A comprehensive mathematical model for the CO₂-catalyzed sintering of CaO is proposed. It takes into account the mechanisms of surface diffusion and grain boundary diffusion, catalyzed by CO₂ chemisorption and dissolution, respectively. In addition, the model proposed here considers the change in pore size distribution during sintering, grain growth, and the densification by lattice diffusion, which is the intrinsic sintering mechanism of the CaO. Model predictions are validated using experimental data on the sintering of two CaO samples, one of them derived from pure CaCO₃ and the other from limestone. It is found that impurities in limestone-derived CaO do not significantly affect the CO₂ dissolution or chemisorption processes; however, they strongly increase the rate of sintering by lattice diffusion. It is also established that low temperatures and CO₂ partial pressures promote the coarsening by surface diffusion, whereas high temperatures and CO₂ partial pressures favor densification.

Keywords: mathematical modeling, sintering, calcium oxide, carbon dioxide

Introduction

Reactions involving CaO have been widely studied for their industrial applications such as desulfurization of waste gases, cement manufacturing, and CO₂ sorption in the well-known Ca-looping process. Since most of these reactions occur at high temperatures, the sintering phenomenon strongly affects the CaO microstructure, the gas diffusivity, and the overall reactivity. In addition, many of the above-mentioned processes involve the presence of CO₂, which catalyzes solid-state diffusion mechanisms besides the intrinsic CaO mechanism, and also modifies the sintering rate of the calcium oxide.

The catalytic effect of CO₂ on CaO sintering has been largely investigated using an experimental approach. One of the most recognized studies on CO₂-catalyzed sintering of CaO is the work of Beruto et al. who described, for the very first time, the mechanisms involved in the catalytic process. Beruto et al. proposed that the first step in the catalytic phenomenon is the chemisorption of CO₂ that reacts with the surface O²⁻ anions to produce CO₃²⁻. Subsequently, adsorbed CO₃²⁻ diffuses on the surface causing a fast coarsening process without significant change in porosity. Finally, a slower dissolution process within the sample (at grain boundaries or into the bulk) begins, which enhances the densification process. This catalytic mechanism has been accepted over the years by several authors and has been experimentally confirmed in a more recent study. These studies indicate that both CO₂ chemisorption and its subsequent dissolution are the required steps to achieve an effective catalytic effect on the CaO sintering.

Modelling of CO₂-catalyzed sintering of CaO

Regarding CO₂-catalyzed sintering of CaO, the modelling approach has been semi-empirical. One of the most popular models is the classical German-Munir model, which predicts the drop in surface area at both initial and early-intermediate stages of sintering as follows

$$\left(\frac{S_0 - S}{S_0}\right) = K_c t$$

where $S_0$ is the initial specific surface area, $S$ is the instantaneous specific surface area, $\gamma$ is a mechanism-dependent exponent that varies between 1.1 and 3.5, $K_c$ is a temperature-dependent function, and $t$ is the time. Since in the original development of Eq. 1 the catalytic effect of CO₂ was not considered, Borgwardt empirically adjusted the values of $K_c$ and $\gamma$ to take into account such effect, and later on Stanmore and Gilot improved the fitting of these values. This modified German-Munir model has been used by several authors; however, it presents significant shortcomings:

The values of $\gamma$ fitted by Borgwardt have no physical meaning, since the original model was developed considering only one operating mechanism at a time. In addition, Eq. 1 was deduced from the widely known geometry of two equally

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sized spheres connected by a neck, assuming that sintering is driven by the gradient of curvature radius in the neck zone. However, this does not occur at the intermediate stage when surface free energy is the main sintering driving force.

Another flaw of the German-Munir model as modified by Borgwardt (1989) is that it only gives correct predictions in certain ranges of temperature and CO$_2$ concentration, due to its semi-empirical nature.\textsuperscript{19}

Another approach is the one adopted by Silcox et al.,\textsuperscript{20} which considers that the driving force of sintering is the interfacial energy gradient. This model obeys a thermodynamic principle ignoring geometric factors, and is expressed as

$$\frac{dS}{dt} = -k_c(S-S_{eq})^2$$  (2)

where $S_{eq}$ is the equilibrium specific surface area; and $k_c$ is a kinetic constant that depends on temperature and CO$_2$ partial pressure, which was empirically adjusted by Silcox. Equation 2 has some weaknesses, among which is that value of $S_{eq}$ must be experimentally determined after a long time of sintering. Furthermore, this model does not consider the CaO microstructure and also takes into account the CO$_2$ catalytic effect in a completely empirical manner similar to that of Borgwardt.\textsuperscript{13} More recently, other authors\textsuperscript{19,21} have used a model known as the empirical general power law expression (GLE). It follows the spirit of the Silcox model,\textsuperscript{20} incorporating both a mechanism dependent exponent and the initial specific surface area effect on the sintering kinetics. Nevertheless, despite the improvements in the GPLE, it suffers from the above drawbacks of Eq. 2.

