

Preparation of Ultra-fine Calcium Carbonate by a Solvent-free Reaction using Supersonic Airflow and Low Temperatures

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ABSTRACT

The treatment of calcium chloride with sodium carbonate under solvent-free conditions with a supersonic airflow and at a low heating temperature leads to the synthesis of ultra-fine calcium carbonate. The reaction not only involves mild conditions, a simple operation, and high yields but also gives a high conversion rate.

KEYWORDS

Supersonic airflow, solvent-free reaction, low temperature, calcium carbonate.

Introduction

The traditional solid-state reaction refers to a reaction at high temperature. Such a reaction can be a complex process and have limitations such as high energy consumption,¹ while furthermore it can be especially difficult to operate on a large scale. By contrast, a solid-state reaction at low temperature, *viz.* from room temperature to 100 °C, has particular advantages: simple manipulation, high selectivity and productivity, low cost, etc.² Therefore, this method is being increasingly used as a green chemistry procedure. An important goal of green chemistry is to develop high-yield reactions that do not require workup for removal of catalysts, supports, solvents or other auxiliaries.³ Thus, the up-scaling of quantitative solid-state reactions in a supersonic airflow and requiring low heating is of technical importance.

Calcium carbonate, which is used in plastics, rubber, chemical building materials, etc.,^{4,5} is an important inorganic chemical product. The preparation of ultra-fine calcium carbonate has

been achieved by high-gravity reactive precipitation,⁶ internal circulating carbonation⁷ and absorption spraying.⁸ In this paper, we report a new solid-state reaction method using solvent-free conditions at low temperature and by application of a supersonic airflow for the preparation of ultra-fine calcium carbonate. This new method could be extended to large-scale production and as a consequence might be applied in industry.

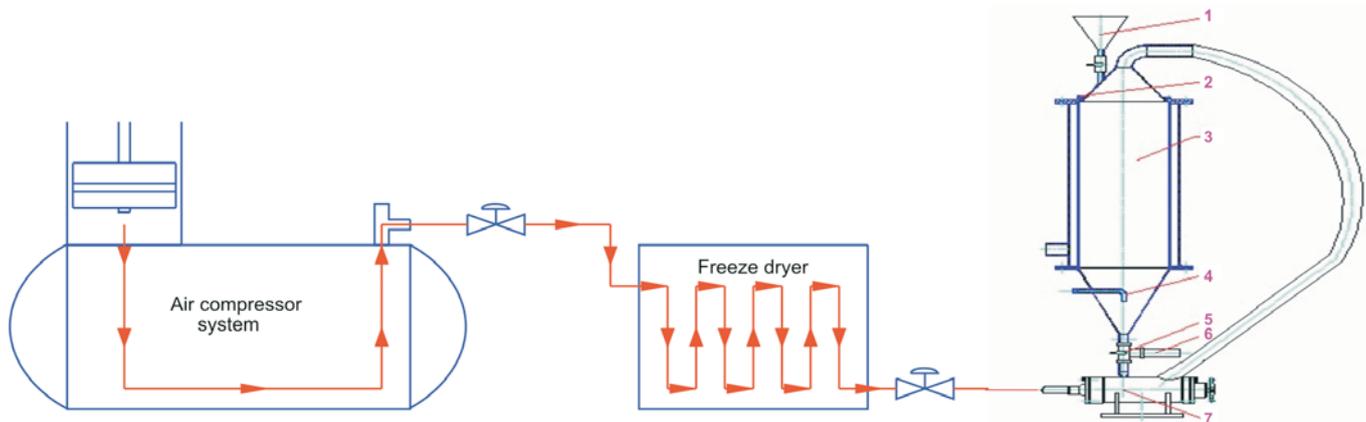
Experimental

Materials and Equipment

All materials used in this study were of analytical reagent (AR) grade. Calcium chloride was purchased from Chengdu Kelong Chemical Reagents Company (Sichuan Province, China) and sodium carbonate was purchased from Beijing Chemical Reagents Company (Beijing, China). All solvents were distilled before use.

