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IN HIGH SURFACE AREA CaO AGGREGATES

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December 1983

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CO₂-Catalyzed Surface Area and Porosity Changes in High Surface Area CaO Aggregates

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Abstract:

The changes in surface area and mesoporosity in aggregates of $\sim 0.01 \mu\text{m}$ cross-section CaO particles when heated in CO₂ at 686°C have been determined from N₂ adsorption isotherms. Initially, the surface area decreases rapidly with little change in porosity. When the surface area has decreased below $\sim 90 \text{ m}^2/\text{g}$, surface area and porosity variations become consistent with expectations for coarsening by grain boundary or bulk diffusion. The initial rapid decrease in surface area must result because CO₃⁻² formation greatly increases the rate of O⁻² ion surface diffusion and probably the rate of Ca⁺² ion surface diffusion also, but the data suggest that surface diffusion is not rate limiting. The rate limiting step may be decomposition of adsorbed CO₃⁻² ions to O⁻² ions and CO₂ gas.

Introduction

CO₂ gas is a remarkably effective catalyst for surface area reductions in high surface area (80-120 m²/g) CaO powders.¹⁻⁴ Measurable reductions have been found at a temperature of only 610°C and at a pressure as low as 0.2 Pa (2x10⁻⁶ atm).⁵ In vacuum, the same CaO powders do not lose surface when heated for several hours at 900°C. This paper reports quantitative measurements of the CO₂-catalyzed surface area and porosity changes produced when the high surface area CaO aggregates characterized by Beruto et al.⁶ are heated in CO₂.

It is important to note that these CaO aggregates, which are formed by decomposing calcite crystals that have cross sections of the order of 1 mm or more, have two different sets of pores. These are mesopores with initial cross sections in the order of 5 nm and macropores with cross sections in the order of 1-2 μm.^{4,6} A consequence of the bimodal pore size distribution is that heating in CO₂ causes coarsening with but little aggregate shrinkage; the decreases in the mesopore volumes are nearly balanced by increases in macropore volumes.

Evidence for two paths of coarsening are found: 1) a surface path that produces initial rapid decreases in surface area with little change in porosity, and 2) a path that causes slower surface area and mesoporosity decreases and growth of the >1 μm cross-section pores with relatively little decrease in total porosity. Changes in surface area with time by the slower path are consistent with expectations for diffusion limited processes,^{7,8} but reasons are given for thinking that a nondiffusional step of CaO transport may govern the rate of the initial rapid process.

The most similar previous study appears to be that of Anderson and Morgan.⁹ They measured the rates of H_2O -catalyzed surface area reductions of high surface area MgO powders as a function of time by means of liquid N_2 adsorption isotherms. Because the slopes of the isotherms approached infinity as the N_2 pressure P approached its standard pressure P_0 , Anderson and Morgan were unable to obtain porosity data.

Experimental

Iceland Spar single crystals, which typically had dimensions of 3.82 mm x 4.71 mm x 0.79 mm, were decomposed to $\text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ in vacuum at 686°C using a dual furnace microbalance apparatus.⁶ The CaO was cooled in the apparatus to 78 K, and N_2 adsorption-desorption isotherms were measured to yield the surface area of sintered CaO .

Sintering was produced by heating the aggregates to 686°C and introducing high purity CO_2 at 1.33×10^3 Pa pressure. The change in sample weight caused by CO_2 pick up during heating was followed continuously. After exposure for a selected time period, the CO_2 was pumped out and the sample was cooled to 78 K for measurement of an N_2 isotherm.

Throughout the sintering experiments, the sensitivity of the thermobalance was set at $2.5 \times 10^{-3} \text{ mg} \times \text{mm}^{-1}$, and CO_2 weight variations were continuously recorded. Tests with dry N_2 were made to evaluate the buoyancy and to tare the apparatus at 686°C throughout the range of pressures investigated.

SEM observations were made on the final samples as well as on samples of the kind of high surface area CaO used in the sintering

studies. To minimize hydration, fresh internal surfaces of samples were coated, as soon as they were formed, with a layer of gold ~ 30 nm thick.

Linear dimensions of the final sintered oxides were measured with a micrometer as soon as the samples were removed. From previous experience with hydration of CaO,¹⁰ the hydration during measurement is estimated at $<3\%$. This level of vapor-phase hydration has an insignificant effect on overall sample dimensions.

