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Preparation of basic magnesium carbonate by simultaneous absorption of NH_3 and CO_2 into $MgCl_2$ solution in an RPB

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ABSTRACT

The preparation of basic magnesium carbonate (BMC) by the simultaneous absorption of NH_3 and CO_2 into $MgCl_2$ solution in a rotating packed bed (RPB) was studied. The influences of the operating conditions including the rotation speed, liquid volumetric flow rate, gas volumetric flow rate, reaction temperature and initial concentration of $MgCl_2$ solution on the crystal structure and morphology of BMC were investigated. The scanning electron microscope image of the as-prepared BMC showed that the BMC particles had a unique rose-like structure with a mean size of 5.3 μm, a petal thickness of 20 nm and a particle size distribution mainly in the range of 2.8–7 μm.

1. Introduction

Basic magnesium carbonate [BMC, xMgCO$_3$•yMg(OH)$_2$•zH$_2$O; $x = 3–5$, $y = 0–1$, $z = 3–8$] is an important material with a wide range of uses in the industry, including paints, pharmaceuticals and dental treatment, cosmetic manufacturing, rubber, precursor of other magnesium-based chemicals, etc. [1,2]. For their complex microstructures, BMC also has potential applications in pigments, catalysts, ceramics, electronics, and so on [3–6]. Therefore, research on its preparation has attracted extensive interest.

The chemical methods, including carbonation [7], hydrothermal treatment [8] and precipitation [9] have been employed to prepare BMC with various morphologies. Guo et al. [9] have prepared needle-like BMC by the reaction of $MgCl_2$ with Na_2CO_3 in a stirred reactor using polyacrylamide as an additive to control the morphology. Mitsuhashi et al. [7] synthesized BMC microtubes with a "house of cards" surface structure by employing needle-like particles of magnesium carbonate trihydrate as a template in a stirred reactor. However, these methods have the limitations of high cost, low product quality and difficulty to scale up.

A rotating packed bed (RPB), also called a Higee device, is an efficient process intensification equipment, which has been applied to absorption [10], ozonation [11], distillation [12], reactions [13], particle preparation [14], and so on. In the RPB, the liquid going through the rotating packing is spread and split into very fine droplets, threads and thin films. This results in intense micromixing and fast mass transfer between the fluid elements, leading to a good control of the particle size distribution (PSD) of the product [15]. Nano-$CaCO_3$ with a particle size of 30 nm and narrow size distribution has been produced by the RPB at a large scale in China, which is a clear indication that the Higee technology is well-suited for nanoparticle preparation [15].

In this work, BMC was prepared in an RPB using $MgCl_2$, NH_3 and CO_2 as the raw materials. The effects of different operating conditions on the shape, structure and size of BMC were investigated. To the best of our knowledge, this is also the first report on the synthesis of BMC in an RPB by the simultaneous absorption of NH_3 and CO_2.

2. Mechanism of BMC preparation in RPB

BMC was prepared by the simultaneous absorption of NH_3 and CO_2 into $MgCl_2$ solution in an RPB. The production process of BMC is dominated by the reaction temperature. In a conventional stirred reactor, the product is mainly magnesium carbonate trihydrate in the temperature range of 308–343 K, whereas the product is mainly BMC in the temperature range of 343–363 K [16]. Therefore, the reaction between NH_3, CO_2 and $MgCl_2$ can be written as

$$Mg^{2+} + 2NH_3 + CO_2 + 4H_2O \Rightarrow MgCO_3 \cdot 3H_2O(s) + 2NH_4^{+} (308-343\,K) \quad (1)$$

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$$5Mg^{2+} + 10NH_3 + 4CO_2 + 10H_2O \Rightarrow 4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O(s) + 10NH_4^{+}(308-343\ K) \quad (2)$$

The simultaneous absorption of NH_3 and CO_2 into $MgCl_2$ solution in the RPB is an exothermic process, and reactions (1) and (2) are very fast. Also, the absorption rate of NH_3 into the solution is faster than that of CO_2. Therefore, the reaction can be easily controlled by the absorption process of CO_2 [17]. There is uniform heat and concentration distribution in the RPB due to intense micromixing. In addition, a short residence time of fluids in the RPB ensures rapid removal of the heat evolved during reaction, hence easy control of the reaction temperature. It can therefore be predicted that BMC prepared by the simultaneous absorption of NH_3 and CO_2 into $MgCl_2$ solution in the RPB will have good quality.

3. Experimental section

The experimental setup for this study is shown in Fig. 1. Industrial magnesium chloride ($MgCl_2 \cdot 6H_2O$, 99.5%, Beijing Chemical Reagent Co.) was dissolved in distilled water and heated to a certain temperature. The prepared solution was pumped into the RPB through the liquid inlet and flowed outwards in the rotor under the action of centrifugal force. Meanwhile, the gas mixture of air, CO_2 and NH_3 (99.99% and 99.9%, respectively; Beijing Tianyoushun Gas Co., Ltd.) was introduced into the RPB from the gas inlet and flowed inwards in the rotor where CO_2 and NH_3 were absorbed into the $MgCl_2$ solution by a counter-current contact of the gas stream with the liquid stream and reacted with $MgCl_2$ to produce BMC at a certain reaction temperature. The resulting slurry flowed into the liquid tank through the liquid outlet of the RPB and was continuously recycled into the RPB to react with CO_2 and NH_3 until $MgCl_2$ was completely consumed. The gas stream was discharged from the gas outlet after the absorption process. The liquid and gas temperatures were monitored with a temperature control system.

