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Synthesis of nano-$CaCO_3$ by simultaneous absorption of CO_2 and NH_3 into $CaCl_2$ solution in a rotating packed bed

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ABSTRACT

This article presents investigations on the synthesis of nano-$CaCO_3$ by the simultaneous absorption of CO_2 and NH_3 into $CaCl_2$ solution in a rotating packed bed (RPB). The influence of the experimental parameters including the high gravity level, gas volumetric flow rate, liquid volumetric flow rate, and initial $CaCl_2$ concentration on the particle size of $CaCO_3$ were studied. Transmission electron microscope image of the as-prepared $CaCO_3$ shows that the mean size of the nano-$CaCO_3$ particles was about 50 nm with a particle size distribution (PSD) of 10–80 nm. X-ray diffraction pattern demonstrates that the nano-$CaCO_3$ has a calcite crystal structure.

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1. Introduction

In many industries, such as the production of soda ash, potassium chlorate, and calcium hydrophosphate by hydrochloric acid extraction, a large amount of waste liquor containing $CaCl_2$ is produced [1–3]. At present, only a small part of the $CaCl_2$ wastewater is concentrated to recover solid $CaCl_2$, while most of the $CaCl_2$ wastewater is directly discharged into rivers or seeps into the ground, which causes a significant environmental impact and resources waste [4,5]. A typical example is the production of soda ash by the classic Solvay method, where 10 m^3 of distiller waste will generate for the production of 1 ton of soda ash [6,7]. The distiller waste contains mainly $CaCl_2$ and NaCl as well as a small amount of $Ca(OH)_2$ and $CaCO_3$. After precipitation treatment of the distiller waste, the suspended solids are deposited and the overflow containing $CaCl_2$ will be discharged into the sea or the rivers due to the lack of feasible means to recover $CaCl_2$ effectively.

It may be a promising route to produce $CaCO_3$ by using $CaCl_2$ wastewater. Studies on this route in conventional apparatuses have been reported. Hideo et al. [8] synthesized hollow $CaCO_3$ particles by continuously bubbling CO_2 gas into $CaCl_2$ aqueous solution in a thermostat-stirring bath reactor, and the hollow $CaCO_3$ particles with a size of about 1 μm were obtained. Zhuang et al. [9] synthesized nanometer $CaCO_3$ in a thermostat-stirring bath reactor by a reaction of $CaCl_2$ with $(NH_4)_2CO_3$ in the presence of alcohol and phosphoric acid compounds, and the as-prepared $CaCO_3$ has a particle size of 50 nm.

Higee is an effective process intensification technology, which is carried out in a rotating packed bed (RPB) and has been applied to deaeration, distillation, reaction, absorption, mass transfer, nanoparticles preparation, and so on [10–17]. In the RPB, the liquids going through the packing are spread or split into very fine droplets, threads, and thin films under the high shear field. This results in intense micromixing and enhanced mass transfer between the fluid elements, leading to a good control of the particle size distribution (PSD) of the product [15]. Using limestone as the raw materials, nano-$CaCO_3$ with a particle size of 30 nm and narrow size distribution has been produced by the higee technology. Nano-$CaCO_3$ production lines by this technology have been put into operation in China, varying in capacity from 3000 to 10,000 t/a, which demonstrate that the higee technology is well suited for nanoparticles preparation [18].

In this work, nano-$CaCO_3$ was synthesized in an RPB by a reaction of $CaCl_2$ with gaseous NH_3 and CO_2, aiming at the utilization of $CaCl_2$ wastewater and the treatment of industrial exhausts rich in NH_3 and/or CO_2. The influence of the process parameters on the synthesis of $CaCO_3$ particle by simultaneous absorption of CO_2 and

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Abbreviations: PSD, particle size distribution; RPB, rotating packed bed; TEM, transmission electron microscope; XRD, X-ray diffraction.

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Nomenclature

a_f	specific area of the packing (m^2/m^3)
$c_{A,0}$	initial $CaCl_2$ concentration (mol/L)
d_p	mean particle size of nano-$CaCO_3$ (nm)
g_r	mean acceleration speed in the rotator (m/s^2)
G	gas volumetric flow rate (L/h)
h	axial length of the packing (m)
L	liquid volumetric flow rate (L/h)
N	rotation speed (rpm)
r	arithmetic mean radii of the packing (m)
r_i	inner radius of the packing (m)
r_o	outer radius of the packing (m)
t	operation time (min)
t_m	micromixing characteristic time (s)
V_B	volume of the rotor (m^3)

Greek symbols

ε	voidage of the dry packing (m^3/m^3)
θ	diffraction angle (°)
τ	induction time (s)
ω	rotational speed (rad/s)

NH_3 into $CaCl_2$ solution in the RPB was explored. To our best knowledge, this is also the first report on the synthesis of nanoparticles in an RPB by the simultaneous absorption of two gases.

2. Nucleation mechanism of nano-$CaCO_3$ in the RPB

The synthesis of nano-$CaCO_3$ by the simultaneous absorption of NH_3 and CO_2 into the $CaCl_2$ solution is a typical gas–liquid reaction. The reaction equation can be written as:

$$CaCl_2(l) + 2NH_3(g) + CO_2(g) + H_2O(l) = CaCO_3(s) + 2NH_4Cl(l) \quad (1)$$

where the symbols g, l, and s in the parentheses denote the phase states corresponding to gas, liquid, and solid, respectively. The gaseous NH_3 is much easier to be absorbed by aqueous solution compared with CO_2. Because of the very high solubility of NH_3 in the solution, the solution is alkaline with a pH value of 9 (±1), and there is no $Ca(HCO_3)_2$ produced.