Results and Discussion

The pressure of CO_2 at which calcite formation from bulk CaO begins at 686°C is calculated from standard tables to be 2.7×10^3 Pa.¹¹ The high surface area CaO, however, reacted with CO_2 to form calcite when its pressure exceeded 2.2×10^3 Pa. The weight increase reported by Ewing et al.³ when high surface area CaO was held at a CO_2 pressure just below the standard decomposition pressure undoubtedly also reflected calcite formation. The present studies were carried out at 1.33×10^3 Pa.

Before CO_2 is introduced, the CaO is composed of rod-shaped particles with cross sections of the order of $0.01 \mu\text{m}$ and lengths of the order of $0.1 \mu\text{m}$.^{12,6} The rods tend to be aligned with their long axes parallel along the bisectors of the obtuse angles of the rhombohedral faces of the parent calcite crystal. As noted in the introduction, the CaO aggregates contain mesopores of ~ 5 nm cross sections and macropores with ~ 1 - $2 \mu\text{m}$ cross sections.^{4,6}

Figure 1A is an SEM photograph of the CaO particles formed along the outer surface of an initial calcite crystal. Figure 1B is an SEM photograph taken in the same orientation after a sintering time of

60 hours. Figure 2 is a cross section of a broken surface through a CaO aggregate after it has been sintered for 60 hours. These pictures show that the heating in CO_2 produces particles which retain preferred alignments along the initial rod axes.

Three N_2 adsorption-desorption isotherms of the kind which were used to investigate the changes in surface area and mesoporosity produced by heating in CO_2 are reproduced in Fig. 3. Surface areas were obtained by the standard multipoint BET method. When, as seen in Fig. 3, the isotherms have finite slopes as P/P_0 approaches 1, the volume of liquid N_2 adsorbed gives the total volume of pores smaller than $0.2 \mu\text{m}$ in cross section.¹³ The decrease in volume of mesopores with time of heating in CO_2 is evident in Fig. 3 from the successive intercepts at $P/P_0 = 1$ for the initial CaO (curve a) and for CaO heated for a shorter time (curve b) and longer time (curve c).

When, in agreement with TEM and SEM observations, the mesopores are assumed to have cylindrical symmetry, pore-size distributions like those of Fig. 4 are obtained. Figure 4 shows that the decrease in mesopore volume is accompanied by a shift towards higher average mesopore cross sections. The curve labeled d was obtained for a sample which was heated in CO_2 for 30 hours.

Each point in Fig. 5 records a surface area or mesoporosity obtained by the kinds of experiments just described, and with each sample heated in CO_2 in one uninterrupted run at 686°C for the time indicated before it was cooled for surface area and mesoporosity determinations. When a single sample was heated over a similar total time period but with interruptions of the heating operation for surface area determinations, lower surface areas and mesoporosities were

obtained after the first cooling and reheating cycle than were measured for samples held at 686°C for the same total time without cooling. From comparison of the weight of CO₂ held by the sample before cooling for liquid N₂ adsorption measurements to the weight of CO₂ gained when the sample was first reheated to 686°C, the changes produced by a thermal cycle could be calculated. The weight of CO₂ adsorbed on a sample which showed a surface area of ~87 m²/g, for example, decreased by 9.6% as a result of cooling to liquid N₂ temperatures and reheating to 686°C. Thermal cycling also reduced the mesoporosity by several percent. Evidently the cycling causes the CaO rods to repack more closely together so that the rates of surface area reduction are increased when CO₂-catalyzed sintering is resumed.

Figure 6 shows the, at first, puzzling results obtained when the quantity of CO₂ absorbed by a sample was followed as a function of time. An explanation for the existence of two maxima in the curve of Fig. 6 was found by comparing the weight of CO₂ taken up by the sample at a given time to its specific surface area (Fig. 7). The initial rapid rise to the maximum shown in the inset of Fig. 6 is produced by CO₂ adsorption on the CaO surface, but sintering causes the surface area available for adsorption to decrease. A slower process of CO₂ penetration into the sample (presumably at grain boundaries but possibly in the bulk) arrests and then reverses the weight decrease. About six hours after sintering has begun, the grain boundaries (or bulk sample) are essentially saturated and the continued decrease in surface area causes the reduction in CO₂ content of the sample to resume. This interpretation is substantiated by measurements of CO₂ adsorption and

absorption of surface areas $< 20 \text{ m}^2/\text{g}$, for which sintering rates were slow.¹⁴

Surface area changes were examined in terms of the equation

$$(\Delta S/S^\circ)^n = BN_o^n t \quad (1)$$

where S° is the initial surface area; ΔS is the change in area; n is the mechanism-characteristic exponent; B is a constant which includes the particle size, temperature, and geometric terms; N_o is the particle-packing coordination; and t is the time.^{7,8} Figure 8 shows a log-log plot of $\Delta S/S^\circ$ against time.

