



Preparation of magnesium hydroxide flame retardant from light calcined powder by ammonia circulation method



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ABSTRACT

Lamellar magnesium hydroxide (MH) with a purity of 99.5% was synthesized using industry lightly calcined powder as raw material and ammonium salt solution as circulating mother liquid by ammonia circulation method. The structures and morphologies of MH were characterized by X-ray diffraction, scanning electron microscope, laser particle size analyzer and thermo gravimetric analysis. The experimental results showed that the hexagonal flake MH products were about 0.86 μm in mean particle size (D50) and nanometers in thickness, and were loose enough for filtering. The BET surface area was about $8 \text{ m}^2 \cdot \text{g}^{-1}$, indicating that the products can be applied as additives of the macromolecule compounds. The diffraction intensity of the (001) direction was higher than that of the (101) direction and the decomposition temperature of products was about 400 °C.

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1. Introduction

Superfine MH as a smoking- and toxic-free flame retardant filler has attracted much attention and widely used in many applications such as plastic, rubber, and other halogen-free polymeric materials. MH was decomposed into MgO and H₂O at a relatively higher temperature (300 °C) than the most widely used aluminium trihydrate fillers. In the flame phase, water vapor forms an envelope around the flame, which tends to exclude the air and dilute the flammable gases. The MgO residue forms a thermally inert layer that could create a protective barrier on the polymer substrate [1–10]. However, all these chemical syntheses were characterized by problems such as being limited to one or two morphological preparations, relatively low yields and being economically unacceptable. A simple fabrication method of MH nanoparticles with several morphological structures is still a challenge.

The raw materials frequently used for preparing MH include sea biter (MgCl₂), bischofite (MgCl₂), magnesite (MgCO₃), and dolomite (MgCO₃ · CaCO₃) [7,11–13]. Magnesite (MgCO₃) is a plentiful mineral worldwide that can be calcined to an inexpensive MgO product called

lightly calcined magnesia (MgO content of 80–93%). Compared to the commonly used MgCl₂ obtained from seawater and brine, light calcined powder is particularly suitable for preparing chlorine-free MH. The direct hydration method [MgO + H₂O → MH] can be used to prepare MH from light calcined powder [6]. However, this method cannot remove the impurities in the lightly calcined magnesia (such as SiO₂), so only low-end MH product is produced. Another usable method is as follows: The MgO in lightly calcined magnesia is first converted into a soluble magnesium salt with acid, for example, into MgCl₂ or MgSO₄ with HCl or H₂SO₄, respectively, and then Mg²⁺ is precipitated with an alkali, such as NaOH, Ca(OH)₂, or ammonia. However, the cost is obviously increased because of the use of acid. In addition, new impurities are introduced, such as Cl[−] from HCl and SO₄^{2−} from H₂SO₄.

To overcome these disadvantages, we developed the ammonia circulation method to prepare MH in a large ammonia-bubbling setup designed by our group (see Fig. 1) [14,15]. The flow contains two main units, namely, an ammonia-evaporation unit and a MH-precipitation (ammonia-adsorption) unit. Lightly calcined magnesia (85% MgO) was used as a magnesium precursor, nitrogen fertilizer (NH₄NO₃, (NH₄)₂SO₄, NH₄Cl, (NH₄)₂SO₄) was used as leachate. The concentration of nitrogen salt solutions was about 3 mol/L. Circulation NH₃ was used as precipitator. The formulas were given as following:

① Ammonia-evaporation process



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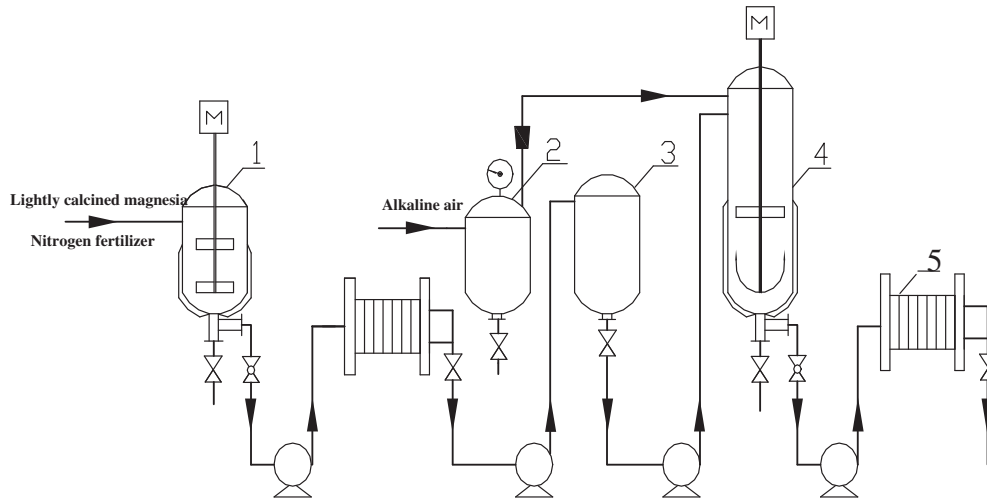
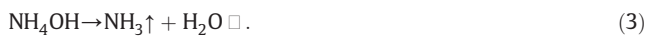
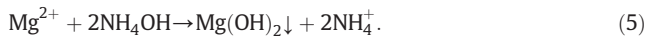


