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Controlled preparation and characterization of nano-sized hexagonal $Mg(OH)_2$ flame retardant

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ABSTRACT

Nano-sized hexagonal magnesium hydroxide ($Mg(OH)_2$) with good dispersibility was synthesized by a double injection-hydrothermal method, utilizing polyvinylpyrrolidone (PVP) as an additive and with optimized processing parameters. SEM and BET analysis showed that the mean particle size and specific surface area of the $Mg(OH)_2$ particles were 174 nm and 50.77 m^2/g, respectively. The FT-IR spectra and the XRD patterns showed that PVP was adsorbed on the surface of the $Mg(OH)_2$ crystal, thus effectively limiting particle agglomeration and hindering crystal growth along the (1 0 1) plane. TGA showed a decrease in the decomposition temperature and an increase in the weight loss of the $Mg(OH)_2$ particles due to addition of PVP.

1. Introduction

Recently, flame retardants have been widely used in polymers, electric cables, and building and decoration materials. As a prominent flame retardant, magnesium hydroxide ($Mg(OH)_2$), especially the nano-sized variety, has attracted much attention due to its relatively high decomposition temperature, good compatibility with organic material, and environmental friendliness (Wu, Hu, Wang, & Yang, 2008). However, $Mg(OH)_2$ particles synthesized at room temperature usually show relatively high surface activity and a large strain due to their predominant growth in the (1 0 1) plane direction, which results in poor compatibility and poor mechanical properties of the corresponding composite.

One effective strategy to reduce the surface activity and surface strain of $Mg(OH)_2$ is to recrystallize the particles under hydrothermal conditions. This process is capable of inhibiting the growth of $Mg(OH)_2$ along the (1 0 1) plane direction. Henrist, Mathieu, Vogels, Rulmont, and Cloots (2003) obtained larger, well-defined $Mg(OH)_2$ particles after hydrothermal treatment at 443 K for 7 d with an intensity ratio of the (0 0 1) to (1 1 0) reflections of 5.02. Results from Wu, Xiang, and Jin (2006) showed that the hydrothermal treatment of $Mg(OH)_2$ in a 1.0 g/L $CaCl_2$ solution at 473 K for 4 h decreased the specific surface area (BET) of the $Mg(OH)_2$ particles from 28.5 to 10.5 m^2/g and increased the average particle size from 0.1–0.2 to 0.3–0.7 μm. Ji et al. (2011) found that the rough lamellar crystals of $Mg(OH)_2$ turned into well-dispersed spherical crystals with a diameter of 450 nm after an 8 h hydrothermal treatment at 453.15 K in a 4 mol/L quadrol solution. The work done by Xiang, Jin, and Jin (2003) indicated that hydrothermal treatment of $Mg(OH)_2$ agglomerates in a 5 mol/L NaOH solution at 473 K for 4 h increased and decreased the BET surface area from 35.0 to 6.3 m^2/g. However, nano-sized $Mg(OH)_2$ particles are often not available, due to the fast growth of the $Mg(OH)_2$ crystals during the hydrothermal process. Dispersants have been proposed as a means to control the growth of the crystal. For instance, Yan et al. (2008) obtained well-dispersed $Mg(OH)_2$ with an average particle size of 400 nm and a thickness of 60 nm after hydrothermal treatment of irregular lamellar $Mg(OH)_2$ crystals in the presence of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) at 423 K for 6 h with a Mg^{2+}/CTAB molar ratio of 80. Xue, Yan, and Wang (2009) synthesized hexagonal nanoplates with a diameter of 700 nm after hydrothermal treatment at 453 K in sodium dodecyl sulfate solution for 8 h. The drawback to these methods was that the particles exhibited either irregular morphology or a large particle size. Among all types of dispersants, polyvinylpyrrolidone (PVP) is extensively used as a template to construct various morphologies, such as plates, lamellar, rod, and needle-like (Long, Guo, & Li, 2008; Lv, Qiu, & Qu, 2004). However, $Mg(OH)_2$ crystals prepared at ambient temperature in the presence of PVP are often limited by poor crystallinity and agglomeration. Few investigations so far have focused on the synthesis of $Mg(OH)_2$ via hydrothermal treatment in the presence of PVP. To prepare nano-sized hexagonal $Mg(OH)_2$

