to make it more adherent to some theoretical and experimental observations.

2. Experimental Materials and Methods

2.1. Sorbent Preparation. Pure Li_2ZrO_3 powders were prepared by the solid-state method. Starting materials were reagent-grade Li_2CO_3 and ZrO_2 (from Aldrich) in a 1:1 molar ratio. The materials were weighed, mixed, and ground in an agate mortar with a suitable amount of acetone. Then, the mixtures were dried and calcined in air at 850 °C for 6 h. Both temperature increase and decrease ramping rates were set to 60 °C/h. After calcination the products were ground to powder again in the agate mortar for later analysis.

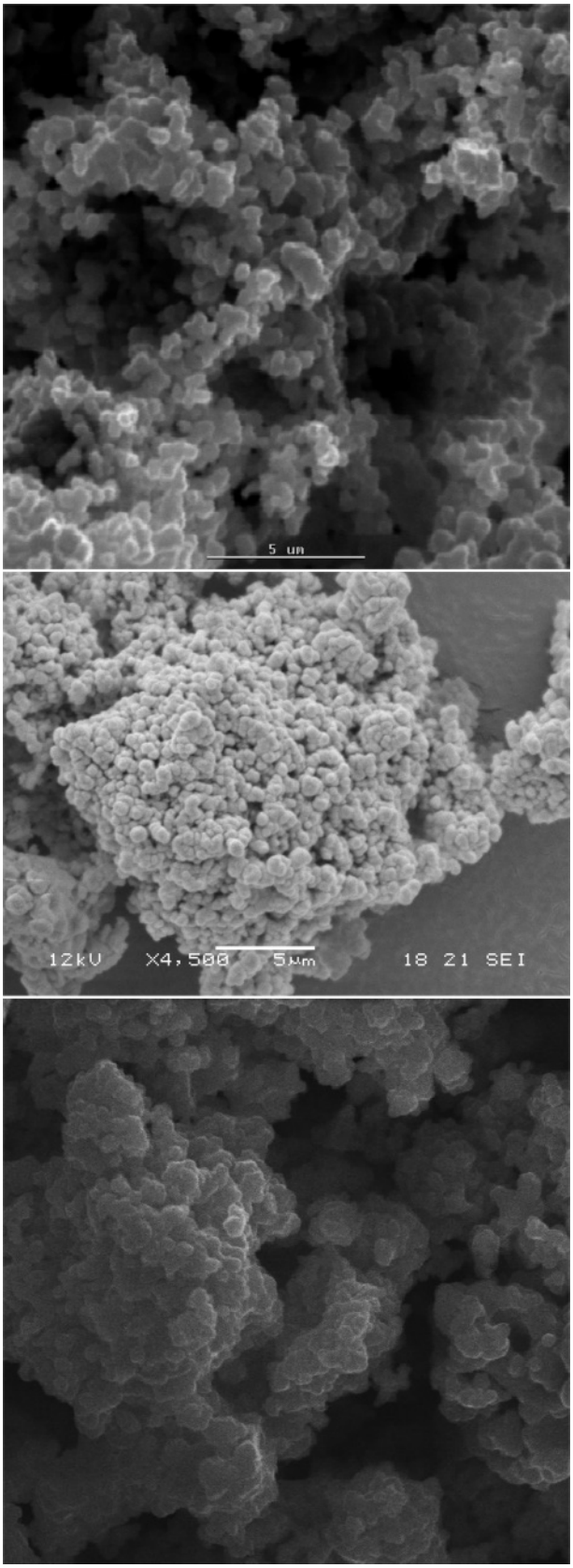

Figure 3. SEM images of pure (top), Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 (middle), and Li_2ZrO_3 prepared with addition of Y_2O_3 (bottom).

Powders of Li_2ZrO_3 with K_2CO_3 (from Aldrich) were also prepared using the same preparation procedure mentioned above. Two different compositions of sorbents were tested. It is known that the mixture of Li_2CO_3 and K_2CO_3 can form a eutectic

