

Study of Limestone Calcination with CO₂ Capture: Decomposition Behavior in a CO₂ Atmosphere

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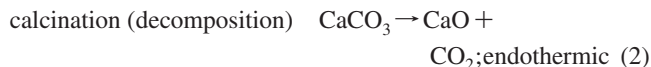
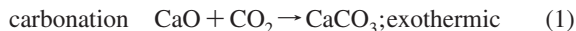
In the present work, the effects of temperature (up to 1293 K) and residence time on the decomposition behaviors of limestone particles (0.25–0.5 mm) in a CO₂ atmosphere were investigated using a continuously operating fluidized bed reactor for CO₂ capture. The results show that the rate of limestone decomposition was strongly dependent upon the pressure difference between the equilibrium CO₂ pressure and CO₂ partial pressure in experiments ($P^* - P_{\text{CO}_2}$) with temperature. Decomposition conversions ($\text{CaCO}_3 \rightarrow \text{CaO}$) were 73% at 1193 K and 95% at 1293 K, with a 70 min average residence time of particles in the bed. A model was proposed to describe the distribution of limestone particles in the fluidized bed reactor with residence time. The hydration and carbonation reactivities of CaO produced by the limestone decomposition were also tested. The results show that CaO hydration [CaO to $\text{Ca}(\text{OH})_2$] can be completed within 11 min; however, the conversion of CaO to CaCO_3 in the CaO carbonation test was below 60%.

1. Introduction

Carbon dioxide (CO₂) is a contributor to the greenhouse effect that causes global warming. Most anthropogenic CO₂ emissions are due to the combustion of fossil fuels. Some limestone calcination processes, such as limestone calcination in the cement industry, and some processes of CO₂ separation using CaO base sorbent also release CO₂ into the atmosphere. To prevent rapid climate change, it will be necessary to stabilize the CO₂ concentration in the atmosphere by better reduction of CO₂ emissions.

At present, a reliable method for the interception of CO₂ emissions consists of three steps: capture, transport, and sequestration. Lyngfelt et al.¹ reviewed the feasibility of this sequence and reported that the cost of the CO₂ capture step is much higher than that of the transport and sequestration steps.

Calcined lime (main content of CaO) can be used for CO₂ absorption in some industrial processes by carbonation of CaO with CO₂ to yield the carbonate CaCO_3 (eq 1), after which the carbonate CaCO_3 is thermally decomposed (calcined) to CaO and CO₂ (eq 2).



The calcination step (eq 2) is also used in the cement industry to decompose natural limestone (main content of CaCO_3) to obtain lime (main content of CaO), releasing CO₂.

Using CaO to absorb CO₂ from flue gas has previously been studied by several authors.^{2,3} Gupta and Fan³ provided an

overview of the advantages of this absorption process, including the operating conditions, CO₂ sorbents, gas products, and so forth. Curran et al.⁴ first studied the use of CaO to absorb CO₂ internally in a coal gasifier. Lin et al.^{5,6} also proposed that internal absorption of CO₂ in a coal gasifier can improve the purity of the hydrogen produced and that CO₂ can be captured by one reactor (the hydrogen production by a reaction-integrated novel gasification process, HyPr-RING). If CaO is used to absorb CO₂, whether from flue gas or inside the reactor, the CaCO_3 produced needs to thermally decompose to CaO in a calciner for cyclic use. On the other hand, to obtain a purified stream of CO₂ from the calciner, the atmosphere should be CO₂. Therefore, it is necessary to clarify the decomposition characteristics of CaCO_3 in a CO₂ atmosphere in the calciner.