The process developed is based on jet milling, with the equipment utilized for the reaction being shown in Fig. 1. Reactant particles are accelerated to treble the velocity of sound by the

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1, loading hopper; 2, delivery valve; 3, circulation collecting system; 4, adjustable jet pipeline; 5, tee globe valve; 6, outlet port; 7, reaction zone.

Figure 1 Schematic drawing of the reaction equipment.

high pressure airflow and sprayed on to the fixed target at high speed. Particle collisions at the fixed target lead to their fracture and their activation and subsequent reaction through an intense energy exchange between the fixed target and themselves.

Preparation of Ultra-fine Calcium Carbonate

Ultra-fine calcium carbonate was prepared as follows: equimolar quantities of ground calcium chloride (0.380 kg) and sodium carbonate (0.363 kg) were thoroughly mixed, and the mixture transferred to the reaction equipment. The working temperature in the reaction zone was 9 °C. The flowing mixture entered into the circulation collecting system at a speed of 30 m s⁻¹. The reaction particles separated in the circulation collecting system through a gravitational sedimentation process and were re-introduced into the reaction zone through the feeding tube. The product was collected after different reaction times and washed three times with distilled water, then twice with absolute ethyl acetate before being dried at 120 °C.

Ultra-fine Calcium Carbonate Tests

A LTD S440 scanning electron microscope at 25 kV voltage (Leica, Cambridge, England) was used to determine the size and morphology of the particles. A D/max-RB X-ray diffractometer (Japanese Neo-Confucianism, Tokyo, Japan) using monochromatic high-intensity CuK_α radiation (tube current 60 mA, voltage 35 kV, electric current 60 mA, scanning velocity 8° min⁻¹, step extent 0.02) was used to perform qualitative analyses.

Results and Discussion

XRD Pattern of the Ground Mixtures of CaCl₂ and Na₂CO₃

Figure 2 shows the XRD pattern of the ground mixture of CaCl₂ and Na₂CO₃ at different reaction times. After 30 min, the intensities of the calcium chloride and sodium carbonate diffraction peaks were considerably reduced while their shapes had broadened. This indicated that the crystallite size of the mixture had become small, that the crystal lattices had deformed and that unformed grains had developed. New diffraction peaks assigned to sodium chloride appeared but the intensities were very weak. After 45 min the peaks of the calcium chloride and sodium carbonate were much weaker while the intensities of the diffraction peaks for sodium chloride had strengthened. However, the diffraction peaks for calcium carbonate were not observed in the 45 min spectrum. The reason for this might be that the quantity of calcium carbonate formed was small and that its weak diffraction peaks overlapped with others. After 60 min, the diffraction peaks of the calcium chloride and sodium carbonate were replaced by the peaks for both calcium carbonate and sodium chloride. After 75 min the spectrum was essentially identical to the 60 min one and the crystallite size of calcium carbonate remained essentially unchanged, reflecting that at this stage the growth and loss of crystallites were in dynamic equilibrium. The reaction is thus complete within 60 min, but the XRD spectra did reveal the existence of small quantities of impurities in the sample after 60 min, resulting from friction between reaction particles and the reactor wall.

From this XRD spectral study it is clear that calcium carbonate can be prepared by solvent-free reaction at supersonic airflow and a low heating temperature.

XRD and SEM Studies

As shown in Fig. 3 the XRD powder pattern for calcium carbonate was consistent with the standard powder diffraction card