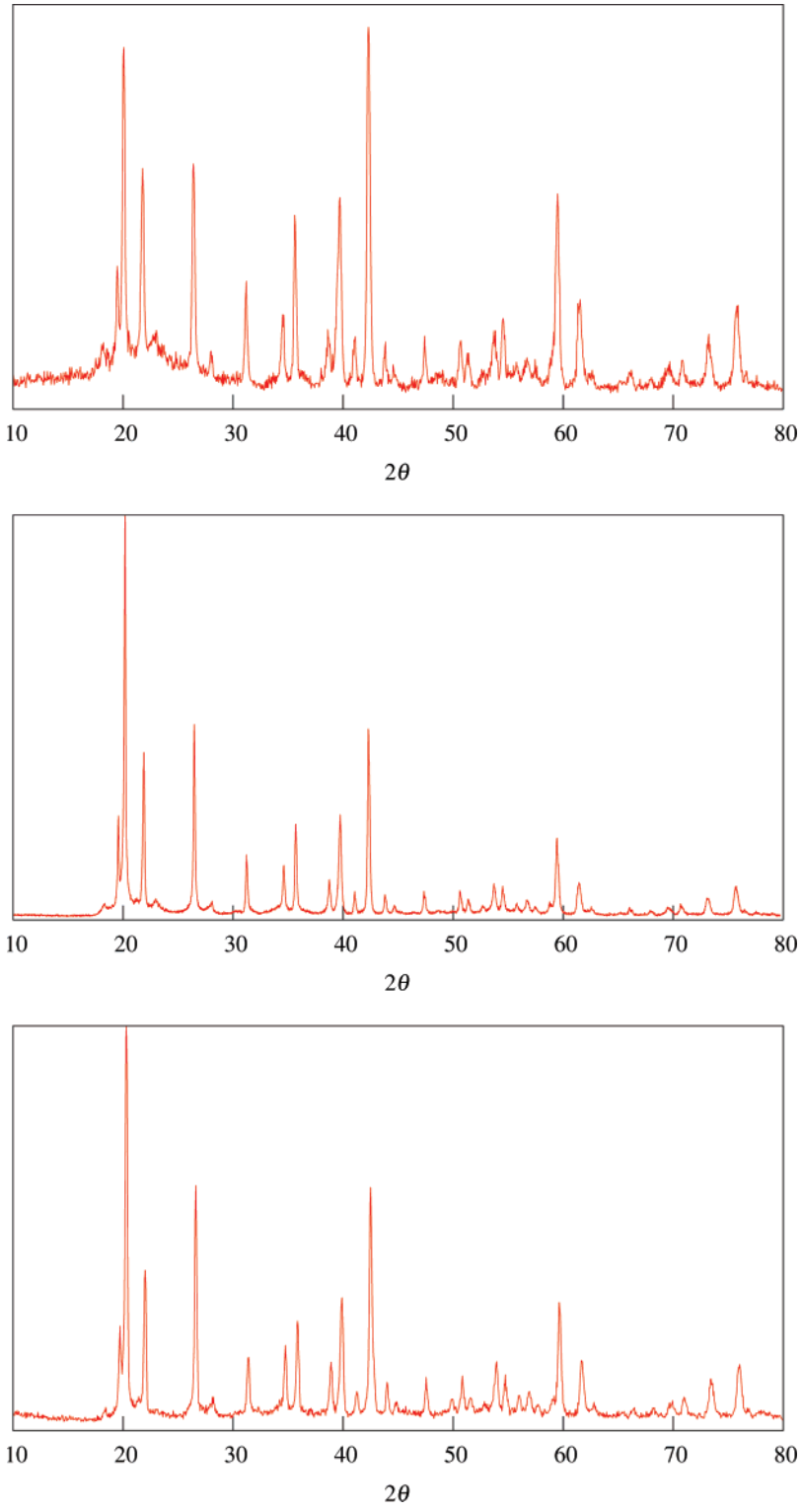

Figure 4. XRD patterns of pure Li_2ZrO_3 (top), Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with 10% excess Li_2CO_3 (middle), and Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with 15% excess Li_2CO_3 (bottom).

mixture having melting point of 498 °C, as shown in Figure 2. At the sorption temperature (e.g., 550 °C) the mixture of Li and K carbonates is partially or totally liquid depending on their composition ratio in the mixture. Thus, the molar ratios of the starting materials (Li_2CO_3:ZrO_2:K_2CO_3) considered in this work were 1.1:1.0:0.2 (typical composition suggested in the literature[6,8]) and 1.15:1.0:0.2, in order to have a completely molten carbonate at the start of the sorption reaction. For the typical potassium-doped lithium zirconate, the reaction of calcination can be represented as follows:

$$1.1Li_2CO_3 + 1.0ZrO_2 + 0.2K_2CO_3 \rightleftarrows 1.0Li_2ZrO_3 + 0.1Li_2CO_3 + 0.2K_2CO_3 + CO_2 \quad (4)$$

in which one can notice that a 10% excess of Li_2CO_3 is used. Using this excess of Li_2CO_3, a 0.33 Li_2CO_3 mole fraction in

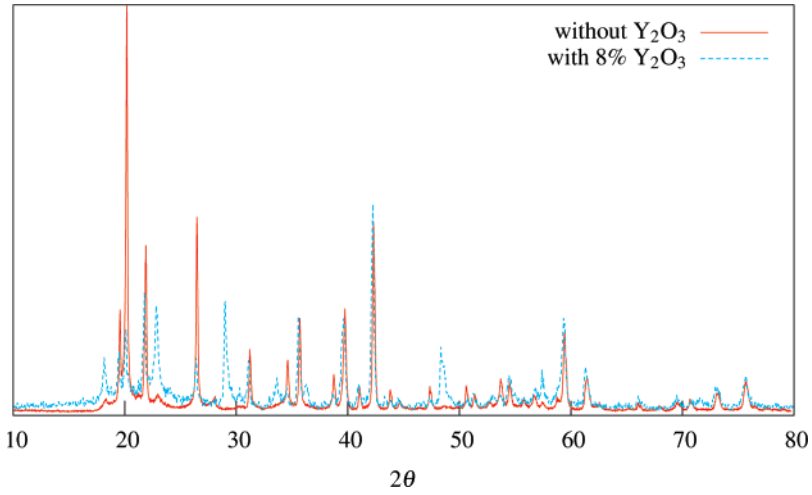

Figure 5. XRD patterns of Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with 10% excess Li_2CO_3 prepared from pure ZrO_2 and with addition of 8% Y_2O_3.

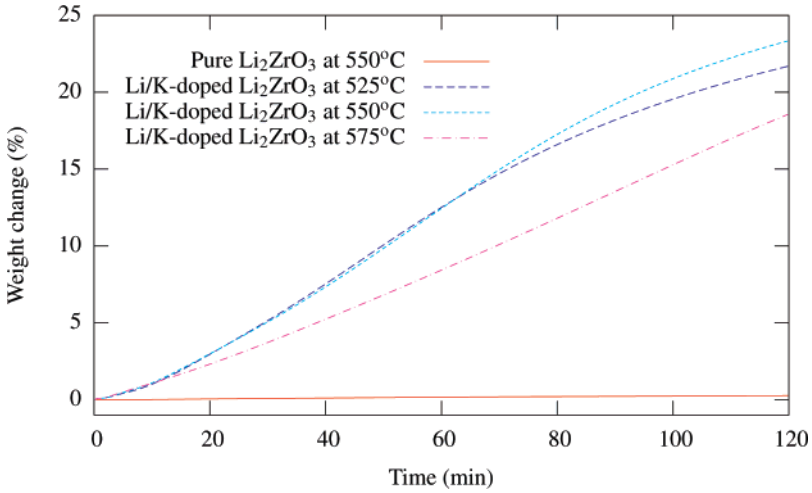

Figure 6. CO_2 uptake of pure and Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with 10% excess Li_2CO_3 at different temperatures.