**Distributed models in sintering**

Sintering is essentially characterized by two phenomena, densification and coarsening.\textsuperscript{22} These two processes depend not only on surface area, but also on several structural variables as pore size distribution, grain size, porosity, and pore coordination number. Incorporation of these structural variables has permitted the development of models that take into consideration the non-uniformity of the solid microstructure. One of the first approaches of this type was the so called statistical theory of sintering,\textsuperscript{23} which was later enhanced\textsuperscript{24,25} by considering the effect of pores trapped within the grains. In the statistical theory of sintering, the solid sample is modeled as a non-uniform sized population of pores or grains changing their sizes due to sintering, while obeying a population balance equation. However, in the original development of the model,\textsuperscript{23} the main simplification was the assumption of a quasi-stationary distribution with no experimental support. However, models for predicting the evolution of pore/grain size distribution have regained relevance,\textsuperscript{26-33} largely due to the progress in numerical simulation in the last decades. These latest models make no a priori assumption about the behavior of the distribution function, and instead numerically calculate its time evolution. Nevertheless, some of these models\textsuperscript{27-29} fall short in the distinction of the operative sintering mechanisms. Conversely, Maya and Chejne\textsuperscript{33} and Fierro et al.\textsuperscript{34} modeled the sintering as a phenomenon of coalescence of grains and pores, respectively. In these two last works, the pore shrinkage effect was not taken into account, so that such models\textsuperscript{33,34} should be used only at early stages of sintering when densification is not yet significant. Li et al.\textsuperscript{35} modeled the CaO sintering by using a discrete form of the population balance equation, and Maya et al.\textsuperscript{32} presented a distributed model for the same phenomenon that takes into account densification and allows to differentiate between the operative mechanisms in sintering. However, in these last two models the catalytic effect of CO$_2$ on the CaO sintering was not considered.

In summary, the commonly used models for the CO$_2$-catalyzed sintering of CaO only predict the change in surface area and empirically consider the CO$_2$ catalytic effect. Those models have shown quite reasonable agreement with experimental data despite their simplicity. However, they do not allow elucidating the phenomena involved in the CO$_2$-catalyzed sintering of CaO. Conversely, the distributed sintering models have greater merit since they consider the non-uniformity of the solid microstructure. Nevertheless, phenomena such as the CO$_2$-catalyzed sintering of CaO or any gas-catalyzed sintering process (e.g., H$_2$O-catalyzed sintering of MgO, H$_2$O-catalyzed sintering of CaO) have not been considered in these models. As can be seen above, although the CO$_2$-catalyzed sintering has been extensively studied from an experimental approach, the mathematical models related to this phenomenon have several weaknesses. Taking all the above into consideration, the goal of this work is to develop a detailed mathematical model considering the non-uniformity of the CaO sample, the steps of the CO$_2$ catalytic process (reversible chemisorption and dissolution within the CaO sample), and all the involved solid-state diffusion mechanisms. For this purpose, a population balance-based model that predicts the temporal-evolution of the pore size distribution, mean grain size, porosity, and surface area is developed. It is based on the distributed model of Maya et al.,\textsuperscript{32} but taking into account the catalytic effect of CO$_2$ in the atmosphere. The model is validated using experimental data of pore size distribution taken by gas adsorption porosimetry, and CO$_2$ chemisorption and dissolution measurements acquired through thermogravimetry.

**Experimental**

**Calcination**

CaO samples were prepared by the calcination of two precursors: limestone (97.3 wt % CaCO$_3$, 0.3 wt % MgCO$_3$, 2.3 wt % SiO$_2$, 0.1 wt % others; initial porosity = 0.03) and high purity CaCO$_3$ (99.9% CaCO$_3$, initial porosity = 0.02). In order to obtain CaO samples with high surface area, the effect of sintering during calcination was minimized. To this end, calcination was carried out at a low temperature of 950 K in N$_2$ atmosphere, and under chemical control conditions to minimize the CO$_2$ catalytic effect on the CaO sintering.

Chemical control conditions were found by using a thermogravimetric balance LINSEIS STA PT1600. (Each test was performed three times and an average was taken) with different gas flows, particle sizes, and sample amounts were carried out to determine the conditions in which the mass transfer resistances (external, intra-particle, and inter-particle) are removed. Thus, it was observed that interparticle mass transfer resistance is minimized by using amounts of sample smaller than 30.2 mg, the intra-particle diffusion step disappears with particles <3 μm in size, and the external mass transfer resistance is negligible at the above-mentioned operating conditions (950 K and N$_2$ atmosphere). Complete conversion times for calcination of the limestone and pure CaCO$_3$ under chemical control conditions were 1.5 and 2 min, respectively. These times differ because, under chemical control conditions, conversion depends only on the surface reaction rate that is proportional to the specific surface area.
the pure CaCO$_3$ due to the smaller specific surface area of MPD, it was possible to calculate the mean grain size:

\[ X-ray \text{ diffractometer X'Pert PRO Brand Panalytical reference temperature and fixed CO}_2 \text{ partial pressure. The CaO samples were immediately moved to a sintering muffle at constant temperature. The CaO samples of limestone-derived CaO (LC) were withdrawn from the heating muffle in 1.7 min and the CaCO}_3\text{-derived CaO (CC) samples were removed in 2.1 min. The times in which the samples were withdrawn from the heating muffle were determined from the complete conversion times under chemical control conditions found in the thermogravimetric balance.}