For simple geometries the value of n is expected to be a function of the path by which surface areas are reduced. Because the geometries of the CaO particles and of the pores in the CaO aggregates are complex, the plot of Fig. 8 can only be qualitatively interpreted.¹⁵ The plot certainly suggests that a change in the rate-limiting process occurs when the surface area reaches $\sim 90 \text{ m}^2/\text{g}$. By the time surface areas have decreased below $\sim 90 \text{ m}^2/\text{g}$ the quantity of CO_2 absorbed into the CaO, probably primarily as $\text{CO}_3^{=}$ at grain boundaries, is of the order 1 mole %.¹⁴ The high value of n measured for the lower surface area samples is consistent with expectations for a process limited by a diffusional process.

In the short time regime, the physical evidence clearly indicates that the initial rapid surface area reduction at nearly constant mesoporosity (insert of Fig. 5) must be produced by surface diffusion: (1) the rapid process occurs only when CO_2 is present and begins when the CO_2 has not yet had time to penetrate far from the CaO surface;

(2) an evaporation and condensation mechanism is ruled out because there are no known vapor molecules which could be formed by reaction of CO_2 with CaO to account for the sintering observed.

Surface diffusion is expected to produce large decreases in surface area with little change in porosity, as observed in the inset of Fig. 5. But the low value found for n in the short time regime, less than 1.6 at $t=0$, suggests that the rate-limiting step of the overall CaO surface transport process is not any of the diffusional processes. For surface, bulk, or grain boundary diffusion $n > 4$ is predicted for simple geometries. Reasons can be suggested for thinking that the dissociation of adsorbed CO_3^{-2} ion to adsorbed O^{-2} may be rate limiting in this short time regime.

Infrared measurements indicate CO_2 to be adsorbed on CaO surfaces as CO_3^{-2} ions.¹⁶ Equilibrium adsorption measurements indicate the CO_2 of these surface CO_3^{-2} ions to be as tightly bound as is CO_2 in CO_3^{-2} of calcite, and show that 50-80% of the surface O^{-2} are converted to CO_3^{-2} under the conditions of our sintering experiments.¹⁴

The very high rates of surface area reduction in CO_2 require rapid transport of both the Ca^{+2} and O^{-2} ions. It seems unlikely that the intrinsic surface diffusion coefficient of Ca^{+2} ions on CaO is high enough to permit the observed rates. Chemisorption on metal surfaces is known to increase the metal surface diffusion coefficients by as much as 10^5 .^{17,18} For metals, the high rates are found when surface coverage by the chemisorbed molecules is high, like the CO_2 coverage of the present study, and the formation of two-dimensional solid or liquid-like phases has been suggested.¹⁸ Probably the conversion of surface O^{-2} ions to

CO_3^{-2} ions produces a two-dimensional CaCO_3 -like phase and increases the effective surface diffusion rates of both the Ca^{+2} and O^{-2} ions.

From the apparent activation enthalpy measured for chemisorption of CO_2 on CaO , 61 ± 8 kJ/mole, and the equilibrium enthalpy of adsorption, -199 kJ/mole, the activation enthalpy for desorption by the reaction $\text{CO}_3^{-2}(\text{ad}) = \text{O}^{-2}(\text{ad}) + \text{CO}_2(\text{g})$ is calculated to be 260 ± 18 kJ/mole.¹⁴ This high enthalpy step of decomposition of adsorbed CO_3^{-2} ions at the site of formation of new CaO layers could well make the decomposition of adsorbed CO_3^{-2} ions to deposit O^{-2} ions at CaO growth sites the rate limiting process for CO_2 -catalyzed coarsening of CaO .

Morgan and Anderson found that the H_2O -catalyzed sintering of MgO powder formed from $\text{Mg}(\text{OH})_2$ decomposition occurs primarily within the aggregates formed from each initial $\text{Mg}(\text{OH})_2$ particle rather than between these aggregates.⁶ A similar result is found for CO_2 -catalyzed sintering of CaO aggregates which have highly nonuniform pore sizes. After 16.3 hours heating, the mesopore volume of a $(3.82 \times 4.71 \times 0.79) \text{ mm}^3$ specimen had decreased by 79%, but micrometer measurements showed the total specimen volume to have decreased by only $\sim 10\%$. Thus, the principal consequences of the CO_2 -catalyzed processes are to reduce surface areas and mesopore volumes with growth of the $>1 \text{ }\mu\text{m}$ cross-section pores that are present in the CaO aggregates formed from decomposition of large calcite crystals.