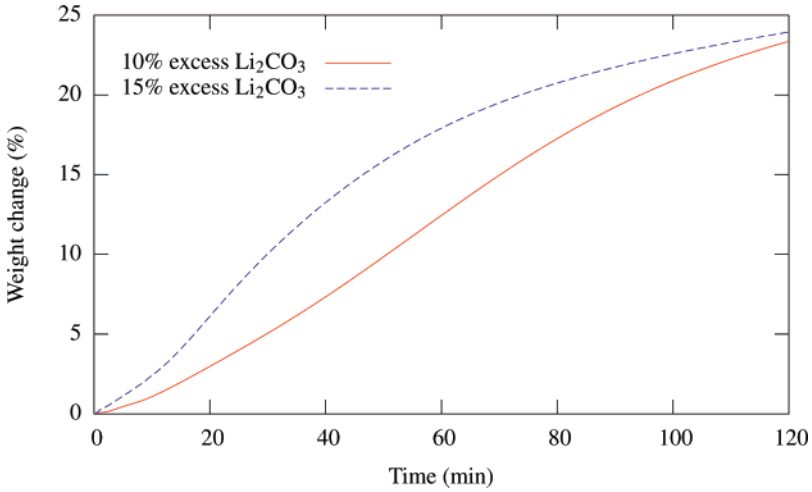

Figure 7. CO_2 uptake on Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with different excess amounts of Li_2CO_3 (at 550 °C).

the carbonate mixture is achieved, and from Figure 2 we can see that, at the operating temperature (between 500 and 600 °C, as discussed later on), a solid phase is also present along with the eutectic liquid phase. For the sorbent prepared with a 15% excess of Li_2CO_3, instead, a 0.43 Li_2CO_3 mole fraction in the carbonate mixture is achieved, and from Figure 2 we can see that only a liquid phase is present at the operating temperature.

The samples with K_2CO_3 and Y_2O_3 (from Aldrich), for producing yttrium-doped lithium zirconate, were prepared by the solid-state method suggested by Zou and Petric,[10] as described above. Y_2O_3 was used in order to improve the O^{2-} ion diffusion rate in the ZrO_2 shell. It is well-known that oxygen ions diffuse through ZrO_2 via oxygen vacancies in ZrO_2 crystals. Pure ZrO_2 has a monoclinic structure at room temperature. When doped with yttrium oxide, ZrO_2 is

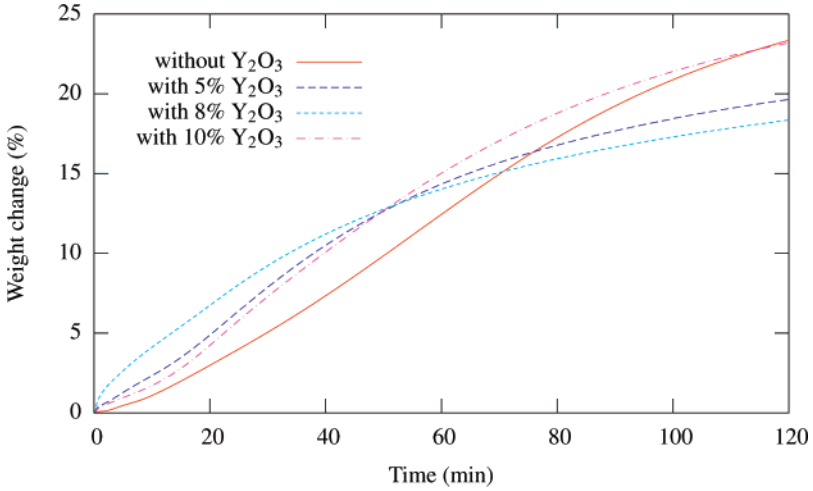

Figure 8. CO_2 uptake of Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with 10% excess Li_2CO_3 prepared from pure ZrO_2 and with addition of Y_2O_3 at different molar ratios (at 550 °C).

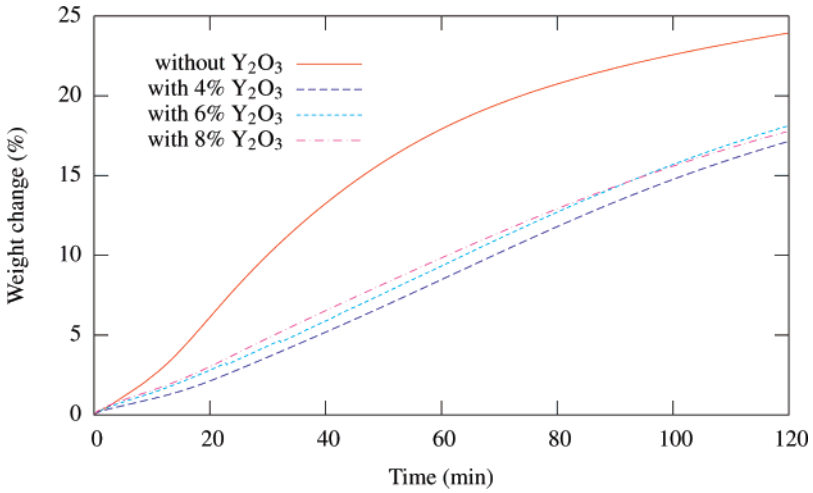

Figure 9. CO_2 uptake of Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with 15% excess Li_2CO_3 prepared from pure ZrO_2 and with addition of Y_2O_3 at different molar ratios (at 550 °C).

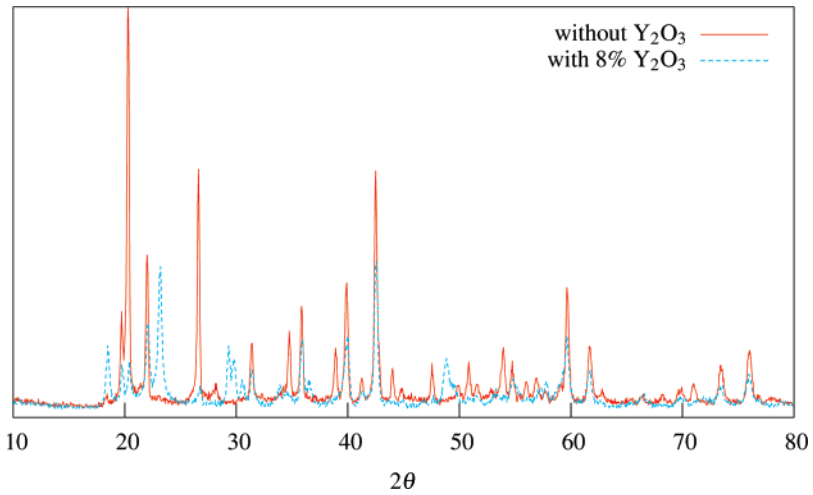

Figure 10. XRD patterns of Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with 15% excess Li_2CO_3 prepared from pure ZrO_2 and with addition of 8% Y_2O_3.

fully stabilized. The replacement of Zr^{4+} by Y^{3+} give rise to a higher concentration of structural oxygen vacancies for charge compensation and stabilizes the cubic phase. At high temperatures, these oxygen vacancies are highly mobile and give rise to oxygen ionic conductivity via a vacancy diffusion mechanism. The highest ionic conductivities were reported for Y_2O_3 concentrations of 7−10%.[11] In particular, in this work for sorbents prepared with a 10% excess of Li_2CO_3, lithium zirconate was doped with 5, 8, and 10% Y_2O_3, whereas for sorbents prepared with a 15% excess of Li_2CO_3, lithium zirconate was doped with 4, 6, and 8% Y_2O_3.

