



Onset sintering-coarsening-coalescence kinetics of calcite powders

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Abstract

An onset sintering-coarsening-coalescence (SCC) event based on a significant decrease of specific surface area relative to the dry pressed samples after isothermal firing in the 450–600 °C range in air was determined by N₂ adsorption–desorption hysteresis isotherm for submicron-sized calcite powders. The apparent activation energy for such a rapid SCC event was estimated as 57.5 ± 1.0 kJ/mol based on the time for 50% reduction of specific surface area without appreciable phase change of calcite. The minimum temperature to activate the SCC process, as of concern to industrial CaCO₃ applications and natural limestone formation, is 317 °C based on the extrapolation of steady specific surface area reduction rates to null. © 2013 Elsevier Ltd. All rights reserved.

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1. Introduction

Calcium carbonate is commonly used as property modification filler in adhesive,¹ rubber/plastics,² paints³ and oil fluids.⁴ Marine shells and coral reefs are common natural resources of calcium carbonates which have been deposited over geological time scale to contain hydrocarbon fluid inclusions.⁵ Such biogenic calcium carbonate was originally crystallized, under the influence of biochemistry and capillarity effect, as high-pressure stabilized aragonite (space group *Pmcn*) which then transformed into calcite (space group *R $\bar{3}c$*) under crustal metamorphic conditions.⁶ Calcite is in fact the dominant carbon-bearing phase in the Earth's crust, and acts as a buffer for the long-term cycling of CO₂ among the atmosphere, oceans and the solid Earth.⁷ Calcite is also of concern to household or industrial operation because of its deposition within water pipe as a hard scale^{8,9} whose removal is difficult even by magnetic water treatment¹⁰ taking advantage of a magnetohydrodynamic force on charged species.^{11,12} It is of interest to know if a pack of calcite powder becomes bulk polycrystal by a sintering-coarsening-coalescence (SCC) process when fired above a critical temperature under dry condition in air.

Regarding the SCC process, fine sized particles having relatively high specific surface area and low melting point,¹³ and hence a beneficial high homologous temperature (T/T_m where T_m is melting point in Kelvin¹⁴) than the bulk are expected to be activated at relatively low temperatures. (In general thermal activity such as diffusion coefficients of all materials with a given bond type is approximately the same at the same fraction of their melting temperatures. Such a normalized temperature T/T_m is so called homologous temperature.¹⁴) This has been proven for close-packed oxide nanoparticles with varied shape, i.e. equiaxed γ -Al₂O₃,¹⁵ platy cobalt oxide,¹⁶ hexagonal rod of ZnO¹⁷ and dioxide of ZrO₂ vs. less refractory TiO₂,¹⁸ based on electron microscopic observations coupled with kinetic BET/BJH measurements of specific surface area and pore size/shape change of the dry-pressed samples subjected to isothermal firing at temperatures for minutes. (BET and BJH denote Brunauer–Emmett–Teller method¹⁹ and Barrett–Joyner–Halenda method,²⁰ respectively.) The specific-surface-area change rate in the steady state was used to determine the apparent activation energy of a vigorous onset SCC event for these oxide nanoparticles.^{15–18} In addition, the minimum temperature for {0 1 $\bar{1}$ 0} - and (0 0 1)-specific coarsening/coalescence of hexagonal ZnO nanorods was estimated to be 516 °C based on the extrapolation of steady specific surface area reduction rates to null.¹⁷ Following the same method, the minimum temperature for SCC of ZrO₂ and TiO₂ nanoparticles were estimated as 710 and 641 °C,

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respectively.¹⁸ The apparent activation energy for such a SCC process being rather low (77 ± 23 kJ/mol) for ZrO_2 nanoparticles was attributed to phase transformation plasticity.¹⁸ Recently an onset sintering-coarsening-coalescence-polymerization (SCCP) event of amorphous SiO_2 nanoparticles was found to have accompanied change of medium range orders, i.e. forming Si_2O_5 while retaining Si-2^{nd} O yet losing Si-2^{nd} Si without appreciable crystallization.²¹ The minimum temperature for SCCP of amorphous silica, as of concern to industrial applications and sedimentary/metamorphosed sandstone formation, was determined as 1120°C based on the extrapolation of steady specific surface area reduction rates to null.²¹

Here the BET/BJH method is further employed to study the onset SCC kinetics of CaCO_3 powders with the ambient-pressure stabilized calcite structure. We focused on the activation energy and minimum temperature for the submicron-sized calcite powder to undergo the SCC process without polymorphic phase change or decomposition. This knowledge is of concern to engineering applications of fine sized CaCO_3 particles at temperatures and sheds light on CO_2 retention in limestone since its accretion from individual particles.

