Preparation of Flowerlike Porous Mg$_5$(CO$_3$)$_4$(OH)$_2$.4H$_2$O by CO$_2$ Bubble Templating

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Abstract: Flowerlike porous basic magnesium carbonate (Mg$_5$(CO$_3$)$_4$(OH)$_2$.4H$_2$O) were obtained successfully using magnesium chloride hexahydrate and ammonium bicarbonate as raw materials. We investigated the effect of reaction time and reaction temperature on the Mg$_5$(CO$_3$)$_4$(OH)$_2$.4H$_2$O preparation. In the first three hours’ reaction, Magnesium carbonate trihydrate (MgCO$_3$.3H$_2$O) whiskers generated, and transferred to the flowerlike porous Mg$_5$(CO$_3$)$_4$(OH)$_2$.4H$_2$O as the reaction time prolonged. During the transformation, the flowerlike Mg$_5$(CO$_3$)$_4$(OH)$_2$.4H$_2$O crystals firstly appeared at the head of the MgCO$_3$.3H$_2$O whisker.

1. Introduction

The morphology and properties of particles are closely related. To fabricate materials with certain morphology to achieve better performance, there has been increasing interests in controlled synthesis of inorganic microstructure with desirable shape and size[1-2].

Because of the special structure, spherical porous materials have advantages in easily moving, closely packing and occupying the available vacancies, which implies potential applications[3]. In recent years, in particular, spherical porous materials have attracted much attention and many studies have been carried out on the superiority of spherical porous materials. For example, Wang et al. have synthesized spherical porous CaCO$_3$ microparticle which could be applied as relatively safe drug vehicles. Yu et al have prepared spherical porous LiFePO$_4$/C particles which provide better contact with electrolyte and are easier to bind than isolated LiFePO$_4$ particles[4-5].

This paper presents the formation process of flowerlike porous Mg$_5$(CO$_3$)$_4$(OH)$_2$.4H$_2$O. By investigating particles under various reaction times, the shape evolution of these flowerlike porous particles is discussed in detail. CO$_2$ bubble template was introduced to simulate the formation of flowerlike porous Mg$_5$(CO$_3$)$_4$(OH)$_2$.4H$_2$O, and the equation of reaction temperature and the pore size was given by the derivation of Laplace and Clapyeron equations.

2. Experimental

Magnesium chloride hexahydrate (MgCl$_2$.6H$_2$O) and ammonium bicarbonate (NH$_4$HCO$_3$) were used and were of analytical grade. In this experiment, 0.4 mol/L of MgCl$_2$.6H$_2$O and NH$_4$HCO$_3$ (1/2 molar ratio of MgCl$_2$.6H$_2$O) were mixed well and transferred into automatic Control Reaction Kettle. Then, the homogeneous reaction solution was heated at a constant pressure of 4 atm. The reaction temperature was maintained at 80 °C for a given reaction time. The reaction time was set as 3–6 h. After reaction finished, the special autoclave was taken out for ageing for 3 h. Afterwards, a filtration
was implemented by vacuum suction filter method and washed with distilled water as well as ethanol. The washed residue was dried in vacuum oven for 2 h.

The crystal phases of the products were determined by XD-5A-type powder X-ray diffraction (XRD) with Ni-filtered Cu Ka radiation. The morphology of the product was observed using a JSM-5510LV scanning electron microscope (SEM).

3. Results and discussion

Figure 1 shows XRD patterns of the mixtures produced under 80 °C for different duration times. The XRD pattern of the mixture prepared by reacting 3 h displays only the peaks of MgCO$_3$·3H$_2$O. The XRD pattern of the mixture obtained after reacting 4 h are dominated by the peaks of MgCO$_3$·3H$_2$O, with the main characteristic peaks of Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O just starting to show up in the XRD. 5 h later, Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O becomes the dominant phase in the mixture. Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O is the only phase present in the XRD pattern of the mixture when reaction time was increased to 6 h.