**Sintering**

After withdrawal from the heating muffle the CaO samples were immediately moved to a sintering muffle at constant temperature and fixed CO$_2$ partial pressure. The CaO samples were periodically removed from the sintering muffle, rapidly cooled and measurements of specific surface area and porosimetry conducted. This procedure was performed at different temperatures (1000–1200 K) and CO$_2$ partial pressures (0–70 kPa). The specific surface area and micro/mesoporosity measurements were performed with a surface and porosity analyzer TriStar II Plus from Micrometrics, by means of gas physisorption. Pore size distribution of pores with sizes below 1 nm was calculated from CO$_2$ adsorption measurements, whereas N$_2$ measures were used for calculating the pore size distribution function of pores larger than 1 nm in size.

The calculated initial BET surface areas for LC and CC were of 102.5 ± 4.9 m$^2$/g and 103.6 ± 4.1 m$^2$/g, respectively. Figure 1 shows the initial pore size distributions of the two CaO samples. It can be seen that most of the pores belong to the mesoporous range with mean pore radii of 2.7 and 2.9 nm for LC and CC, respectively, and porosities of 0.52 and 0.53 for LC and CC, respectively. These values of BET surface area, porosity and mean pore size are close to those found by other authors for nascent CaO.$^{10,36}$ Conversely, the two initial samples showed a type H1 hysteresis loop in the N$_2$ adsorption/desorption tests. This kind of hysteresis is associated with cylinder-like pores,$^{37}$ which is consistent with observations of other authors regarding the initial geometry of CaO pores.$^{10}$

From X-ray diffraction measurements determined using an X-ray diffractometer X’Pert PRO Brand Panalytical reference MPD, it was possible to calculate the mean grain size:

\[ G = \frac{C \lambda}{B \cos \beta} \]  

(3)

where $C$ is a dimensionless numerical constant, $\lambda$ is the wavelength of the X-rays, $\beta$ is the Bragg angle, $B$ is the line broadening at the half maximum intensity (FWHM) and $G$ is the mean grain size. The initial mean grain sizes were 17 and 18 nm for CC and LC, respectively.

**CO$_2$ chemisorption and dissolution**

Chemisorption and dissolution measurements must be carried out at constant surface and grain size; however, these two variables are strongly affected by both the sintering at the temperatures and CO$_2$ partial pressures studied in this work. Therefore, the CaO samples were initially sintered during 60 h at 1000 K and a CO$_2$ pressure of 3 kPa, and then pumped under vacuum for 9 h. At the end of this long-time sintering process, samples reached stable specific surface areas of 8.6 ± 0.7 m$^2$/g and 10.9 ± 0.9 m$^2$/g for LC and CC, respectively, and almost constant grain sizes of 199 and 159 nm for LC and CC, respectively. Then, the measurements of CO$_2$ adsorption and dissolution were undertaken in the above-described thermogravimetric balance. The highly sintered CaO samples were heated into the thermobalance (under N$_2$ atmosphere) until the desired temperature was reached. At this time, the required CO$_2$ was allowed to flow and the data of mass change over time were collected. A first equilibrium point was reached few seconds after CO$_2$ was admitted; however, the amount of CO$_2$ taken up by the sample continued to grow slowly until a second equilibrium point was reached several hours later. Therefore, it was assumed that the first fast process corresponds to the CO$_2$ chemisorption on the CaO surface and that the second slower step is associated with the CO$_2$ dissolution process, since it is known that chemisorption step occurs at a much faster rate than dissolution. The above procedure was carried out at several temperatures (1000–1150 K) and pressures (0.5–70 kPa) using new samples in every experiment (three times at each experimental condition).

**The Model**

As mentioned above, the model of this article is based in the distributed model of Maya et al.$^{32}$ but considering the catalytic effect of CO$_2$ on the CaO sintering. Thus, the assumptions adopted in the model of presented here are the following: The CaO is represented as a population of pores of different initial radius that grow or shrink because of sintering.

As mentioned above, the initial CaO samples showed a type H1 hysteresis loop, whereby it is assumed that pores are...
initially cylindrical. As sintering proceeds and the porosity reaches a value of about 0.08, the cylindrical pores become isolated pores that are represented by spheres;

It is supposed that CO$_2$ chemisorption catalyzes the sintering by surface diffusion and CO$_2$ dissolution within CaO catalyzes densification. Because the highly defective nature of grain boundaries, it is reasonably assumed that CO$_2$ dissolves within CaO through a grain boundary path. Therefore, it is also supposed that the catalyzed densification process occurs by grain boundary diffusion.

