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Continuous precipitation of calcium carbonate using sonochemical reactor

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ABSTRACT

The continuous production of calcium carbonate ($CaCO_3$) by precipitation method at room temperature was carried out in a stirred reactor under ultrasonic environment and was compared with the conventional stirring method. The effect of various operating parameters such as $Ca(OH)_2$ slurry concentration, CO_2 flow rate and $Ca(OH)_2$ slurry flow rate on the particle size of $CaCO_3$ was investigated. The calcium carbonate particles were characterized by Fourier transform infrared (FTIR), wide angle X-ray diffraction (WXRD) and particle size. The morphology was studied by using scanning electron microscopic (SEM) images. The particle size obtained in the presence of ultrasonic environment was found to be smaller as compared to conventional stirring method. The particle size is found to be reduced with an increase in the concentrations of $Ca(OH)_2$ and increased with increasing CO_2 flow rate for both the methods. The slurry flow rate had a major effect on the particle size and the particle size decreased with increased slurry flow rate. Only calcite phase of $CaCO_3$ was predominantly present as confirmed by the characterization techniques for both the preparation methods. In most of the cases rhombohedral calcite particles were observed.

1. Introduction

Calcium carbonate ($CaCO_3$) is a widely used inorganic material in various industries and it is an abundant mineral comprising approximately 4% of the earths crust occurring as limestone, chalk, and biominerals [1,2]. Because of the harmless properties and inexpensiveness, it has been used for a variety of purposes and finds applications in diverse areas such as in the manufacture of toothpastes, lubricants, paints, textiles, plastics, adhesives, waste water treatment, rubber, ink, paper, ceramic materials, food and horticulture [3–6]. Therefore, the precipitation of calcium carbonate has received much attention of the researchers. Different applications of calcium carbonate necessitate various granulometric, physical and chemical properties. These specific requirements are generally achieved by preparing the substance under carefully controlled conditions with specific morphology, structure, specific surface area, particle size and particle size distribution etc. [4,7–8]. So as to achieve these specific properties, the kinetics of precipitation of calcium carbonate has been thoroughly investigated [9]. For the manufacturing of precipitated $CaCO_3$, the carbonation of lime is industrially practiced method [10–11]. In recent years nano-$CaCO_3$ has found large commercial importance because of its utility in diversified areas [12]. Inorganic nano-particle synthesis is a growing area of research and the change in the properties of materials with nanometric scale makes them increasingly suitable for a variety of applications. Some of the properties of nanomaterials like large surface area, different crystal geometries and hydrophobicity make them more suitable for the applications such as surface coatings, photocatalytic degradation, and catalytic activity [13].

The crystallization phenomenon of $CaCO_3$ is a complicated process involving three different phases of $CaCO_3$, namely calcite, aragonite, and vaterite. The operating variables such as pH of the solution, solute concentration, temperature of the reaction medium, and ionic strength of the media affect the crystal growth [1]. Three polymorphs of $CaCO_3$ like calcite, aragonite and vaterite have crystal structures of rhombohedral, orthorhombic and hexagonal respectively in nature. Calcite is the thermodynamically stable structure. Aragonite is mainly found in the biosynthetic $CaCO_3$

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such as shells and core and is a less stable form. The most unstable polymorph is vaterite, which rarely occurs in natural fields, but plays an important role in the calcium carbonate formation during precipitation [2,5]. There are various methods available for the $CaCO_3$ synthesis, such as batch carbonization [14], micro-emulsion [11], spray-carbonation, in situ deposition technique and ultrasound-assisted synthesis [12,13]. In carbonation process, CO_2 gas is passed through a slurry of $Ca(OH)_2$. The conventional carbonation process usually produces the precipitated $CaCO_3$ with spindle shape with particle size bigger than 2 μm [8].

However, there are a very few reports of continuous production of $CaCO_3$ which includes synthesis in Couette–Taylor reactor [15], Continuous-flow crystallizer [16], mixed suspension mixed product removal crystallizer (MSMPR) [17,18], MSMPR reactor with microwave radiation as a source of energy [19], and segmented flow tubular reactor [20]. On an industrial scale, it is necessary to produce large quantities of precipitated calcium carbonate (PCC). The issue of the production in large quantity can be resolved by producing $CaCO_3$ in a continuous process. It is also important to note that the batch process has number of limitations such as non-homogeneous mixing of three different phases (gas, liquid, solid), diffusion of solute through highly concentrated slurry, secondary nucleation, variation in the particle size, shape and distribution etc, which needs to be optimized from the batch to batch. Therefore, it is preferable to use continuous process over the batch process; hence number of attempts are made to shift from batch process to continuous process for the production of PCC.