Many studies have been performed on the calcination of limestone or pure CaCO_3 in a vacuum,⁷ as well as in partial CO₂,^{8,9} 100% CO₂,^{10–12} and other atmospheres.¹³ Almost all of

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Table 1. Chemical Analysis of Limestone

	composition (wt %)			
	F_{CaO}	F_{MgO}	F_{CO_2}	F_{others}
Kuzuu (Tochigi, Japan)	50.60	3.98	44.32	1.10

the studies cited focused on the kinetics of limestone or CaCO_3 decomposition, and most of the experiments were carried out at temperatures below 1173 K with a small thermogravimetric analysis (TGA) apparatus. Recently, Lech¹⁴ presented a paper about the influence of limestone properties on calcination time with three limestones (45–95 mm cylindrical samples, 1:1 dimension/height). Lech¹⁴ reported that the kind, sizes, and porosity of limestone have a great impact on the calcination time besides of heat and mass transfer.

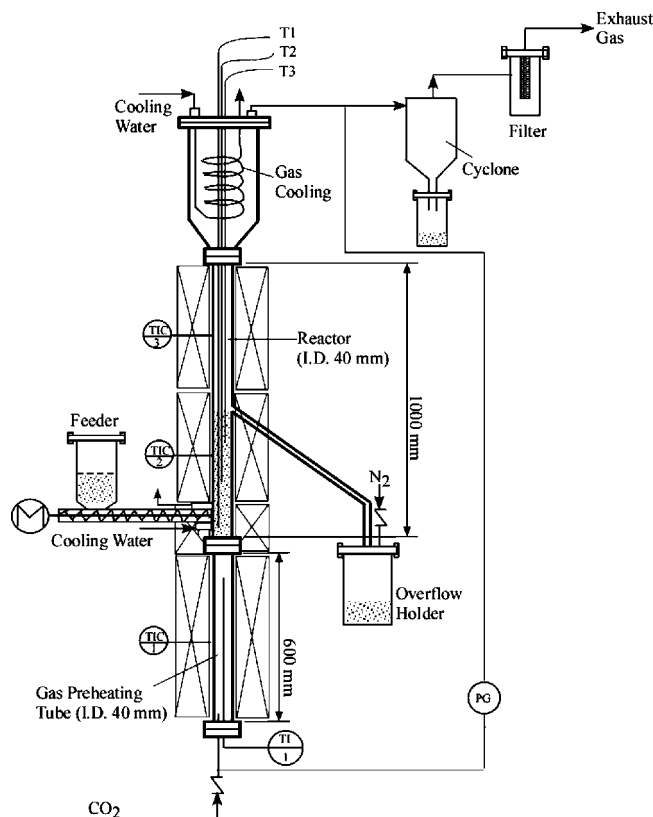
In the present work, the objective was to investigate the optimal thermal decomposition conditions for one kind of limestone with CO_2 absorption. A continuously feeding fluidized bed reactor was used to investigate the effects of temperature (up to 1293 K) and residence time on the limestone decomposition ($\text{CaCO}_3 \rightarrow \text{CaO}$) in an atmosphere of 100% CO_2 . The rate of limestone decomposition was calculated with data from experiments with the continuously operating fluidized bed reactor. Both CaO hydration and carbonation reactivity were also tested.

2. Experimental Section

2.1. Sample. In the present work, a piece of limestone (Kuzuu, Tochigi, Japan) was used for the experimental sample. The limestone was ground and sieved to 0.25–0.50 mm for the experiments and analyzed for its chemical composition (Table 1).

2.2. Fluidized Bed Apparatus. A continuously operating fluidized bed reactor (Figure 1) was used to decompose limestone. The apparatus consists mainly of a fluidized bed reactor, a screw feeder, and an overflow holder. The fluidized bed reactor was made of an Inconel pipe, with an inner diameter of 40 mm and a length of 1000 mm. Underneath the fluidized bed, a gas preheater preheated the supplied carrier gas, in this instance, CO_2 . The carrier gas was supplied from the bottom, passed through the preheater into the fluidized bed reactor, and then flowed out the top of the reactor. The limestone particles were introduced by a screw feeder, made into a fluidized bed in the reactor, and then overflowed into the overflow holder. The temperatures in the fluidized bed were measured by K-type thermocouples located at three points T1, T2, and T3 (Figure 1). The differential pressure (ΔP) between the bottom and top of the fluidized bed was measured during the experiments.