![XRD patterns](image)

**Figure 1.** XRD patterns of the heated mixtures at 80 °C for different duration times (a: 3 h; b: 4 h; c: 5 h; d: 6h)

Figure 2 shows SEM images of the particles synthesized at different reaction time, which indicates an obvious growth process occurring from whisker to flowerlike microsphere with porous structure. As shown in Fig. 2a, a large number of whiskers were obtained by reacting 3 h. Through the phase analysis, the product was determined as MgCO$_3$·3H$_2$O (Fig. 1a). The structure and surface of MgCO$_3$·3H$_2$O whiskers were unbroken and smooth. In addition, the length was about 140 μm and the aspect ratio was about 25. At the time of reacting 4 h, the sample was still whisker with reduced aspect ratio, but the surface became rough and a small number of leaf-like crystals appeared on the surface of the whisker. When the reaction time was increased to 5 h, the sample not only contained whisker product, but also began to appear flowerlike spherical particles. From a magnifying SEM image, it seemed that “connected flakes” gathered on the head of the whisker (Fig. 2c). When the samples were produced for reacting 6 h, the original whisker shape disappeared completely. All samples turned into the flowerlike porous Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O that are assembled by lamella (Fig. 2d).
The conversion reaction giving rise to the \( \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot4\text{H}_2\text{O} \) crystal occurs via the formation of metastable \( \text{MgCO}_3\cdot3\text{H}_2\text{O} \) in the synthetic process\cite{6-8}. The reaction time has a significant impact on the phase transition process. Reactions of the transition process occur as follows:

\[
\text{MgCl}_2\cdot6\text{H}_2\text{O} + 2\text{NH}_4\text{HCO}_3 \rightarrow \text{MgCO}_3\cdot3\text{H}_2\text{O} + 2\text{NH}_4\text{Cl} + \text{CO}_2 \uparrow + 4\text{H}_2\text{O} 
\]

(1)

\[
5\text{MgCO}_3\cdot3\text{H}_2\text{O} \rightarrow \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot4\text{H}_2\text{O} \downarrow + \text{CO}_2 \uparrow + 10\text{H}_2\text{O} 
\]

(2)

As shown in Figure 2d, the surfaces of the flowerlike \( \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot4\text{H}_2\text{O} \) are assembled from a number of lamellae that interconnected to form an open porous structure. Generally, gas bubbles, such as \( \text{CO}_2 \) bubbles, can form open porous structure \cite{9}. With the increase of reaction time, the \( \text{NH}_4\text{HCO}_3 \) slowly releases \( \text{CO}_2 \) bubbles. At the same time, in order to obtain lower surface tension to achieve a relatively stable state, small \( \text{CO}_2 \) bubbles gather into big spheres of micrometer size and preferentially adhere to the head of whisker (see Figure. 3). This process can be explained by Gibbs function:

\[
dG = -SdT + Vdp + \sum_{a} \sum_{B} \mu_{B(a)} n_{B(a)} + \gamma dA_s
\]

(3)

where \( G \), \( S \) and \( V \) are Gibbs function, entropy and volume of system, separately; \( \mu_{B(a)} \) and \( n_{B(a)} \) are chemical potential and amount of substance of component \( B \) in phase \( A \), respectively; \( A_s \) is the interfacial area; \( \gamma \) is the interfacial tension. Since the temperature and pressure are constant, equation 3 can be simplified as follows:

\[
dG = \gamma dA_s
\]

(4)

If \( \gamma \) remains constant, upon integration equation 4 gives

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**Figure 2.** SEM images of the particles synthesized at different reaction time (a: 3 h; b: 4 h; c: 5 h; d: 6 h)
Further differential equation can be obtained:
\[ dG^s = \gamma dA^s + A^s d\gamma \]  \( (6) \)

Under the condition of constant temperature and constant pressure, the decrease of Gibbs function of interface system is a spontaneous process from the thermodynamic view. According to the equation 6, in order to reduce the interfacial Gibbs function to achieve relatively stable state, many small CO\(_2\) bubbles reduce its surface area by gathering into big CO\(_2\) bubbles, and the head of whisker reduce the surface tension by dissolving and adsorbing CO\(_2\) bubbles.

\[ G^s = \gamma A^s \]  \( (5) \)

4. Conclusions
Flowerlike porous Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)4H\(_2\)O have been synthesized successfully using MgCl\(_2\)6H\(_2\)O and NH\(_4\)HCO\(_3\) as raw materials. The formation of porous structure and the control of system temperatures over the pore size of porous Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)4H\(_2\)O were studied.

(1) The products synthesized at 3 h were MgCO\(_3\)3H\(_2\)O whiskers. After a series of phase transition process, it turned out that the final products for 6 h are flowerlike Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)4H\(_2\)O with porous structure. Moreover, flowerlike Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)4H\(_2\)O crystals firstly appear at the head of the MgCO\(_3\)3H\(_2\)O whiskers.

(2) The formation of porous structure of flowerlike Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)4H\(_2\)O could be explained. The growth and gathering of the CO\(_2\) bubbles induced the growth of the Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)4H\(_2\)O flakes and formation of the porous structure.

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