The recycling process was stopped immediately when all Mg^{2+} in the solution was used up as determined by titration analysis. Samples were taken from the BMC slurry for SEM (H-800, Hitachi, Japan) analysis and particle size determination. The BMC slurry was subsequently filtered and dried in an oven (DZF-6020, Shanghai Yiheng Instruments Co., Ltd., Shanghai, China) at 353 K for 24 h to obtain the BMC powder samples for XRD (XRD-6000, Shimazu, Japan, with radiation of CuK) analysis.

The details of the RPB are given in Table 1. The rotation speed was varied from 400 to 1500 rpm, providing a centrifugal acceleration ranging from 197 to 1233 m/s^2 based on the arithmetic mean radius of the rotor. Stainless steel wire mesh (Beijing Hongyahong Mesh Sale Center, Beijing, China) was used as the packing material. The system pressure in the RPB was 0.20 MPa and no chemical inhibitor was added in the reaction system.

4. Results and discussion

4.1. XRD analysis of the product

The experimental conditions were set as follows: the volume of $MgCl_2$ solution was 3 L with an initial $MgCl_2$ concentration of 0.3 mol/L; the liquid and gas volumetric flow rate were 100 and 950 L/h respectively. The NH_3 and CO_2 content were 10.6% and 5.3% respectively. The system pressure was 0.2 MPa and the rotation speed of the RPB was 1100 rpm.

At the end of the reaction, the slurry was sampled for XRD analysis. Fig. 2 shows the XRD patterns of samples obtained at various reaction temperatures.

It can be seen from Fig. 2 that the reaction temperature had a significant effect on the composition of the product. It is seen that the XRD pattern did not match the existing standard pattern of BMC at the reaction temperature of 303–333 K, indicating that the composition of the product was a mixture, while $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ was obtained when the reaction temperature rose to 335 K. A further increase of the reaction temperature to 358 K indicated that the $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ structure remained, signifying that 335 K is a threshold temperature for the formation of $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ structure.

4.2. SEM analysis of the product

4.2.1. Effect of reaction temperature on the morphology of BMC

The operating conditions were set similar to those for the XRD analysis, except for the gas volumetric flow rate, which was maintained at 980 L/h with a mixture composition of 12.2% NH_3 and 6.1% CO_2. The reaction temperature was varied in the range of 303–358 K.

Fig. 3 shows SEM images of BMC obtained at different reaction temperatures. The morphology of BMC was needle-like with a diameter of 1 μm and an aspect ratio of 25 when the temperature was 303 K,

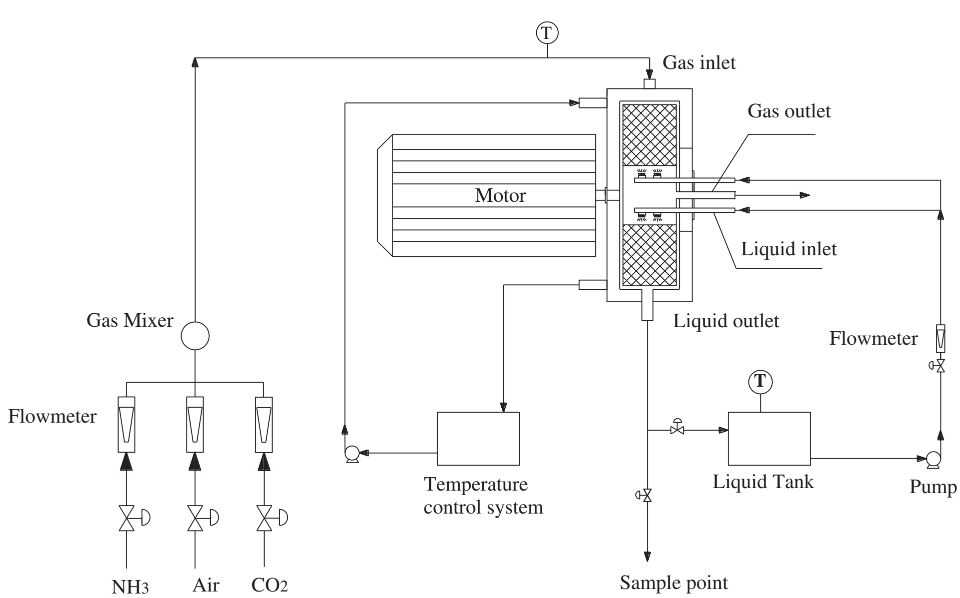

Fig. 1. Experimental setup for preparation of BMC.