2.3. Experimental Procedure. Temperatures of the fluidized bed reactor and the preheater were raised by an electric furnace to the target values while injecting the CO_2 stream at a given flow rate, for instance, $0.20 \times 10^{-3} \text{ m}^3/\text{s}$ (Table 2). A purge gas (nitrogen, $0.83 \times 10^{-6} \text{ m}^3/\text{s}$) was injected into the overflow holder, passed through the overflow pipe, and flowed out of the reactor with the CO_2 coming from the fluidized bed. When the temperatures of the reactor reached the preset values, the limestone particles were introduced into the reactor to start decomposition. The temperatures T1, T2, and T3 and the differential pressure (ΔP) were measured continuously (Figure 2). When limestone particles were introduced to the reactor, the temperatures T1, T2, and T3 decreased and the differential pressure (ΔP) increased. At an overflow beginning time, the differential pressure (ΔP) began to decrease and eventually reached a stable value. After the differential pressure (ΔP) and bed temperatures were stable, the experiment was then performed, lasting about 70 min. In the present work, the time between the start of the particle introduction and the beginning of the overflow, t_0 , was defined as the average residence time of the particles in the

**Figure 1.** Continuously operating thermal decomposition apparatus.**Table 2. Experimental Conditions**

limestone feed rate (g/s)	CO_2 flow rate [$\times 10^{-3} \text{ (m}^3/\text{s)}$]	bed average temperature (K)
0.093	0.20	1193
0.093	0.20	1223
0.093	0.20	1253
0.093	0.20	1273
0.093	0.20	1293
0.18	0.20	1273
0.093	0.32	1223
0.07	0.28	1223
0.07	0.20	1223

bed. After the experiment, the decomposed particles were sampled from the overflow holder. In the present work, the bed temperature was used as the average value of T1, T2, and T3. To test the thermal decomposition of limestone under certain times and temperatures, some batch experiments (time up to 60 min and temperature up to 1373 K) were also performed and compared to the results of the fluidized bed experiments.

2.4. Analysis of the Solid CaO . The conversion of CaCO_3 to CaO in the sample after limestone decomposition was confirmed by a TGA (Rigaku ThermoPlus 8120) technique. The conversion of CaCO_3 to CaO in the sample was defined as

$$X = \left[1 - \frac{(100 - F_{\text{CO}_2})W_{\text{change}}56}{F_{\text{CaO}}(W_0 - W_{\text{change}})44} \right] \times 100\% \quad (3)$$

where F_{CaO} and F_{CO_2} are CaO and CO_2 contents in raw limestone (wt %), respectively, and W_0 and W_{change} are the initial weight and weight change of the sample (product from the overflow holder) analyzed in the TGA measurement (in grams), respectively.

The reactivity of CaO in the sample after limestone decomposition was tested by steam hydration and CO_2 carbonation with a TGA apparatus.¹⁵ Hydration was measured under 923 K and 2.0

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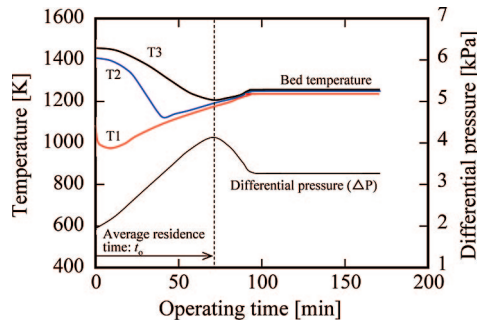


Figure 2. Variations of temperature in the reactor and the differential pressure between the bottom and top of the bed versus the operation time.

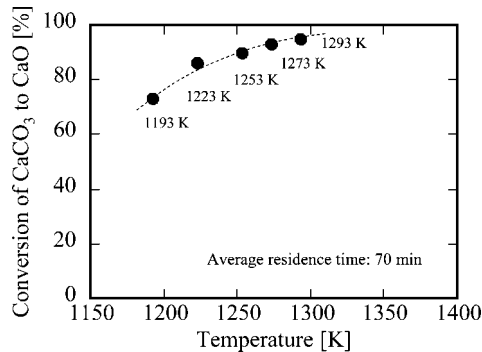


Figure 3. Effect of the temperature on the conversion of CaCO₃ to CaO in limestone decomposition.