Conclusions

1. For specimens of CaO in which the particles and pores are too small for conventional sintering studies, N_2 adsorption-desorption isotherms provide measurements of changes in surface areas, mesopore volumes, and pore-size distributions.

2. At 686°C , CO_2 reacts with high surface area CaO to form calcite at pressures which exceed $\sim 81\%$ of the equilibrium calcite decomposition pressure for CaO of negligible surface.

3. At lower pressures, CO_2 catalyzes CaO surface area and mesoporosity reductions. The high initial surface area decreases rapidly with little change in porosity. After the surface area has decreased to $< 90 \text{ m}^2/\text{g}$, further surface area and porosity changes occur at a slower rate and by a different principal path. In a CaO specimen in which most pores are initially $\sim 5 \text{ nm}$ in cross section and some are $\sim 1 \text{ }\mu\text{m}$ in cross section, the volume of pores less than $0.2 \text{ }\mu\text{m}$ in cross section decreases $\sim 78\%$, and the volume of larger pores increases as the total specimen volume decreases $\sim 10\%$.

4. For the slower process, the experimental data agree with expectations for coarsening by grain-boundary or bulk diffusion. The experimental evidence indicates that the rapid initial reduction in surface area must occur by CO_2 -catalyzed surface diffusion, but the change in relative surface area with time is not consistent with expectations for a surface diffusion limited process--perhaps because the rate-limiting step of the sintering process is not diffusion but decomposition of adsorbed CO_3^{-2} ions to O^{-2} ions and CO_2 gas.

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Figure Captions

Fig.1 SEM pictures for: a) top surface of the initial CaO; b) top surface of the CaO treated for more than 50 h in CO₂ at 686°C and at 1.33×10^3 Pa.

Fig.2 SEM pictures of cross section of CaO sample treated for more than 50 h in CO₂ at 686°C and 1.33×10^3 Pa.

Fig.3 Adsorption-desorption N₂ isotherms at 78 K for:

a) initial CaO ($S_{\text{CaO}} = 120 \text{ m}^2/\text{g}$, $V_p = 2.7 \times 10^{-1} \text{ cm}^3/\text{gr}_{\text{CaO}}$);

b) CaO sample treated for about 57 min at 686°C and at 1.33×10^3 Pa of CO₂ ($S_{\text{CaO}} = 81 \text{ m}^2/\text{g}$, $V_p = 2.6 \times 10^{-1} \text{ cm}^3/\text{gr}_{\text{CaO}}$);

c) CaO sample treated for about 7 h at 686°C and at 1.33×10^3 Pa of CO₂ ($S_{\text{CaO}} = 59 \text{ m}^2/\text{g}$, $V_p = 2.2 \times 10^{-1} \text{ cm}^3/\text{gr}_{\text{CaO}}$).

Fig.4 Mesopore size distribution for:

a) initial CaO ($S_{\text{CaO}} = 120 \text{ m}^2/\text{g}$, $V_p = 2.7 \times 10^{-1} \text{ cm}^3/\text{gr}_{\text{CaO}}$);

b) CaO sample treated for about 57 min at 686°C and at 1.33×10^3 Pa of CO₂ ($S_{\text{CaO}} = 81 \text{ m}^2/\text{g}$, $V_p = 2.6 \times 10^{-1} \text{ cm}^3/\text{gr}_{\text{CaO}}$);

c) CaO sample treated for about 30 h at 686°C and at 1.33×10^3 Pa of CO₂ ($S_{\text{CaO}} = 30 \text{ m}^2/\text{gr}$, $V_p = 1.2 \times 10^{-1} \text{ cm}^3/\text{gr}_{\text{CaO}}$).

Fig.5 Evolution of the specific surface area and of the volume of mesopores with time.

Fig.6 Relative amount of CO₂ taken up by the sample at 686°C and at 1.33×10^3 Pa vs time. $W_{\text{CO}_2}^t$ is the total amount of CO₂ for complete reaction of CaO to form calcite. The time scale between 0 and $t^* = 25$ min is expanded in the box.

Fig.7 Relative amount of CO₂ on and in the CaO vs CaO specific surface area. The slope change occurs at $\approx t^* = 25$ min.

Fig.8 Plot of $\ln (\Delta S/S_0)^n$ vs $\ln t$, where ΔS is the change in initial surface area S_0 , and t is time in minutes.

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Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5

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Figure 6

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Figure 7

XBL 829-6527

Figure 8

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