2.2. Experimental Procedures. Carbon dioxide sorption on prepared powders was studied using a TGA Q500 (from TA Instrument). About 20 mg sample was placed in the sample

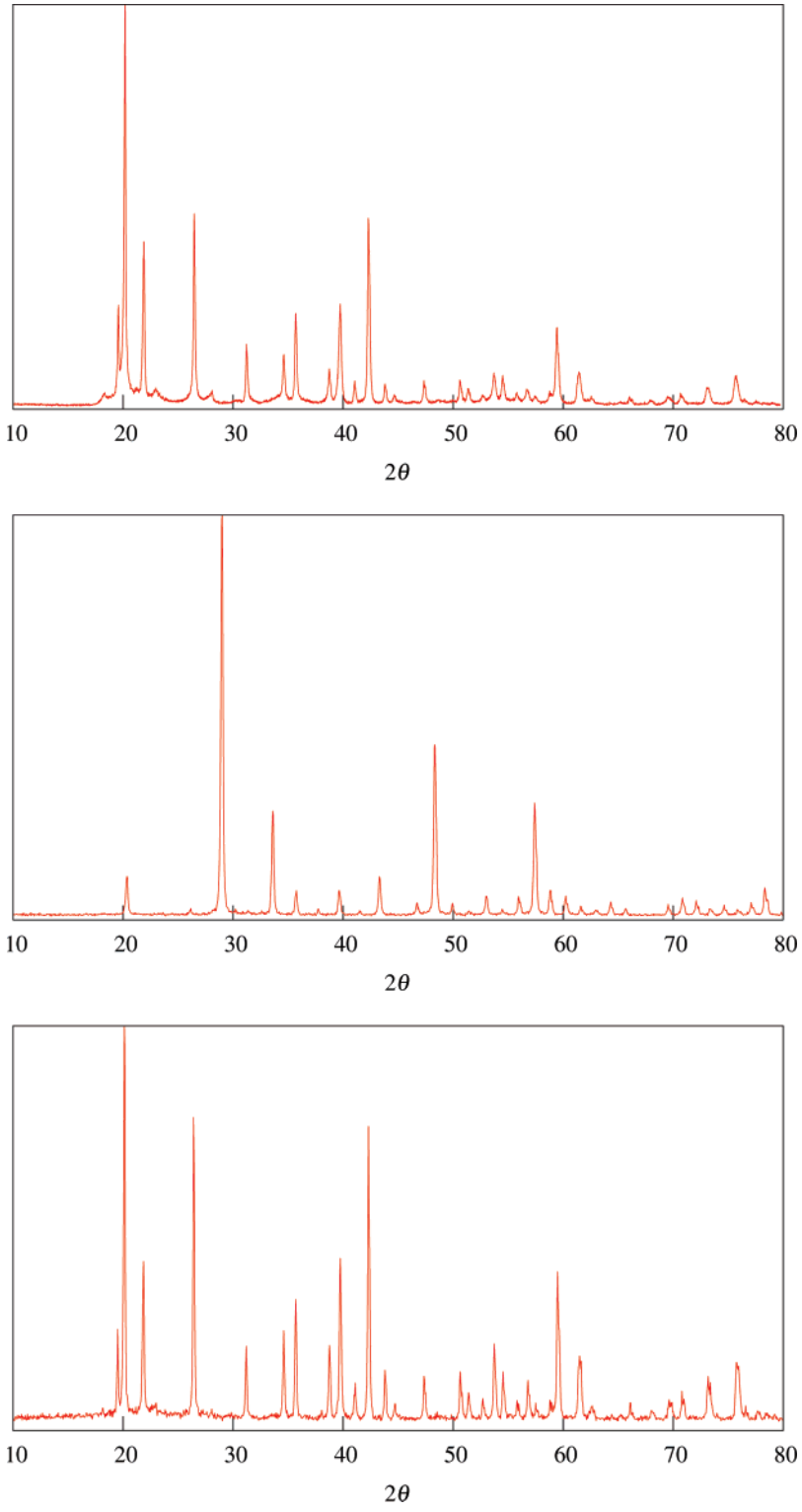

Figure 11. XRD patterns of Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 before (top) and during (middle) CO_2 sorption and after CO_2 desorption (bottom).

pan, and before adsorbing carbon dioxide the sample was dried at the operating temperature by passing nitrogen flow until the sample weight became stable. CO_2 partial pressures were set up by controlling the composition of the feed (CO_2/N_2) using mass flow controllers. The total feed gas flow rate was maintained at 100 mL/min (60% CO_2, 40% N_2). The sample was heated to the desired temperature with a ramp rate of 10 °C/min and the measurement of the sample weight gain versus time after the inlet flow was changed from N_2 to the premixed CO_2/N_2 mixture was recorded. After that, CO_2 desorption was performed by raising the temperature to 800 °C with ramp rate of 10 °C/min and changing from CO_2/N_2 mixture to nitrogen. A tubular furnace was used to control the temperature, and CO_2 sorption was conducted at different temperatures in order to study the temperature effect on the sorption rate.