There are no thermodynamic constraints for shrinkage and the sintering process is isothermal. The temporal variation of the pore size distribution function follows:

$$\frac{\partial F}{\partial t} = - \frac{\partial}{\partial r_p}(vF)$$

(4)

Where $F$ is the pore radius distribution function, $r_p$ is the pore radius, and $v = \frac{d}{dr_p}$ is the total rate of pore radius change. It is commonly assumed that sintering mechanisms operate independently. Therefore, $v$ can be expressed as the sum of the rates of pore radius change related to all the operative mechanisms in the CO$_2$-catalyzed sintering of CaO:

$$v = v_l + v_g + v_s$$

(5)

where $v_l$ is the rate of shrinkage of pores due to mass transport by lattice diffusion, which is the intrinsic mechanism in the CaO sintering under inert atmospheres. The term $v_g$ represents the pore shrinkage rate owing to the grain boundary diffusion catalyzed by the CO$_2$ dissolution at grain boundaries. Finally, $v_s$ is the rate of pore radius change due to the surface diffusion mechanism catalyzed by CO$_2$ chemisorbed on the CaO surface.

**Rate of pore radius change due to lattice diffusion**

From studies of various authors, it has been determined that the intrinsic mass transport mechanism in the CaO sintering is lattice diffusion, which operates in any kind of atmosphere. In the literature, several sintering models for pore shrinkage can be found; however, in the derivation of these expressions, it is assumed that pores are attached to a fixed number of grain boundaries. The latter assumption is inaccurate, since in real powders the number of grain boundaries in contact with a pore changes over time because of grain growth. Hence, in this work the equation for $v_l$ proposed by Fang and Palmour is used. This expression takes into account the change in the number of grain boundaries attached to the pores and may be as:

$$v_l = N \times v_{b0}$$

(6)

where $v_{b0}$ is the rate of change of pore radius due to lattice diffusion assuming that the pore is in contact with just one grain boundary, and $N$ is the pore coordination number representing the number of grains around the pore (i.e., the actual number of grain boundaries attached to the pore). Expressions for $v_{b0}$ can be taken from the well-known sintering models for uniform structures at intermediate and final stages of sintering. Thus, for cylindrical pores, $v_{b0}$ is given by the classical Coble model for lattice diffusion sintering at intermediate stage:

$$v_{b0} = -D_l \gamma_s V_m \frac{\mu_0}{RTG^2 \rho_p}$$

(7)

where $D_l$ is the lattice diffusion coefficient, $\gamma_s$ is the specific surface energy, $R$ is the ideal gas constant, $V_m$ is the molar volume, $T$ is the temperature, and $\varepsilon$ is a dimensionless geometric constant. If pores are spherical, the model of Kang and Jung for lattice diffusion controlled sintering at final stage can be written as:

$$v_{b0} = -\varphi_1 \frac{D_l \gamma_s V_m \varepsilon^{1/3}}{RTG^2 \rho_p^2}$$

(8)

where $\varepsilon$ is the porosity and $\varphi_1$ is a dimensionless geometric constant.

**Rate of pore radius change due to grain boundary diffusion**

As has been mentioned above, grain boundary diffusion is catalyzed by the CO$_2$ that dissolves at grain boundaries as CO$_2^-$, improving the mobility of Ca$_2^+$ and CaO. Therefore, it can be reasonably assumed that the rate of pore radius change due to grain boundary diffusion is proportional to the amount of CO$_2$ dissolved at grain boundaries. Thus, $v_g$ may be expressed as:

$$v_g = \sigma_g \times q_g \times N \times v_{b0}$$

(9)

where $\sigma_g$ is a dimensionless proportionality constant, $q_g$ is the moles of CO$_2^-$ taken up by grain boundaries per mass unit of sample, and $v_{b0}$ is the rate of shrinkage of a pore in contact only with one grain boundary for a non-catalytic system when the operating mechanism is grain boundary diffusion.

The variable $q_g$ is calculated using an appropriate model for CO$_2^-$ dissolution at grain boundaries, and $v_{b0}$ may be expressed from the usual sintering models for simplified geometries. In the case of cylindrical pores, $v_{b0}$ is derived from Coble’s model for densification by grain boundary diffusion at intermediate stage:

$$v_{b0} = -\varphi_2 \frac{D_l \gamma_s V_m \delta_g}{RTG^2 \rho_p^2}$$

(10)

where $\varphi_2$ is a dimensionless geometric constant.