MPa of steam partial pressure, and carbonation was measured under 923 K and 0.04 MPa of CO₂ partial pressure.

3. Results and Discussion

3.1. Behavior of Limestone Decomposition in a CO₂ Atmosphere. **3.1.1. Temperature and CO₂ Partial Pressure Effects.** We studied the conversion of CaCO₃ to CaO of limestone decomposition with various fluidized bed temperatures (Figure 3). The average residence time (t_0) of particles in the fluidized bed was about 70 min in this case. It can be seen that conversion of CaCO₃ to CaO was dependent upon the fluidized bed temperature. For example, the conversion was 73% at 1193 K, 90% at 1253 K, and 95% at 1293 K. This means that the rate of CaCO₃ decomposition increased with temperature. However, the magnitude of the rate increase decreased with an increasing temperature. When the temperature increased from 1193 to 1253 K (Figure 3), the conversion increased about 17% but increased only 5% from 1253 to 1293 K. Stanmore and Gilot¹⁶ investigated the limestone decomposition rate under various temperatures and CO₂ partial pressures using the TGA technique and reported the rate of CaCO₃ decomposition to be

$$R = K_D(P^* - P_{CO_2}) = \left[A \cdot \exp\left(\frac{-E}{RT}\right) \right] (P^* - P_{CO_2}) \quad (4)$$

$$A = 0.012 \quad (\text{mol m}^{-2} \text{s}^{-1} \text{kPa}^{-1}) \quad (5)$$

$$E = 33.47 \quad (\text{kJ mol}^{-1}) \quad (6)$$

$$P^* = 4.192 \times 10^9 \exp\left(\frac{-20474}{T}\right) \quad (\text{kPa}) \quad (7)$$

where P_{CO_2} is the partial pressure of CO₂ in the experiment, P^* is the equilibrium CO₂ pressure for CaCO₃ decomposition and

Table 3. Values of P^* , $(P^* - P_{CO_2})$, and K_D with Temperature

temperature (K)	P^* [$\times 10^2$ (kPa)]	$(P^* - P_{CO_2})$ [$\times 10^2$ (kPa)]	K_D [$\times 10^{-2}$ (mol m ⁻² s ⁻¹ kPa ⁻¹)]
1173	1.101	0.088	0.039
1223	2.249	1.236	0.045
1273	4.341	3.328	0.051
1323	7.971	6.958	0.057
1373	14.004	12.991	0.064

is calculated with the fluidized bed temperature, A is the frequency factor, and E is the activation energy.

Because P_{CO_2} was held constant at about 101.325 kPa in the present work and P^* was a function of temperature only, the term of $(P^* - P_{CO_2})$ in eq 4 was dependent upon temperature (Table 3). The temperature dependence of K_D and $(P^* - P_{CO_2})$ within the temperature range of the present study (Figure 4) shows that the temperature dependence of the term $(P^* - P_{CO_2})$ was stronger than that of K_D . For example, when the temperature increased from 1173 to 1223 K, compared to an increase of a factor of 1.15 times K_D , the increase of $(P^* - P_{CO_2})$ was about a factor of 14.0. Also, the temperature dependence of $(P^* - P_{CO_2})$ decreased with an increasing temperature. For example, $(P^* - P_{CO_2})$ increased 169% for a temperature rise from 1223 to 1273 K, 109% from 1273 to 1323 K, and only 87% from 1323 to 1373 K. This may explain the observed behavior of CaCO₃ decomposition (Figure 3): the conversion increase was rapid in the temperature range of 1193–1223 K but comparatively slow in the temperature range of 1253–1293 K.

Lowering the CO₂ partial pressure P_{CO_2} , for instance, when diluted by other gases (eq 4), can increase the value of term $(P^* - P_{CO_2})$, i.e., an increase of the rate of CaCO₃ decomposition, which we will discuss elsewhere.