The phase structure of the prepared samples was examined by powder X-ray diffraction analysis (XRD) using a Siemens D 500 XRD with Cu Kα radiation. The XRD patterns were recorded over a 2θ range of 10°−80°. Phase identification was verified by comparison against the powder diffraction patterns reported in ref 8. The morphology of the obtained powders was observed using a JEOL 5600LV scanning electron microscope

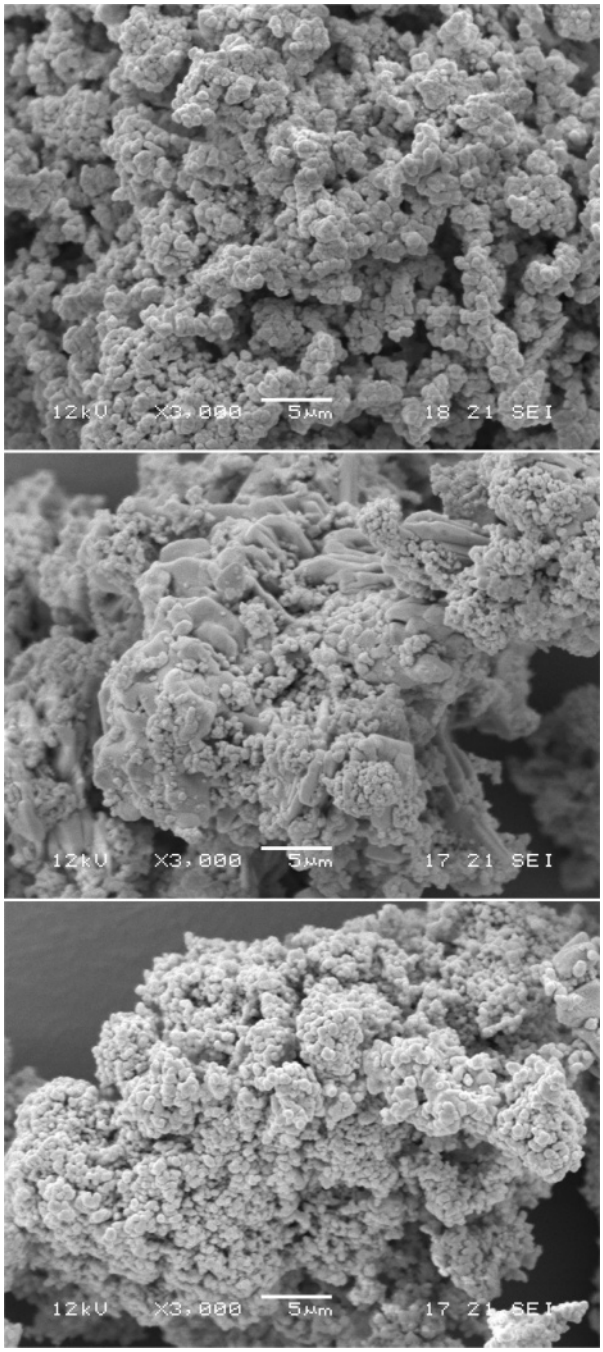

Figure 12. SEM images of Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 before (top) and during (middle) CO_2 sorption and after CO_2 desorption (bottom).

(SEM). XRD and SEM analyses were also used to evaluate the structural changes of the sorbent during a CO_2 sorption/desorption cycle. In particular, in order to characterize the sorption products, the sorbent was rapidly quenched to room temperature after CO_2 sorption at 550 °C, and the obtained powder was analyzed. Similarly, the sorbent was characterized after CO_2 desorption at 800 °C.

3. Experimental Results and Discussion

3.1. Sorbent Characterization. Microscopic views of the pure Li_2ZrO_3, Li_2CO_3/K_2CO_3-doped Li_2ZrO_3, and lithium zirconate prepared with addition of 8% Y_2O_3 are presented in Figure 3. Particles have relatively uniform size and they stick together to form a large porous agglomerate. Moreover, the average particle size is around 1 μm: the particle size of Li_2ZrO_3 was controlled by ZrO_2 because during the preparation (calcination) only ZrO_2 particles remained in the solid state due to its high melting point (2700 °C). Therefore, ZrO_2 particles acted as cores to control the particle size of product Li_2ZrO_3.[6] In this work, ZrO_2 powder of particle size below 1 μm was used. In the case of Li_2CO_3/K_2CO_3-doped Li_2ZrO_3, the mixture of lithium and potassium carbonates are also in the liquid state during the preparation process because the melting point of their mixture is much lower than the preparation temperature. In this case, an excess amount of lithium/potassium carbonates may remain on the surface of the Li_2ZrO_3 after the Li_2ZrO_3 formation reaction is completed.

The X-ray diffraction patterns of the prepared Li_2ZrO_3 powders, pure and modified with carbonates, are presented in Figure 4. As can be seen, the prepared pure lithium zirconate presents most diffraction peaks assigned to Li_2ZrO_3 monoclinic.[8] Patterns of the Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 sample also present characteristic peaks of pure lithium zirconate, independently of the Li_2CO_3 excess.

Figure 5 shows XRD patterns of Li/K-doped Li_2ZrO_3 with a 10% excess of Li_2CO_3 prepared from pure ZrO_2 and with the addition of 8% Y_2O_3. As can be seen, the diffraction peaks for the sample prepared with the addition of Y_2O_3 can be matched with those of Li_2ZrO_3 except for two small peaks, which may be assigned to zirconia. The XRD results also show that the diffraction peaks systematically shift toward lower diffraction angles. Since the geometry of the crystal structure is correlated to the angular position of the diffraction peaks (according to Bragg's law), the observed shift suggests an increase of the distance between crystallographic planes due to the presence of Y_2O_3 in the crystal structure of zirconia. Hence, these results indicate that we obtained a solid solution of Y_2O_3-doped Li_2ZrO_3.[10]

3.2. Sorption Properties. The CO_2 uptake curve on the pure lithium zirconate sorbent is reported in Figure 6. As can be seen, the sorption rate is very low (the weight change after 40 min was only 0.10%). Figure 6 also shows sorption curves, at different temperatures (525, 550, and 575 °C), on Li_2ZrO_3 with carbonates having a molar ratio Li_2CO_3:K_2CO_3:ZrO_2 equal to 1.1:1.0:0.2. As shown, the sorption rate on modified Li_2ZrO_3 is much higher than that on pure lithium zirconate. This higher sorption rate on Li/K-doped Li_2ZrO_3 can be explained by the formation of a liquid phase of potassium lithium carbonate (which is molten at temperatures above 500 °C) between sorbent particles during the carbonation reaction. Diffusion of CO_2 in the molten carbonate is several orders of magnitude higher than that in the solid carbonate, which instead forms in the case of pure Li_2ZrO_3. Then, for Li/K-doped lithium zirconate the rate-limiting step is now switched to diffusion of Li^+ and O^{2-} through the zirconium oxide shell which forms surrounding the unreacted lithium zirconate core during the sorption reaction. From Figure 6 we can also see that the sorption rate increases as the temperature increases from 525 to 550 °C. However, when the temperature continues to increase from 550 to 575 °C, the sorption rate decreases. This suggests that temperature affects the sorption rate in two opposite directions. Increasing the temperature can increase the reaction rate constant. However, increasing the temperature would increase the equilibrium carbon dioxide partial pressure and thus reduce the driving force for sorption at the constant operation CO_2 pressure. The temperature effect on the sorption rate depends on both thermo-