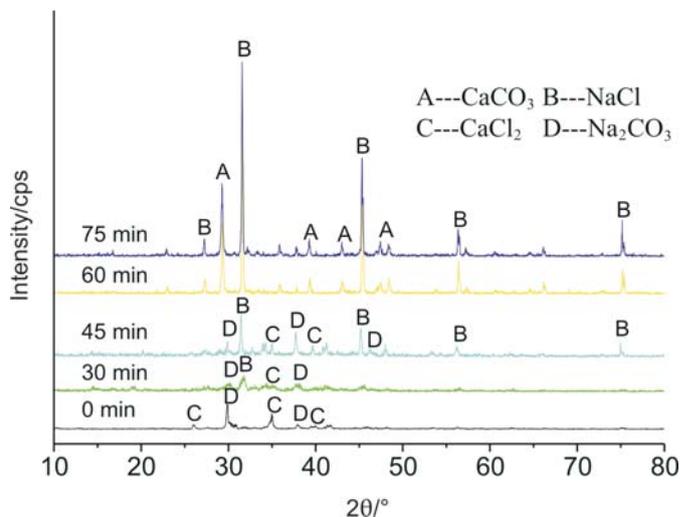


Figure 2 XRD spectra of the ground mixtures of CaCl₂ and Na₂CO₃ at different times.

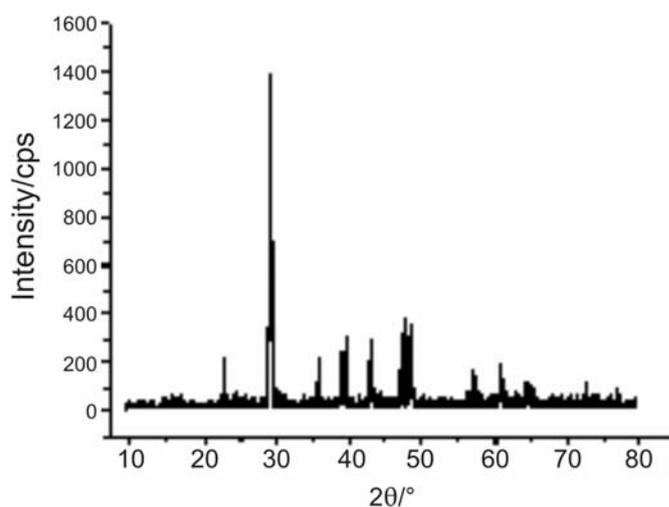


Figure 3 XRD spectrum of CaCO₃.

(PDF = 29-0304) for calcite. The SEM image showed that the particles of calcium carbonate were irregular and the average size of the particles was 0.5 μm (Fig. 4). The larger particles occurred as agglomerates of smaller ones resulting from van der

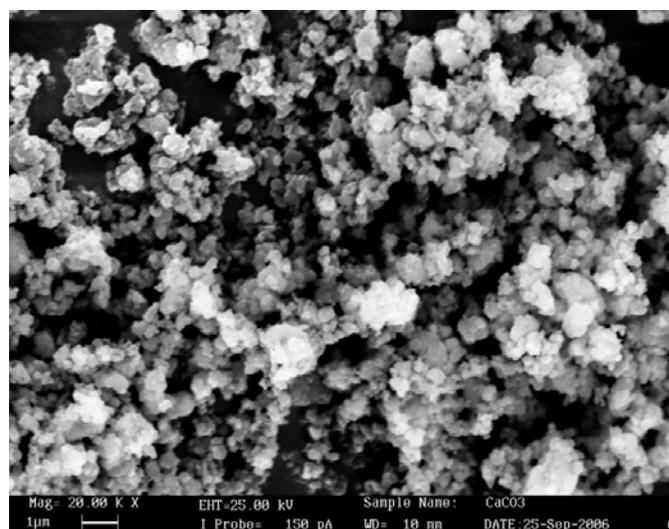


Figure 4 SEM image of CaCO₃.

Waals and Coulombic forces between the particles. The agglomerated particles could easily be dispersed by using chemical processes or a mechanical force, processes used in traditional solid-state reactions.^{9–12}

Conclusions

- a) The solid-state reaction of calcium chloride and sodium carbonate does occur under conditions of supersonic airflow and low temperature.
- b) Under an airflow treble the velocity of sound, the reaction is completed within 60 min, and the average size of the product particles is 0.5 μm .
- c) The reaction mechanism of the solvent-free reaction using supersonic airflow and low temperature is complex, and further studies are in progress to explore the mechanism.

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