**Pore coordination number**

It is very difficult to experimentally determine the pore coordination number of each pore within the sample; however, it is possible to get an approximate average value by assuming that $N$ is proportional to the ratio between the mean pore surface area and the projected area of the grain. Hence, for cylindrical pore we have

$$N = \beta_1 \frac{\mu_1}{\mu_0} \frac{1}{G^2}$$

(12)

where $\mu_0 = \int r_p^2 Fdr_p$ is the moment of the pore radius distribution function and $l$ is the mean pore length. For spherical pores, the pore coordination number is given by

$$N = \beta_2 \frac{\mu_2}{\mu_0} \frac{1}{G^2}$$

(13)

where $\beta_1$ and $\beta_2$ are geometric constants.
Coarsening by surface diffusion

It has been experimentally found that, at the initial stage of the CaO sintering in CO₂ atmosphere, a large drop in surface area without considerable mesoporosity decrease occurs. This phenomenon has been associated with the CO₂ that chemisorbs on the CaO surface and catalyzes the sintering by surface diffusion; hence, it is reasonable to assume that the rate of sintering by this mechanism is proportional to the surface concentration of chemisorbed CO₂. Thus, the rate of change of pore radius due to the catalyzed effect of surface diffusion mechanism may be expressed as

\[ v_s = \sigma_s \times X_s \times \nu_{so} \]  

where \( \sigma_s \) is a proportionality constant, \( X_s \) is the surface concentration of chemisorbed CO₂, and \( \nu_{so} \) is the pore radius rate of change due to the surface diffusion mechanism for a non-catalytic system. Since sintering by surface diffusion is characterized by increase in the mean pore size at constant porosity, this phenomenon may be modeled as an Ostwald ripening process. Thus, by using the mean field approach, we employed the following expression for cylindrical pores:

\[ v_m = \frac{D_s \gamma_s V_m \delta}{RT_p^4} (r_p - r^*) \]  

where \( D_s \) is the surface diffusion coefficient, \( \gamma_s \) is a geometric constant, \( \delta \) is the diffusion thickness of the surface diffusion, and \( r^* \) is the critical pore radius given by

\[ r^* = \frac{\mu_2}{\mu_3} \]  

Surface area and porosity

The surface area and porosity are related to the moments of the pore radius distribution. These moments can be calculated by transforming Eq. 4 into moment equations. Thus, multiplying Eq. 4 by \( r_p^n \) and integrating from 0 to \( \infty \) yields

\[ \frac{d\mu_n}{dt} + r_p^n \left( \frac{dr_p}{dt} \right) F \int_0^{\infty} r_p^{n-1} \left( \frac{dr_p}{dt} \right) F dr_p = 0 \]  

For cylindrical pores, the porosity may be expressed as function of the second moment:

\[ \varepsilon = \frac{\pi \mu_1 l}{V} \]  

where \( V \) is the total sample volume. For spherical pores, porosity is related to the third moment, following

\[ \varepsilon = \frac{4\pi \mu_3}{3V} \]  

For pores of cylindrical geometry, the specific surface area in mass basis is a function of the first moment of pore radius distribution function:

\[ S = \frac{2\pi \mu_1 l}{m} \]  

where \( m \) is the mass of the sample. Finally, for spherical isolated pores, the specific surface area on a mass basis can be expressed as function of the second moment as shown below

\[ S = \frac{4\pi \mu_3}{m} \]  

Total rate of pore radius change

Equations 7, 8, 10, 11, and 12 depend on several terms that can be considered as constants, so Eq. 5 can be rewritten as follows

\[ v = -N \frac{\dot{k}_s(T)}{TGrp} - N \frac{\dot{k}_g(T)}{Te^{1/2}G^2_{sT}} q_g + \frac{\dot{k}_i(T)}{TGrp} (r_p - r^*) X_s \]  

for cylindrical pores, where \( \dot{k}_i(T) = \frac{D_s \gamma_s V_m \delta}{RT_p^4} \) and \( \dot{k}_i(T) = \frac{D_s \gamma_s V_m \delta}{RT_p^4} \). For isolated spherical pores, the total rate of pore radius change may be written as

\[ v = -N \frac{\dot{k}_L(T)e^{1/3}}{Trp^2} X_p - N \frac{\dot{k}_G(T)}{TGrp} q_g \]  

where \( \dot{k}_L = q_0 \frac{D_s \gamma_s V_m \delta}{RT_p^4} \) and \( \dot{k}_G = q_0 \frac{D_s \gamma_s V_m \delta}{RT_p^4} \). The constants \( k_L, k_G, k_i, k_s, k_g \), and \( k_m \) depend only on temperature, and are expressed by the following Arrhenius type equation:

\[ k_i = k_{i0} \exp \left( \frac{EA_i}{RT} \right) \]  

where \( k_{i0} \) is a pre-exponential factor and \( EA_i \) is the activation energy associated with the mechanism \( i \) (i,e,g,s,L,G). Regarding the solution of the model, an improved version of the extended method of moments (EMOM), which was described in detail in a previous paper, was used. All the simulations were carried out using Matlab 7.10.0.499 (R2010a) software.