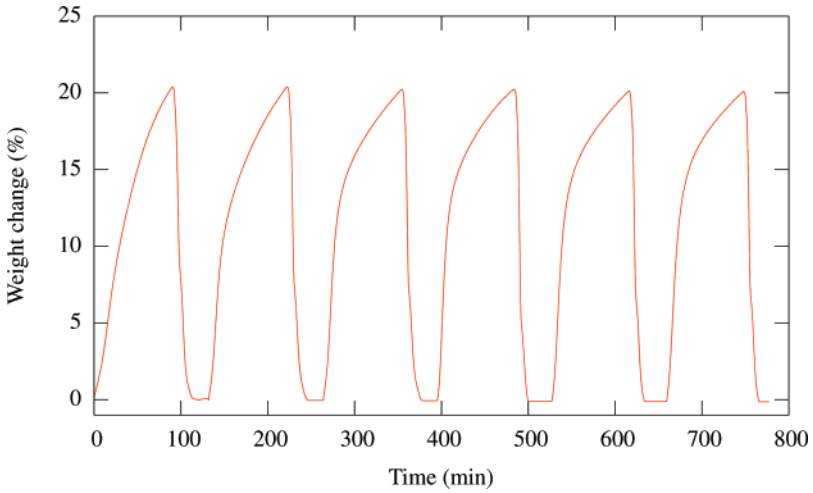

Figure 13. CO_2 uptake and release of Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with 15% excess Li_2CO_3 during six cycles of sorption at 550 °C and desorption at 800 °C.

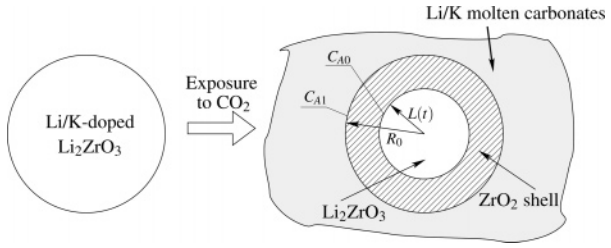

Figure 14. Schematic illustration of kinetic model for CO_2 sorption on Li_2CO_3/K_2CO_3-doped Li_2ZrO_3.

dynamic and kinetic factors. A moderate temperature range, e.g., around 550 °C, would be desirable for carbon dioxide sorption.

CO_2 uptake curves on lithium zirconate with different proportions between carbonates in the starting mixture are reported in Figure 7. As can be seen, during the first 120 min of operation, the sorption rate on a sorbent prepared with a 15% excess of Li_2CO_3 is higher than that of a sorbent prepared with a 10% excess of Li_2CO_3. This higher sorption rate depends on the different condition of the Li_2CO_3/K_2CO_3 mixture at the sorption temperature (550 °C) at the start of the carbonation (Figure 2): in the case of a 15% excess of Li_2CO_3 the mixture is completely molten; thus the CO_2 diffusion is enhanced in the liquid phase.

In order to improve the O^{2-} ion diffusion rate in the ZrO_2 shell, lithium zirconate with carbonate was prepared with addition of Y_2O_3. Figures 8 and 9 show CO_2 uptake curves on these sorbents. The operation temperature is 550 °C. In the case of sorbents with composition Li_2CO_3:ZrO_2:K_2CO_3 = 1.1:1.0:0.2, the sorbent with yttria gives a higher CO_2 sorption rate, during the first 60 min of operation, than the sample without yttria in accordance with the increase of oxygen vacancies due the introduction of Y_2O_3 into ZrO_2. Moreover, during the first part of the sorption process, the sorption rate decreases for Y_2O_3 concentration higher than 8%. Although an increasing number of vacancies is obtained when the dopant concentration is raised, the vacancy mobility decreases, and at sufficiently high concentrations, the latter factor starts to dominate leading to a decrease of conductivity.[12] In particular, 8% Y_2O_3 substitution for ZrO_2 leads to a composition close to the lower limit for stabilization of the zirconium oxide with the highest value of electrical conductivity.[13] The samples having composition Li_2CO_3:ZrO_2:K_2CO_3 = 1.15:1.0:0.2 do not present the same trend. This difference can be explained by the XRD patterns of the sorbents. Figure 10 reports results of X-ray analysis of this sorbent without yttria and with 8% Y_2O_3. As can be seen, the shift of diffraction peaks toward lower diffraction angles is absent. This suggests that the presence of a larger excess of carbonates may prevent Y_2O_3 from doping the crystal structure to increase oxygen vacancies.

To summarize, based on the experimental results presented in this section, as well as other ones not shown for the sake of space, we believe that the most promising sorbent among those compared in this study is that having composition Li_2CO_3:ZrO_2:K_2CO_3 = 1.15:1.0:0.2, without the necessity of adding such an expensive component as yttrium.

3.3. Sorbent Characterization during Sorption/Desorption Cycles. For the sorbent of choice, we conducted further studies in order to assess its regeneration properties and stability during several cycles of sorption and desorption. Figure 11 shows, by means of X-ray analysis, the microstructure changes of the Li/K-doped Li_2ZrO_3 before and during CO_2 sorption and after CO_2 desorption. Compared to XRD patterns of the original sorbent (top of Figure 11), XRD patterns of the sorption product (middle of Figure 11) show that the peaks assigned to Li_2ZrO_3 completely disappeared and that ZrO_2 peaks are present instead. This result indicates that during the CO_2 sorption process Li_2ZrO_3 reacts with CO_2 to become ZrO_2 and Li_2CO_3. However, the peaks of Li_2CO_3 were undetectable: Li_2CO_3 produced by the carbonation reaction is in liquid state; thus the carbonate becomes amorphous and undetectable by XRD after it is quenched. XRD patterns of the regenerated sorbent (bottom of Figure 11) only show peaks assigned to monoclinic Li_2ZrO_3, without other peaks. This means that, after CO_2 desorption at 800 °C, Li_2CO_3 and ZrO_2 react to produce again Li_2ZrO_3 with a monoclinic structure by releasing CO_2. Figure 12 shows SEM images of Li/K-doped Li_2ZrO_3 before and during CO_2 sorption and after CO_2 desorption. By comparison of SEM images of the original sorbent (top of Figure 12) and of the sorption product (middle of Figure 12), we can notice in the latter SEM image the presence of an amorphous phase associated with the quenched liquid carbonates. Furthermore, the SEM image of the regenerated sorbent (bottom of Figure 12) is essentially "identical" to that of the original sorbent. Hence, the sorbent appears to be fully regenerable.