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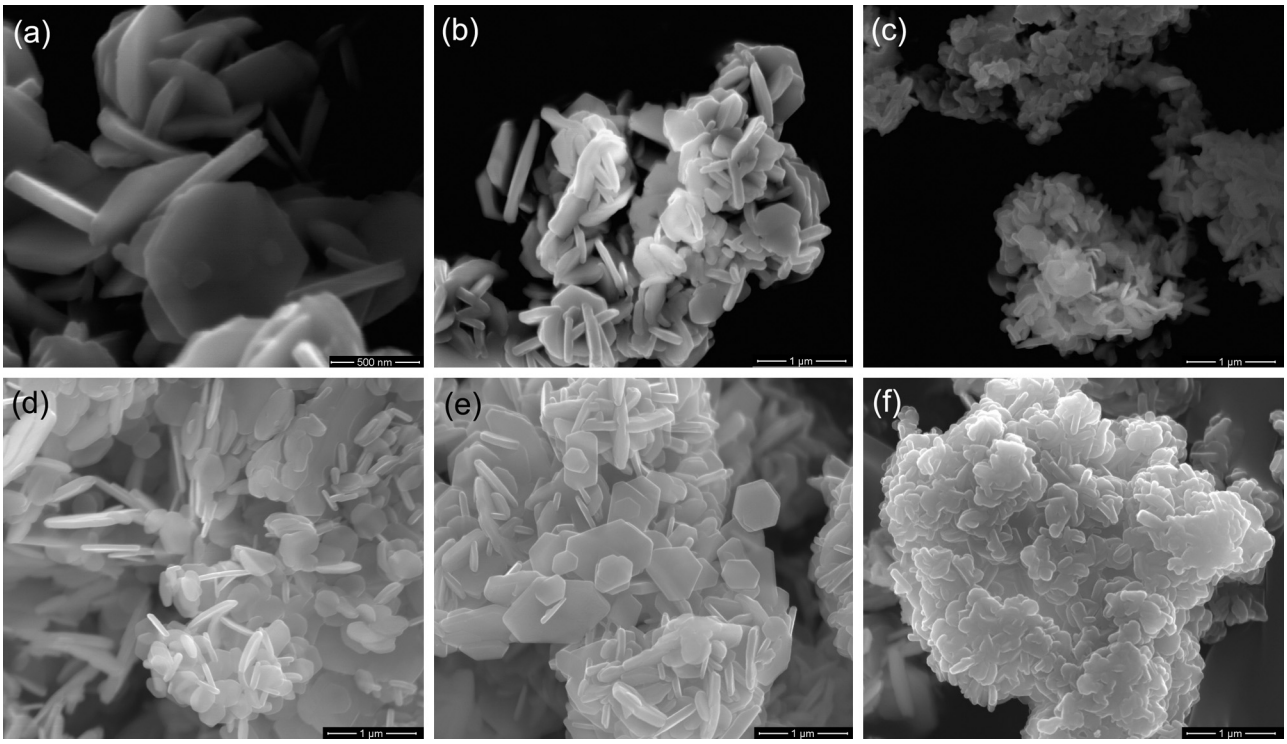

Fig. 1. SEM micrographs of $Mg(OH)_2$ particles prepared at reaction temperature of 333 K and different reactant concentrations of $MgCl_2$: (a) 0.5, (b) 3.0, (c) 4.0 mol/L; and at $MgCl_2$ concentration of 3.0 mol/L and different reaction temperatures: (d) 278, (e) 318, (f) 363 K; all under solution pH of 7.0, PVP amount of 3.0 wt%, hydrothermal temperature 453 K, and hydrothermal duration 3 h.

with good dispersibility and high crystallinity, PVP was therefore selected to control the orientation of the crystal growth and the size of the crystals during hydrothermal treatment.