Analysis and Results

CO₂ chemisorption and dissolution equilibrium

Figures 2a, b show the adsorption isotherms experimentally measured for CC and LC, respectively. For both samples a good fit with the experimental data was achieved by using the well-known Langmuir adsorption isotherm (solid lines in Figures 2a, b), which is expressed by

\[ q_{xe} = q_{s,max} \frac{K_s P_{CO_2}}{1 + K_s P_{CO_2}} \]  

where \( q_{s,max} \) is the amount of surface sites occupied by CO₂ at equilibrium, \( K_s \) is the adsorption equilibrium constant, \( P_{CO_2} \) is the CO₂ partial pressure and \( q_{s,max} \) is the total number of surface active sites, which is assumed proportional to the specific surface area. The good fit of the Langmuir model is expected since CO₂ is chemisorbed on the CaO surface to form a CO₁⁻ monolayer. As can be seen in Figures 2a, b, equilibrium isotherms for CC and LC are very similar, and yielded adsorption enthalpies of \(-202 \pm 6 \text{ kJ/mol}\) and \(-200 \pm 8 \text{ kJ/mol}\) for CC and LC, respectively. This suggests that LC impurities do not significantly affect the CO₂ chemisorption equilibrium. It must be said that the amount of surface sites occupied by CO₂ is slightly smaller than that of CC; however, this is not due to differences in the adsorption equilibrium constant, but the slightly lower relative number of active sites of LC \( q_{s,max} = 0.53 \) for CC and 0.51 for LC). The latter is probably due to unknown details of the LC surface or the occupation of some active sites by LC impurities.

Since the amounts of CO₂ dissolved in the sample during all the experiments were very small (<2% mol), the well-known
Henry’s law is expected to show good agreement with the experimental data. Nonetheless, since it is assumed that CO₂ dissolves at grain boundaries, the number of available active sites for the CO₂ dissolution must depend on grain size. Hence, assuming a constant grain boundary width, the following modified Henry’s law is used to model the CO₂ dissolution equilibrium

$$q_{g,eq} = \frac{K_gP_{CO_2}}{G}$$

where $$q_{g,eq}$$ is the number of grain boundary sites occupied by the CO₂ at equilibrium and $$K_g$$ is a dissolution equilibrium constant. Good agreement of Eq. 26 with the experimental data confirms that CO₂ dissolves at the grain boundaries and not into the bulk, which was not clear until now. In addition, the fact that CO₂ dissolves through grain boundaries supports the assumption that CO₂ dissolution catalyzes the sintering by grain boundary diffusion.

**CO₂ chemisorption and dissolution kinetics**

Assuming that adsorption rate is proportional to the CO₂ partial pressure, the net rate of CO₂ chemisorption is given by

$$\frac{dq_s}{dt} = k_aP_{CO_2}(q_{s,max} - q_s) - k_dq_s$$

where $$q_s$$ is the amount of surface sites occupied by the chemisorbed CO₂, $$k_a$$ is the adsorption kinetic constant and $$k_d$$ is the calculated dissolution equilibrium constants for the two samples were very similar, implying that LC impurities do not significantly affect the CO₂ dissolution equilibrium in the range of experimental conditions studied in this work. The calculated dissolution enthalpies (200 ± 10 kJ/mol for CC and 197 ± 8 kJ/mol for LC) were very close to the adsorption enthalpies, suggesting that strength of repulsive interactions between CO₂⁻ ions chemisorbed on the surface is similar to that of ions dissolved within the sample.

Finally, it must be said that the good agreement of Eq. 26 with the experimental data confirms that CO₂ dissolution occurs at the grain boundaries and not into the bulk, which was not clear until now. In addition, the fact that CO₂ dissolves through grain boundaries supports the assumption that CO₂ dissolution catalyzes the sintering by grain boundary diffusion.
desorption kinetic constant. Since $K_s = \frac{k_a}{k_d}$, Eq. 27 may be rewritten as

$$\frac{dq_s}{dt} = k_a P_{CO_2} \left( q_{(s, \text{max})} - q_s \right) \frac{q_s}{K_s}$$

(28)

For the dissolution process, the following pseudo-first-order rate equation is used:

$$\frac{dq_g}{dt} = k_g q_g - q_g; \text{eq} \frac{q_g}{C_0/C_1}$$

(29)

where $k_g$ is the pseudo-first-order rate constant that depends on temperature, and $q_g$ is the number of grain boundary sites occupied by the CO$_2$. Thus, the total CO$_2$ uptake $q_T$ is given by

$$q_T = q_s + q_g$$

(30)

Figure 4 shows the CO$_2$ taken up by the CC sample at different temperatures and $P_{CO_2} = 4$ kPa once CO$_2$ is admitted. Within the first 5 s (see inset in Figure 4) the CO$_2$ uptake is primarily due to the chemisorption, whereas after the second 5 is mainly because of the CO$_2$ dissolution phenomenon. It is observed that the kinetic model used has remarkable fit with the experimental data for both regimes, although it slightly overpredicts the CO$_2$ uptake during the first seconds of process. The latter is probably because a few seconds are required for the desired CO$_2$ partial pressure to be reached, right after CO$_2$ is admitted.