Finally, we tested the stability of the sorbent undergoing several cycles of CO_2 sorption and desorption. In particular, Figure 13 shows CO_2 uptake and release of the sorbent during six cycles of sorption and desorption. It can be seen that no

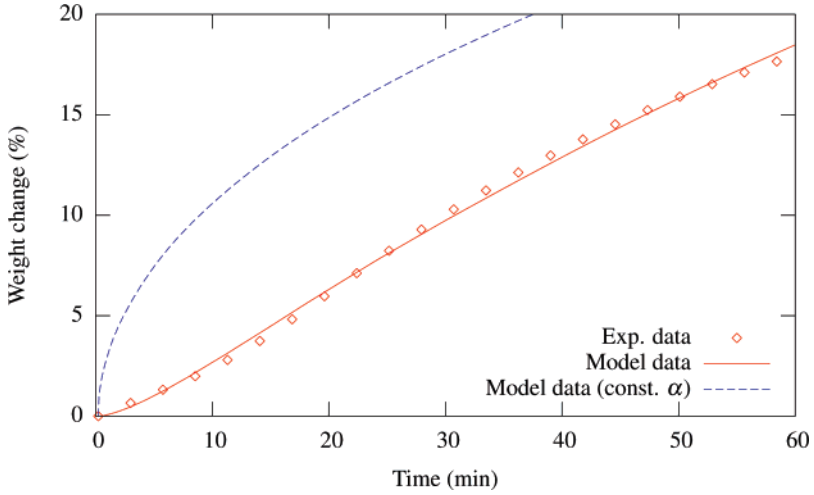

Figure 15. Experimental and model CO_2 uptake curves on Li_2CO_3/K_2CO_3-doped Li_2ZrO_3 with 15% excess Li_2CO_3 at 550 °C.

Table 1. Optimized Model Parameters at Different Temperatures

temp (°C)	500	550	600
τ (min)	14.6	14.3	15.0
$\bar{\alpha}$ (s^{-1})	0.74×10^{-6}	1.90×10^{-6}	0.16×10^{-6}

differences are noticed in terms of sorption capacity among different cycles, and therefore the sorbent appears fully stable.

4. Model Development

4.1. Introduction. Ida and Lin[2] proposed a double-shell model, schematically depicted in Figure 1, to describe the CO_2 sorption mechanism on Li_2ZrO_3 from a qualitative point of view. A mathematical formulation based on this model was proposed by Ida et al.[8] for the case of CO_2 sorption on pure Li_2ZrO_3, and was appropriately modified by Xiong et al.[6] for the case of Li_2ZrO_3 sorbent modified with Li_2CO_3/K_2CO_3 (it must be noticed that, despite the publication year, ref 8 was submitted slightly earlier than ref 6). The main difference between these two mathematical models is that in the case of pure Li_2ZrO_3 the rate-limiting step is assumed to be the CO_2 diffusion in the solid Li_2CO_3 shell, whereas in the case of Li/K-doped Li_2ZrO_3 the rate-limiting step is assumed to be the oxygen ion diffusion in the solid ZrO_2 shell, because the diffusion rate of CO_2 in the molten Li_2CO_3/K_2CO_3 shell is much higher.

From a theoretical point of view we can expect that, during the sorption process and after an initial transient, solid particles composed by an internal core of unreacted Li_2ZrO_3 and an external shell of ZrO_2 are surrounded by a Li_2CO_3/K_2CO_3 liquid phase. This expectation is also supported by the experimental evidence shown in Figures 11 and 12. From the SEM images shown in Figure 12 it is also clear that the solid particles can be considered approximately spherical in shape. For these reasons, we propose a slightly different model representation to describe the sorption mechanism, which is depicted in Figure 14. Furthermore, we propose a modification to better describe the initial part of the uptake curves, which cannot be accurately captured by the original model based on quasi-steady-state assumption.[6]

According to the model depicted in Figure 14, the overall reaction rate depends on the CO_2 diffusion rate in the Li_2CO_3/K_2CO_3 molten phase and on Li^+/O^{2-} diffusion rates in the ZrO_2 shell. However, since the diffusivity of CO_2 in the liquid phase is much higher than the diffusivity of lithium/oxygen ions in (solid) zirconia, it is reasonable to consider the latter one as the rate-limiting step. Moreover, since the dimension of O^{2-} is much larger than that of Li^+, the former ion should have much lower diffusivity. For these reasons, we can assume that the overall reaction rate is controlled by the rate of diffusion of O^{2-} in the zirconia shell. This diffusion process can be modeled by the following equation:

$$\frac{\partial C_A}{\partial t} = D_A \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_A}{\partial r}\right) \tag{5}$$

in which C_A is the oxygen ion concentration at time t and generic radius r inside the ZrO_2 shell; D_A is the diffusivity of O^{2-} in zirconia. In order to simplify the model, we can make use of a quasi-steady-state assumption to obtain the following differential equation:

$$D_A \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dC_A}{dr}\right) = 0 \tag{6a}$$

with associated boundary conditions

$$C_A = C_{A0} \qquad \text{at } r = L(t)$$
$$C_A = C_{A1} \qquad \text{at } r = R(t) \tag{6b}$$

in which $L(t)$ is the radius of the Li_2ZrO_3 unreacted core and $R(t)$ is the external radius of the ZrO_2 shell, whereas C_{A0} and C_{A1} are the oxygen ion concentrations at inner and outer boundaries of the zirconia shell, respectively (see Figure 14). If we assume that $R(t)$ does not change significantly, i.e., if we consider the molar density of Li_2ZrO_3 to be approximately equal to that of ZrO_2, and denote with R_0 the "constant" value of $R(t)$, we can obtain after some manipulations the following equation (more details can be found in ref 6):