3.1.2. Conversion of CaCO₃ Decomposed in the Fluidized Bed. At 1223 and 1273 K, the conversion of CaCO₃ to CaO increased with increasing average residence times of the

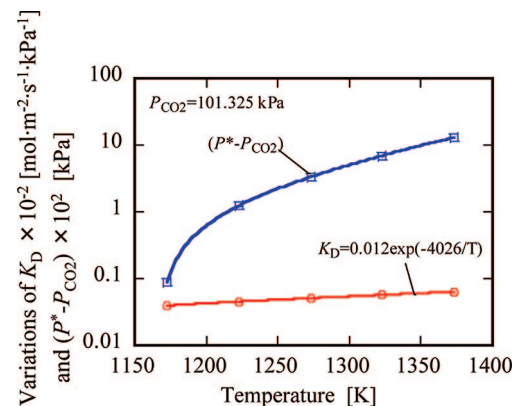


Figure 4. Variation of K_D and $(P^* - P_{CO_2})$ with temperature.

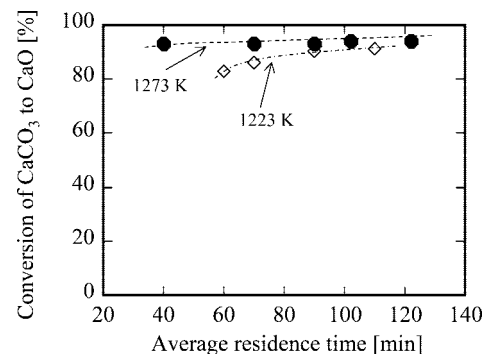


Figure 5. Effect of the average residence time in the fluidized bed on the conversion of CaCO₃ to CaO in limestone decomposition.

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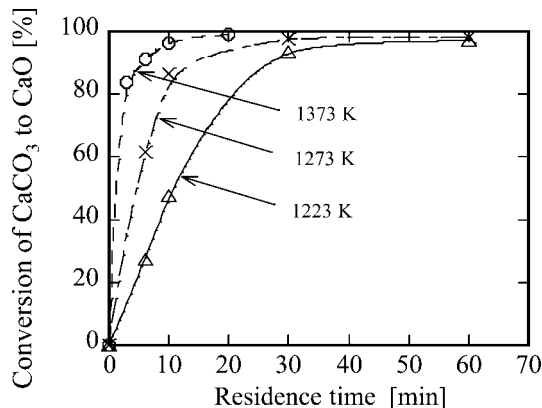


Figure 6. Effect of the residence time on the conversion of CaCO_3 to CaO in batch experiments.

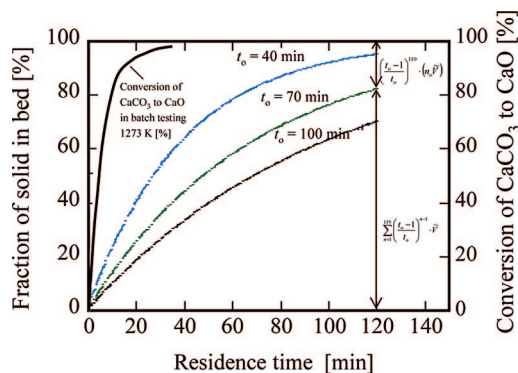


Figure 7. Fraction of solid in the bed with the residence time and the conversion of CaCO_3 to CaO in batch testing.

particles in the bed (Figure 5). However, the increase was slower by a comparison to the effect of the temperature (Figure 3). For example, at 1223 K with an average residence time of 70 min, the conversion was 86%, at 90 min, the conversion was 90%, and at 110 min, the conversion was only increased to 91%.

To clarify the effect of the reaction time on the decomposition of limestone particles, a batch experiment was performed with the same apparatus: about 3 g of limestone particles was put in a platinum basket (φ of 25 mm and height of 15 mm) and then hanged down in the reactor, in which all particles in the basket were under the same conditions, including the average residence time and temperature (Figure 6). High conversion (over 98%) of CaCO_3 to CaO was achieved at 20 min for 1373 K, at 40 min for 1273 K, and at 60 min for 1223 K. The limestone decomposition was therefore faster in the batch experiments than in the fluidized bed experiments (Figure 5).