Chemical reaction, nucleation, and crystal growth are three main steps in a reactive precipitation process. In the preparation process of nano-$CaCO_3$ via reactive precipitation in the RPB, the reaction (1) is so fast that a high degree of $CaCO_3$ supersaturation will be achieved in the local sites. For the very high turbulence and dispersion, large interface renewal rate and thin films (10–80 μm) of liquid in the RPB, mass transfer of CO_2 is greatly enhanced, resulting in a great increase of the nucleation rate. Therefore, the nucleation of nano-$CaCO_3$ in the RPB is mainly controlled by the homogeneous nucleation mechanism [19].

To obtain nano-$CaCO_3$ with narrow size distribution, a high degree of supersaturation, uniform spatial concentration distributions and identical growth time for all crystals are essential. Macromixing and micromixing are occurring simultaneously in the reactors. Uniform spatial concentration distribution of any component on the vessel scale can only be achieved by macromixing, while uniform spatial concentration distribution on the molecular scale can only be reached by intense micromixing [18]. Micromixing is a key factor determining the degree of the supersaturation concentration of the solute and its local spatial distribution. Nucleation kinetics is often examined by the induction time of nucleation τ. τ is the time from the beginning of $CaCO_3$ homogeneous nucleation to the establishment of a steady-state nucleation rate. t_m is the characteristic time of micromixing for species reaching a maximum mixed state at the molecular level. From the viewpoint of chemical reaction engineering, the reaction rate and subsequent nucleation in precipitation will be controlled by the intrinsic kinetics without the influence of micromixing in the region of $t_m < \tau$ and controlled or influenced by micromixing when $t_m > \tau$ [15]. $t_m < \tau$ is thus an ideal environment for nanoparticles preparation.

t_m is estimated to be the order of 5–50 ms in a stirred tank reactor, the value of τ is often on the order of 1 ms or less in water solutions. It is thus difficult to control the PSD and the scale-up effect will play an important role in a conventional reactor because of the poor micromixing [15]. Nevertheless, t_m is estimated to be 10–100 μs in the RPB as a result of a good micromixing effect, and the macro flow pattern in the RPB is close to the plug flow [20]. Therefore, the PSD and particle size can be controlled well in the RPB, which is thus regarded as an ideal reactor for the preparation of nano-$CaCO_3$ [18].

Since it took 17–30 min to prepare $CaCO_3$ by consuming Ca^{2+} completely in this study, a large number of $CaCO_3$ nuclei were produced at the beginning of this process, and the growth of the nuclei might dominate in the subsequent time due to the presence of $CaCO_3$ particles in the feed. It is deduced that the $CaCO_3$ PSD can be controlled well in this process as a result of the good micromixing and strong shearing force in the RPB.

3. Experimental

Anhydrous calcium chloride (A. R.) was purchased from Beijing Chemical Reagent Company, China. N_2 and CO_2 gases were purchased from Beijing Tianyoushun Gas Co., Ltd., China. Distilled water was used through all the experiments. $CaCl_2$ solution was prepared by dissolving a certain amount of anhydrous calcium chloride in distilled water.

Fig. 1 shows the experimental setup for nano-$CaCO_3$ synthesis. The gas stream containing N_2, CO_2 and NH_3 flowed inward from the outer edge of the rotor in the RPB, and the $CaCl_2$ solution stored in the liquid tank was pumped to the inner edge of the rotor and flowed to the outer edge of the rotor under the action of the centrifugal force. The gas stream and liquid stream contacted countercurrently in the packing where CO_2 and NH_3 were absorbed by the $CaCl_2$ solution and reacted with $CaCl_2$ to form $CaCO_3$. The as-formed $CaCO_3$ and $CaCl_2$ mixture flowed back to the liquid tank where the mixture was repumped into the RPB continuously until $CaCl_2$ was completely consumed. The gas stream was discharged from the gas outlet after reacting with $CaCl_2$. The reaction (1) is exothermic, and the temperature of the reaction system was controlled at 20 (±2) °C by an ice-water cooling circulatory system.

This recycling process was stopped when Ca^{2+} in the solution was used up as determined by titration analyses, suggesting that $CaCl_2$ was completely converted into $CaCO_3$. This process (batch operation time) usually took about 17–30 min. The samples were immediately taken from the $CaCO_3$ slurry for the TEM (H-800, Hitachi, Japan) analysis, and the PSD was calculated in terms of the TEM analysis. The $CaCO_3$ slurry was subsequently filtered and the filter cake was dried in an oven (DZF-6020, Shanghai Yiheng Instruments Co., Ltd., Shanghai, China) at around 110 °C for 24 h to obtain the $CaCO_3$ powder samples for XRD (XRD-6000, Shimazu, Japan, with radiation of Cu K_α) analysis.

The specifications of the RPB are given in Table 1. The packing consisted of stainless wire mesh which was purchased from Beijing Hongyahong Mesh Sale Center, Beijing, China. In order to maintain a higher gravity level, the rotation speed was varied from 500 to 1200 rpm, providing a centrifugal acceleration from 192 to 1105 m/s^2 based on the arithmetic mean radius of the RPB. In this work, the pressure of the inlet gas was maintained at 0.20 MPa. No chemical inhibitor was added in the reaction system.

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