The objective of this paper is to investigate the effects of the processing parameters on the particle size and morphology and to determine the optimal processing parameters for the preparation of $Mg(OH)_2$ with relatively small particle size and good morphology.

2. Experimental

In this study, the parameters of nano-sized $Mg(OH)_2$ preparation were optimized by single-factor testing. In a typical procedure, magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, Tianjin Standard Science and Technology Co. Ltd., China) and 3.0 wt% PVP (Sinopharm Chemical Reagent Co. Ltd., China, MW = 40 000, mass ratio to theoretical yield of $Mg(OH)_2$) were dissolved in deionized water at a Mg^{2+} concentration of 3.0 mol/L. 50 mL of both this mixture and a 6.0 mol/L NaOH solution (a $NaOH/Mg^{2+}$ molar ratio of 2) were simultaneously added (2.5 mL/min) into a three-neck flask (filled with 50 mL NaOH solution, pH = 9.5) under vigorous stirring (300 rpm) at 318 K until the pH reached 12 (double injection). Afterwards, the resulting suspension was stirred at the synthesis temperature for 1 h, and then transferred into a 200 mL Teflon-lined stainless steel autoclave. The suspension was treated hydrothermally at 453 K for 3 h. The suspension was allowed to cool to room temperature and then filtered. The obtained filter cake was washed with deionized water four times and then dried in an oven at 393 K for 5 h, yielding loose, white, ultrafine $Mg(OH)_2$ powders.

The morphology of the $Mg(OH)_2$ particles was observed using a scanning electron microscope (SEM, Model Nove NanoSEM 230, FEI, America). The mean particle size was determined from an analysis of the SEM micrographs of 50 particles. The phase and crystallographic structures of the samples were determined with a powder X-ray diffractometer (XRD, Model D500, Siemens, Germany). The thermal behavior of the $Mg(OH)_2$ powders was studied through thermogravimetric analysis (TGA) with a TGA/DSC-1 thermoanalyzer (METTLER, Switzerland). The BET surface area was measured with nitrogen monosorb adsorption equipment (Model TriStar, Micromeritics, America). Fourier transform infrared (FT-IR) spectroscopy was conducted on a Nicolet 6700 FT-IR spectrometer.

3. Results and discussion

3.1. The optimization of the processing parameters

3.1.1. Reactant concentration

To study the influence of the reactant concentration on the particle size and morphology of $Mg(OH)_2$, the synthesis temperature was kept at 333 K, the pH of the substrate solution was set at 7.0, the addition of PVP was 3.0 wt% and the hydrothermal temperature and duration were 453 K and 3 h, respectively. The $MgCl_2$ concentrations studied were 0.5, 2.0, 3.0 and 4.0 mol/L. As shown in Fig. 1(a)–(c), serious agglomeration occurred at all concentrations of $MgCl_2$. The agglomerate, with a flower-like morphology comprised of interwoven hexagonal particles, is approximately 2–10 μm in diameter. Interestingly, the size of the individual particles decreased gradually with increasing concentrations of $MgCl_2$ (919, 695, 450, and 245 nm at 0.5, 2.0, 3.0, and 4.0 mol/L, respectively). It is well-known that nucleation and crystal growth are crucial factors regulating crystal size. Low concentrations of $MgCl_2$ (low supersaturation) favor the growth of the crystal nucleus, thus generating relatively larger particles of $Mg(OH)_2$ (e.g., 0.5 mol/L, Fig. 1(a)). High concentrations (high supersaturation) correspondingly result in rapid and extensive nucleation and a small particle

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