2. Experimental

Micron CaCO_3 (reagent grade) powders were submicron-sized by planetary ball milling under dry condition and at 380 r/min for 6 h. The submicron-sized powders were then die-pressed at 650 MPa into disks ca. 5 mm in diameter and 2 mm in thickness followed by isothermal firing at $450\text{--}600^\circ\text{C}$, corresponding to homologous temperature range 0.46–0.55 given $T_m = 1573$ K.²² The disks were fired in 1–10 min increments in air until an onset SCC event of particles accompanied with pore size/shape change were noted by the type of adsorption–desorption hysteresis isotherm. Microstructure changes of the samples due to dry pressing and heating were studied by scanning electron microscopy (SEM, JEOL 6330 at 10 kV). The phase identity of the dry pressed and heat treated samples was determined by X-ray diffraction (XRD, SIEMENS D5000, $\text{Cu K}\alpha$, 40 kV, 30 mA at 0.05° increment and 3 s per step) from 20° up to $80^\circ 2\theta$.

Nitrogen adsorption/desorption isotherms of the dry pressed and then heated powders were acquired at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2020 instrument. The surface area and pore size distributions were obtained from the N_2 adsorption and desorption branch, using the BET¹⁹ and BJH method,²⁰ in low and high relative pressure (P/P_0) range, respectively where P_0 is the saturation pressure determined as 760–762 mmHg. A filler rod containing ca. 0.1 g of CaCO_3 sample was pumped down to 10^{-3} torr for degassing at 300°C followed by BET/BJH measurements at a relative pressure increment 0.05. The BET isotherm and BJH adsorption/desorption hysteresis type of the samples are classified according to the scheme of International Union of Pure and Applied Chemistry.²³ The H1 type adsorption/desorption hysteresis loop of the type IV isotherm was used as an indicator of cylindrical pores in the samples.

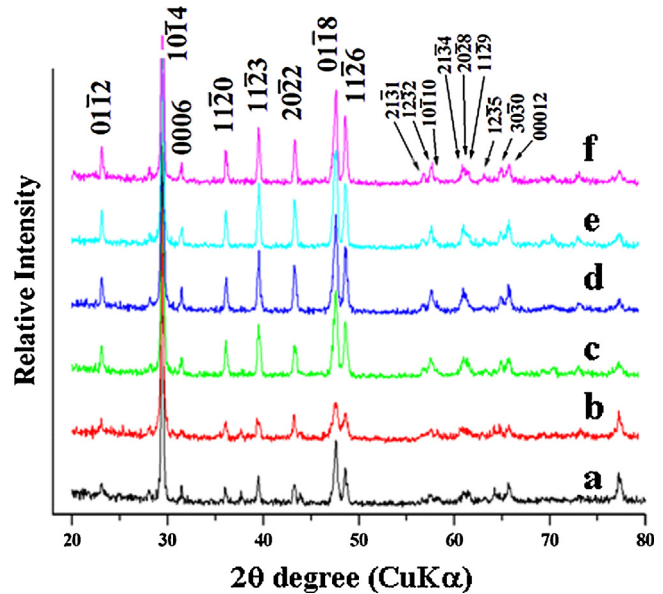


Fig. 1. XRD ($\text{Cu K}\alpha$) traces of the CaCO_3 powders: (a) original micron-size sample, (b) after ball milling for miniature size and hence appreciable diffraction broadening, (c), (d), (e) and (f) further fired at 450°C for 60 min, 500°C for 30 min, 550°C for 15 min and 600°C for 10 min, respectively showing no appreciable phase/orientation change of the calcite structure.

3. Results

3.1. Phase identity of particles

The starting coarse CaCO_3 powders have a single phase of calcite structure according to XRD (Fig. 1a). Ball milling of such calcite powders caused no phase change but significantly finer size (down to submicron) as indicated by diffraction broadening (Fig. 1b) and later SEM observations. The submicron-sized calcite powders subjected to dry pressing and then firing at 450, 500, 550 and 600°C showed no appreciable phase or orientation change within the dwelling time adopted (Fig. 1c–f). Thus, the onset SCC event of the dry-pressed calcite powders, based on the specific surface area reduction in the steady state as addressed later, has nothing to do with phase change at high temperature. In this regard, vaterite is a high-temperature stabilized polymorph of CaCO_3 with controversial structures,^{24–26} which commonly occurs in hot spring or the high-temperature decomposition product of calcite. (Synthetic vaterite was identified as hexagonal structure with space group $P6_3/mmc$.²⁴ However recent study of biogenic vaterite crystals using the aberration-corrected high resolution transmission electron microscopy indicated that vaterite contains two interspersed crystal structures, i.e. a minor unknown structure co-existing with the major hexagonal structure.²⁵ This explains the reported lower symmetry for vaterite crystal when take average over the two structures under 50-nm electron beam.²⁶)

3.2. BET/BJH observations of pore and specific surface area changes by firing

BET data of the fired samples indicated that the specific surface area decreases whereas average pore size increases with

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