The size distribution of nanometer particles is determined by the rate of nucleation and the subsequent crystal growth rate. Accelerated nucleation and inhibited growth, therefore, are the key factors for the synthesis of nanometer particles in aqueous solutions [21]. If the supersaturation and nucleation rates are too high, agglomeration becomes an important growth mechanism, leading to the formation of irregular aggregates. On the other hand, the particle size distribution is dependent on the degree of supersaturation in a reaction system [22]. For an ideal process, before the establishment of a steady-state nucleation rate, mixing of reactive ions should attain homogeneity at the molecular level. Process intensifying devices such as stirrers, jets, tee-mixers, static mixers, and rotating packed beds can be helpful for the improvement in the micromixing and homogenous distribution of reactive ions [22]. Hence, developing new processes and the reactors is always a challenging task for reactive precipitation reactions. Ultrasound can be effectively used for improving micro-mixing of CO_2 gas bubbles during calcium carbonate synthesis, which is demonstrated by Sonawane et al. [13]. Ultrasound synthesis has advantages over other methods in terms of narrower particle size distribution, smaller particle size, controlled morphology and rapid nucleation rate [23]. It has been generally observed that sonication promotes nucleation and inhibits crystal growth. Ultrasound was found to decrease the induction time, which is defined as the time elapsed between the creation of supersaturation and the appearance of crystals [24]. Kumar et al. [25] have utilized ultrasound as an intensification device to induce air into the reaction mass by breaking the interface of liquid/air for the generation of radicals. Lyczko et al. [26] have studied the effect of ultrasound on primary nucleation of potassium sulfate by measuring the induction time and metastable zone width of unseeded solutions.

Aim of the present work was to synthesize $CaCO_3$ particles in continuous mode by using ultrasonic reactor and conventional stirred tank reactor (CSTR). The effect of various operating parameters such as calcium hydroxide slurry concentration, calcium hydroxide slurry flow rate and CO_2 flow rate on the particle size and morphology has also been studied.

2. Experimental

2.1. Experimental setup

The experimental set up used for the continuous synthesis of $CaCO_3$ is shown in Fig. 1. This consists of a reactor with a sonication probe (Dakshin make, 240 W, 22 kHz) along with a gas distributor, magnetic stirrer and CO_2 gas supply. Small bubbles of CO_2 around 1 mm diameter were produced through the gas distributor. The ultrasound probe with tip of 10 mm diameter was used for the generation of ultrasonic waves. The progress of the reaction was continuously monitored using conductivity and pH measurement after regular intervals. Experiments were carried out in a continuous mode with and without ultrasound and the results were compared. While performing the experiments in the absence of cavitation, ultrasound probe was removed and only stirring was used. The temperature of the reactor was maintained constant during the experiments using the constant temperature bath, in which the CSTR assembly was immersed.

2.2. Synthesis of calcium carbonate particles

Initially $Ca(OH)_2$ (LR grade, High Purity Laboratory Chemicals, Mumbai) was dissolved in water to get the desired concentration. The suspension was completely mixed using stirrer (500 rpm) at a

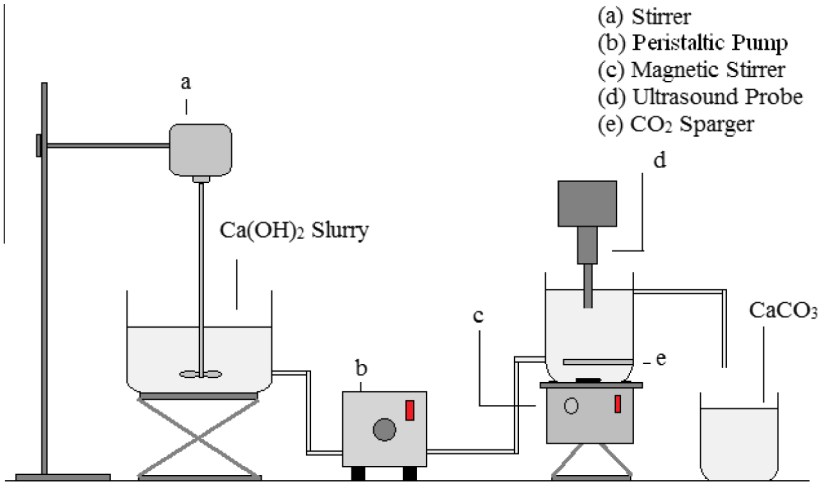

Fig. 1. Schematic of experimental setup for continuous production of $CaCO_3$ particles.