The CO$_2$ uptake rates of the two samples are very much alike for the whole range of experimental conditions studied in this work. The calculated activation energies for the constant $k_a$ are $44 \pm 6$ kJ/mol and $42 \pm 6$ kJ/mol for CC and LC, respectively, whereas activation energies for $k_g$ are $157 \pm 11$ kJ/mol and $161 \pm 11$ kJ/mol for CC and LC, respectively.

As can be seen above, the adsorption and dissolution processes studied in this work are not influenced by the CaO precursor type. Therefore, it can be said that impurities as MgCO$_3$, SiO$_2$, or possible products formed from these compounds during calcination (at 950 K) do not significantly affect the CO$_2$ chemisorption or dissolution.

**Sintering of the CaO**

The model presented here requires the fitting of three parameters ($k_i$, $k_g$, and $k_s$) in case of cylindrical pores or two
for pores of spherical geometry. Nonetheless, these constants cannot be fitted from data taken at any experimental condition. This occurs because CO₂ may catalyze several mechanisms simultaneously and the effect of each of them cannot be easily differentiated. Therefore, in this work the above-mentioned constants were fitted by comparing the model with experimental data taken under conditions in which the operating mechanisms can be differentiated.

First, the model predictions were compared with experimental data of the evolution of pore size distribution measured at different temperatures (1000–1200 K) under N₂ atmosphere. Thus, the only constant to fit is \( k_L \), since the only operating mechanism should be the lattice diffusion, \( k_L \), and furthermore, the pores of the sample are cylindrical. Figures 5a, b show the model predictions for the pore size distribution function development (1173 K, N₂ atmosphere) for CC and LC, respectively. Remarkable agreement of model with the experimental data for the two samples is seen, supporting the assumption that the controlling mechanism in N₂ atmosphere is lattice diffusion.

It was found that the sintering rate of LC is greater than that of CC over the whole temperature range studied here, and that the activation energy for lattice diffusion of LC is smaller than that of CC (385 ± 14 kJ/mol for CC and 281 ± 10 kJ/mol for LC). This behavior was previously observed by Borgwardt, who concluded that the sintering rate of limestone-derived CaO is larger than that of the CaCO₃-derived CaO because of limestone impurities accelerating the lattice diffusion mechanism. In the work of Borgwardt, the decrease of the surface area due to sintering of different types of CaO was studied. In Figure 6, the experimental data of Borgwardt and those of this work for the CaO sintering at 1173 K in N₂ atmosphere are shown. In this figure, it can be seen that CC and the carbonate-derived CaO of Borgwardt have similar sintering rates, whereas our limestone-derived sample (LC) has a different rate from that of Borgwardt. This suggests that the sintering rate is highly sensitive to the amount of impurities, since the sintering rates of the pure calcium oxides are more than five times larger than those of the carbonate-derived CaO samples, although the limestone used by Borgwardt and the one used this work have only about 2–3 wt % of impurities. Moreover, one can also infer that the sintering rate is not only affected by the amount of impurities, but also by the kind of impurities. Thus, although the limestone of Borgwardt (∼2 wt % impurities, mainly SiO₂, Al₂O₃, and Fe₂O₃) and that of this work (∼2.7 wt % impurities, mainly SiO₂ and MgCO₃) have similar
amounts of impurities, sintering rates of limestone-derived CaO samples are very different each other. However, it must be said that this work and in that of Borgwardt, CaO samples derived from limestone with low impurities concentration were studied. Therefore, the conclusions of this article should not be extended to highly impure CaO samples.

The parameter $\hat{k}_s$ was calculated by fitting the model predictions with experimental data taken under conditions in which the only operative mechanisms are lattice diffusion and surface diffusion. Under these experimental conditions, the only constant to be fitted in Eq. 22 is $\hat{k}_s$, because constant $\hat{k}_l$ was previously calculated. To ensure that the only operative mechanisms in the CaO sintering are lattice diffusion and surface diffusion it is necessary to avoid the effect of grain boundary diffusion by minimizing the CO$_2$ penetration within the sample. This is accomplished by using low temperatures (950–1050 K) and low CO$_2$ pressures ($P_{\text{CO}_2} < 4$ kPa) in the experiments, so that the CO$_2$ dissolution rate is minimized. Figures 7a, b show the model predictions of the evolution of pore size distribution function (1000 K and $P_{\text{CO}_2} = 1$ kPa) for LC and CC, respectively. It can be seen that for both samples the mean pore size increases at constant porosity, indicating that coarsening is the dominant phenomenon at low temperature and CO$_2$ partial pressure. It is expected that this coarsening process is due to the surface diffusion, since this mechanism is particularly strong at low temperatures.\textsuperscript{41} The model exhibits remarkable agreement with experimental data, although it slightly overpredicts porosity and mean pore radius at 20 min. This is because at this time densification by grain boundary diffusion becomes significant, which produces a decrease in porosity and mean pore radius. In addition, the calculated activation energies for $\hat{k}_s$ (55 $\pm$ 4 kJ/mol and 58 $\pm$ 7 kJ/mol for LC and CC, respectively) are smaller than activation energies for $\hat{k}_c$, which is consistent with a surface diffusion mechanism. Conversely, it was found that sintering rates of LC and CC were quite similar, implying that LC impurities do not affect the process of coarsening by surface diffusion.