In the fluidized bed reactor, the overflow particles appear to have a conversion distribution, which we can model as follows. Considering a complete mixture of particles in the bed, the fraction of particles with real residence time may be described as

$$M_t = \left(\frac{t_0 - 1}{t_0} \right)^{n-1} \tilde{V} \quad (8)$$

$$\tilde{V} = W/W_{\text{bed}} \quad (9)$$

where M_t is the fraction of particles in the bed with the real residence time t , n is the number of time sections, \tilde{V} is the dimensionless introduction rate of particles, W is the particle introduction weight in one time section (in grams), and W_{bed} is the weight of particles in the bed (in grams).

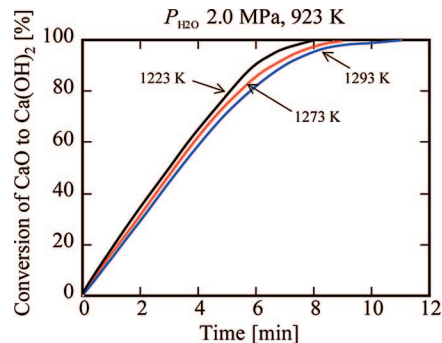


Figure 8. Hydration reactivity of CaO produced at various bed temperatures.

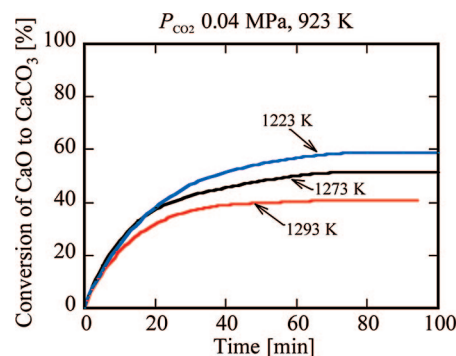


Figure 9. Carbonation reactivity of CaO produced at various bed temperatures.

Figure 7 shows the fraction of solid in the bed with residence time, which is calculated using eq 8. The time section used in the calculation is 1 min. It can be seen that, when the average residence time t_0 is 70 min, about 38% of the particles in the bed have real residence times over 70 min and about 57% of the particles have real residence times in the bed over 40 min.

Expressions

$$\sum_{n=1}^{119} \left(\frac{t_0 - 1}{t_0} \right)^{n-1} \tilde{V} \quad (10)$$

and

$$\left(\frac{t_0 - 1}{t_0} \right)^{119} (n_0 \tilde{V}) \quad (11)$$

in Figure 7 mean the fraction of solid in the bed at 120 min (real residence time) and after 120 min, respectively. n_0 in eq 11 is the number of the time section for the average residence time, t_0 . For a comparison, conversion of limestone decomposition ($\text{CaCO}_3 \rightarrow \text{CaO}$) at 1273 K in the batch experiments is also shown in this figure. Derived from the conversion curve of limestone decomposition, at 40 min, limestone decomposition had proceeded to 98%, meaning that 57% of particles were in the bed for more time than needed for near-complete decomposition. About 34% of the particles in the bed are converted to the range 50–98%, and about 2–3% of the particles still have conversions below 10%.

Increasing the average residence time t_0 can increase the conversion of the limestone in the bed; such that, for t_0 at 40 min, 7% of the particles have a conversion fraction below 10%, for t_0 at 70 min, 3% of the particles have a conversion below 10%, and for t_0 at 100 min, 1% of the particles have a conversion below 10%. However, longer residence times may cause pores and the surface area of the decomposed particles to become smaller and thus reduce their reactivity.