$$\frac{dy}{dt} = \alpha\left(\frac{1}{y^2 - y}\right) \tag{7a}$$

with initial condition

$$y(0) = 1 \tag{7b}$$

in which $y = L(t)/R_0$ and α is defined as follows:

$$\alpha = \frac{D_A(C_{A0} - C_{A1})}{\rho R_0^2} \tag{8}$$

where ρ is the molar density of ZrO_2. Xiong et al.[6] assume that α is constant with time and, hence, solve eq 7 analytically. Then, given the value of y at any time, the relative weight change of the sorbent due to CO_2 uptake can be evaluated as

$$\hat{z} = \frac{\Delta w}{w_0} = \frac{M_{CO_2}\rho}{\rho_0}(1 - y^3) \tag{9}$$

in which Δw is the sorbent sample weight change, w_0 is the initial weight of lithium zirconate present in the sample, M_{CO_2} is the CO_2 molecular weight, and ρ_0 is the mass density of Li_2ZrO_3.

During this work, we experienced that the relative weight change obtained with a constant value of α does not describe accurately the initial part of the uptake curves, and several reasons can be found for this discrepancy. First of all, during the initial part of the CO_2 sorption process a proper zirconia shell surrounding the unreacted Li_2ZrO_3 is not yet formed. Then, even when this shell is completely formed, neither $R(t)$ nor the concentration gradient $(C_{A0} - C_{A1})$ can be necessarily considered constant. Finally, during the initial sorption process a quasi-steady-state assumption may not be appropriate. Thus, we propose to add transient dynamics for α as follows:

$$\tau^2\frac{d^2\alpha}{dt^2} + 2\tau\frac{d\alpha}{dt} + \alpha = \bar{\alpha} \tag{10a}$$

with initial conditions

$$\alpha(0) = 0, \qquad \left.\frac{d\alpha}{dt}\right|_{t=0} = \bar{\alpha}\tau \tag{10b}$$

in which τ is a time constant (e.g., expressed in minutes) and $\bar{\alpha}$ is the asymptotic value of α. It is important to notice that eq 10 assumes that $\alpha(t)$ varies from zero to the steady-state value $\bar{\alpha}$ with second-order dynamics. Furthermore, the lower τ the faster $\alpha(t)$ approaches its steady-state value $\bar{\alpha}$. In a preliminary work,[14] we proposed slightly different dynamics for the evolution of α in the case of Li/K-doped Li_2ZrO_3 sorbent prepared with addition of Y_2O_3.

The overall model composed by eqs 7 and 10 is integrated by means of the Matlab ordinary differential equation implicit solver ODE15I, as long as the two parameters τ and $\bar{\alpha}$ are specified, to obtain the time evolution of y from which the relative weight change of the sorbent can be evaluated by eq 9. The two model parameters τ and $\bar{\alpha}$, which depend on the operating temperature, are evaluated from a numerical optimization procedure based on experimental data as discussed next.

4.2. Results and Parameter Optimization. Given a sequence of N experimental data of sorbent relative weight changes at different times, we can compute the optimal values of the model parameters τ and $\bar{\alpha}$ by solving the following nonlinear optimization problem:

$$\min_{\tau,\bar{\alpha}} \Phi \tag{11a}$$

subject to

$$\tau_{min} \le \tau \le \tau_{max} \tag{11b}$$

$$\alpha_{min} \le \bar{\alpha} \le \alpha_{max} \tag{11c}$$

in which τ_{min}, τ_{max}, α_{min}, and α_{max} are user-defined bounds, and the objective function is defined as

$$\Phi = \sum_{i=1}^{N}(z_i - \hat{z}_i)^2 \tag{12}$$

where z_i is the experimental relative weight change measured at time t_i and $\hat{z}_i$ is the corresponding relative weight change evaluated from eq 9 with y computed by model eqs 7 and 10. The optimization problem is numerically solved using the Matlab constrained minimization routine FMINCON.

Since we are interested in modeling the sorption process in a time window where the reaction rate is still high, we restricted our attention to data collected during the first 60 min of CO_2 uptake. Results for the Li/K-doped Li_2ZrO_3 sorbent with a 15% excess of Li_2CO_3 at 550 °C are shown in Figure 15, in which it is clear that the proposed model with optimized parameters agrees very well with the experimental data. For comparison, Figure 15 also shows the uptake curve for the original model using a constant value of $\alpha(t) = \bar{\alpha}$. It is clear that the initial response of this model is quite different from the experimental curve. Furthermore, even if a lower constant value of α could be chosen in order to reduce the fitting error, the shape of the model uptake curve would still be inconsistent with the experimental curve. We also evaluated the optimal model parameters for CO_2 sorption on Li/K-doped Li_2ZrO_3 sorbent at 500 and 600 °C. These optimized model parameters are reported in Table 1, from which it appears that the temperature mostly affects the value of $\bar{\alpha}$. As expected, the highest value of $\bar{\alpha}$ is obtained at 550 °C, which is a fairly optimal trade-off temperature between kinetic and thermodynamic factors for the CO_2 sorption process.

5. Conclusions

Carbon dioxide sorption kinetics on different Li_2ZrO_3-based sorbents prepared was investigated in this work. Li_2ZrO_3 offers excellent CO_2 sorption characteristics in terms of large CO_2 sorption capacity, infinite CO_2/N_2 selectivity, and good reversibility. A moderate temperature around 550 °C is desirable for CO_2 sorption. The CO_2 sorption rate can increase by the addition of lithium potassium carbonate to Li_2ZrO_3 because a molten phase forms at the operating temperature, which increases significantly the CO_2 diffusion rate. We found that a 15% excess of Li_2CO_3 with 0.43 Li_2CO_3 mole fraction in the carbonate mixture achieves superior results in terms of the sorption rate with respect to other mixtures of carbonates discussed in the literature. Moreover, we found that for this sorbent the addition of Y_2O_3 is not necessary and that superior CO_2 sorption rates are indeed achieved without Y_2O_3. Furthermore, we characterized the regenerability and stability properties of the sorbent, achieving very favorable results. Finally, starting from a double-shell kinetic model described in the literature, we made a number of modifications and proposed a model with two parameters that are found from a nonlinear regression problem based on experimental data. The developed model fits the experimental data very well, and can be readily extended to different operating temperatures by adjusting the two model parameters.

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