Constant $\hat{k}_c$ can be calculated in any experimental condition, because $\hat{k}_l$ and $\hat{k}_s$ are known. The calculated activation energies for $\hat{k}_c$ (249 $\pm$ 11 kJ/mol for LC, and 245 $\pm$ 15 kJ/mol for CC) were larger than those of $\hat{k}_l$ but lower than those of $\hat{k}_s$, which is consistent with the grain boundary diffusion mechanism.\textsuperscript{41} Moreover, the quite similar activation energies of LC and CC signal that impurities in LC do not influence the grain boundary diffusion mechanism.

Model predictions at 1150 K and $P_{\text{CO}_2} = 30$ kPa for LC and CC are shown in Figures 8a, b, respectively. It can be seen that model has good fit with the experimental data and that densification is the dominant phenomenon at these conditions. Conversely, in the insets of Figures 8a, b is observed that for pores with radii smaller than about 1.1 nm, in case of CC, and 0.9 nm, in case of LC, the model overpredicts porosity. However, this is probably not due to a model failure but to the change in pore geometry (i.e., when cylindrical pores are very small in size they become isolated pores, which cannot be detected by adsorption techniques).

As was mentioned above, in the experiments shown in Figures 7a, b coarsening is the dominant phenomenon, whereas in Figures 8a, b the sintering is controlled by the densification phenomenon. Hence, it can be deduced that the CO$_2$-catalyzed sintering of CaO is controlled by different phenomena depending on experimental conditions. The latter may be better understood by analyzing Figure 9, in which the evolution of LC porosity at different temperatures and $P_{\text{CO}_2} = 1$ kPa is shown. It can be seen that at temperatures between 1000 and 1100 K, porosity remains almost constant during the first minutes, implying that at low temperatures coarsening controls the early stage of sintering. As temperature increases, the coarsening phenomenon diminishes its duration until a temperature of 1150 K, when sintering is controlled by densification from the beginning. This behavior is explained by the fact that coarsening is caused by the surface diffusion mechanism, which is particularly strong at low temperatures and during early stages of sintering.

Figure 9 also shows the porosity evolution at 1050 K and $P_{\text{CO}_2} = 10$ kPa, in which the coarsening phenomenon is not observed at any time, indicating that densification is favored by the high partial pressures of CO$_2$. This is because as CO$_2$ partial pressure increases, the CO$_2$ dissolution rate also increases and promotes the densification by grain boundary diffusion. Finally, it is important to note that the good agreement of model presented here with all the experimental data demonstrates that the assumed catalytic mechanism is correct.

Concluding Remarks

In this work, a comprehensive mathematical model for the CO$_2$-catalyzed sintering of calcium oxide has been presented. It considers the simultaneous effects of lattice diffusion, grain boundary diffusion, and surface diffusion on the development of pore size distribution of the calcium oxide. The model takes into account the effects of the CO$_2$ chemisorption and dissolution in the CaO sintering under CO$_2$ atmosphere, which had not been achieved so far.

The model predictions have been compared with experimental data for the evolution of pore size distribution function of two different CaO samples. Remarkable agreement with the experimental data is observed, confirming the two main hypotheses of model: CO$_2$ chemisorption catalyzes the surface diffusion and CO$_2$ dissolution within CaO catalyzes the grain boundary diffusion mechanism.

At low concentrations, impurities such as MgCO$_3$ and SiO$_2$ or possible compounds formed from these during
calcination did not considerably affect the CO$_2$ chemisorption and dissolution on the calcium oxide; however, they strongly affect the CaO sintering process. Thus, the existence of impurities in the CaO increases the sintering rate due to the acceleration of lattice diffusion mechanism, whereas the type of impurities determines the magnitude of such increase.

The sintering of calcium oxide under CO$_2$ atmosphere is dominated by coarsening or densification depending on the temperature and partial pressure of CO$_2$. On one hand, reduction of temperature favors coarsening because this phenomenon is caused by surface diffusion mechanism, which is especially strong at low temperatures. Conversely, densification is favored by increase of CO$_2$ partial pressure, because the CO$_2$ dissolution rate also increases and promotes the densification by grain boundary diffusion.

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