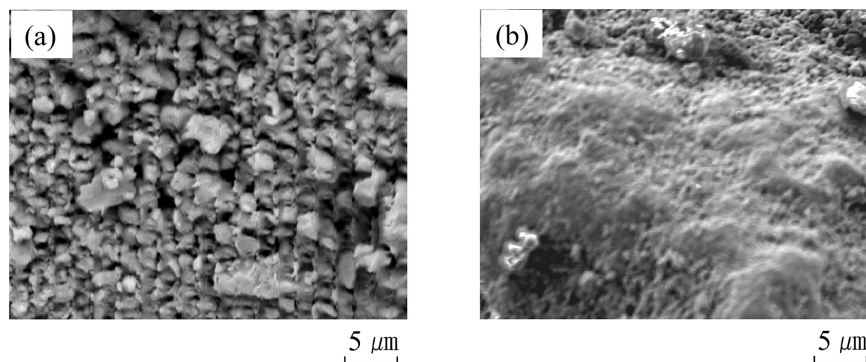


Figure 10. SEM photographs of the particle surface after (a) hydration and (b) carbonation reactions.

3.2. Reactivity of CaO in the Product after Limestone Decomposition. Reactivity of CaO in the product after limestone decomposition in the CO₂ atmosphere fluidized bed was tested by reactions with steam (hydration) and CO₂ (carbonation). In the hydration test at 923 K and a steam partial pressure of 2.0 MPa (total pressure of 3.0 MPa), CaO converted completely to Ca(OH)₂ within 11 min. Times to complete conversion differed for the materials, with limestone decomposed at different temperatures (Figure 8). The complete hydration conversion times were 8, 9, and 11 min for limestone decomposed at 1223, 1273, and 1293 K, respectively.

In the carbonation test at a CO₂ partial pressure of 0.04 MPa and 923 K, the conversion of CaO to CaCO₃ was not higher than 60%, even with a reaction time of 100 min (Figure 9). The final conversion fraction also decreased with the limestone decomposition temperature. For samples with limestone decomposed at temperatures of 1223, 1273, and 1293 K, the conversions at 100 min reached only 60, 52, and 40%, respectively.

Hydration of CaO from the limestone decomposition can sustain higher conversion because the product [Ca(OH)₂] layer of the particles remains porous (Figure 10a), allowing reactant gas diffusion into the particles. Carbonation conversion up to 60% only was due to CaO losing pores and the specific surface area during limestone calcination at high temperatures. The experiments performed at higher temperatures (above 1193 K) caused the rapid sintering of CaO, which gave rise to a sharp reduction in pores and the specific surface area. Further, the production of CaCO₃ comparatively increased the particle volume, causing the prompt

closure of the pores throughout the particles (Figure 10b) and inhibiting CO₂ inaccessible to the unreacted CaO.

4. Conclusions

In the present paper, we investigated the decomposition characteristics (up to 1293 K) of limestone particles (0.25–0.5 mm) with a continuously operating fluidized bed reactor in a 100% CO₂ atmosphere (about 101.325 kPa); reactivities of the hydration and carbonation of CaO from the limestone decomposition were also tested. The following results were obtained: (1) The pressure difference between the equilibrium CO₂ pressure and CO₂ partial pressure ($P^* - P_{\text{CO}_2}$) in experiments has a great influence on the rate of the limestone decomposition ($\text{CaCO}_3 \rightarrow \text{CaO}$), especially at a low temperature stage. With a 70 min average residence time of particles in the fluidized bed, limestone decomposition conversions were 73% at 1193 K and 95% at 1293 K. Above 1293 K is necessary to decompose limestone near completion. (2) An average residence time and a real residence time of limestone particles were used to assess the decomposition conversion. A model was proposed to describe the distribution of limestone particles in the fluidized bed reactor with the real residence time. The model can very well explain the difference of limestone decomposition conversion between the continuous and batch experiments. (3) For CaO produced by limestone decomposition, the hydration conversion can be completed within 11 min at 923 K under 2.0 MPa of steam partial pressure. The conversion of CaO to CaCO₃ in the CaO carbonation test at 923 K under 0.04 MPa of CO₂ partial pressure was below 60% until 100 min.

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