Fig. 1. Experimental setup in large scale. 1. Ammonia-evaporation reactor. 2. Tanks of ammonia gas buffer. 3. Storage tanks. 4. MH-precipitation reactor. 5. Filter.



② MH-precipitation process



In the first unit, MgO reacts with ammonium salt at 98–115 °C to produce ammonia gas and Mg^{2+} solution. After the reaction solution has been filtered to remove insoluble impurities, such as Fe_2O_3 and SiO_2 , refined Mg^{2+} solution is obtained. In the second unit, the refined Mg^{2+} solution is introduced into a bubbling reactor. The ammonia gas obtained in the first unit bubbles through the bubbling reactor to react with Mg^{2+} to produce MH precipitate and NH_4^+ . The MH precipitate is separated from the reaction solution by filtration as the MH product. The filtrate containing NH_4^+ is returned to the first unit as the circulation medium, and thus NH_4^+ or ammonia is recycled, rather than being emitted. The overall reaction of this process is the hydration of MgO [$\text{MgO} + \text{H}_2\text{O} \rightarrow \text{MH} \downarrow$], but MH is actually produced by the reaction of Mg^{2+} with ammonia. No external base as the precipitant of Mg^{2+} , such as NaOH or $\text{Ca}(\text{OH})_2$, is introduced. Using NaOH or $\text{Ca}(\text{OH})_2$ not only produces Na- or Ca- containing byproducts, but also contaminates the MH product. Even industrial aqua ammonia also contains many kinds of impurities. Therefore, the recycling of ammonia gas also improves the purity of the MH product.

Despite the many advantages of the ammonia circulation method described above, the MH product prepared by using $(\text{NH}_4)_2\text{SO}_4$ as the circulation medium tended to agglomerate into a very large particle size [15]. This limits the application of the prepared MH. Furthermore, the issue of shape and size control in fabrication of crystal particles has recently attracted considerable attention due to the unique size and shape-dependent variation of properties and important potential applications of these materials [16–18]. In the present paper, ammonia as precipitant and lightly calcined magnesias as raw materials was discussed in the MH-precipitation unit. The hexagonal flake MH with a narrow particle size distribution can be obtained by controlling the reaction temperature, aging time, ammonium salt and ammonia quality in one step. And then the forming mechanism was also discussed.

2. Experimental

2.1. Preparation of MH

After the ammonia-evaporation reaction had ended, the resulting Mg salt solution was cooled and filtered to remove insoluble impurities, and then refined Mg salt solution for use in the preparation of MH was obtained. In the MH-precipitation unit, Mg salt was reacted with ammonia to produce MH precipitate and NH_4^+ as follows: The samples were obtained by precipitation, at a controlled temperature 100–140 °C, of a magnesium salt solution of concentration 1.0 mol/L by addition of NH_3 used as precipitant. A certain amount of magnesium salt was added to reaction reactor under stirring condition. The suspension was kept at 120 °C for 2 h. The solid phase obtained was recovered by filter and washed twice with distilled water, then vacuum-dried at 100 °C overnight for characterization of powders.

2.2. Characterization of MH

The morphology and element analysis of the MH products were examined by scanning electron microscopy at acceleration voltage of 10 kV (SEM, a LEO, 1530 VP system, with an energy dispersive spectroscopy detector, EDS) and X-ray diffraction (XRD, a Bruker D8 Advance diffractometer, with Cu K α radiation), respectively. The size distribution of MH was characterized by laser particle size analyzer (BT-9300H, Dandong Baite Instrument Co., Ltd., China). The Specific surface area of MH was characterized by BET surface area and void analyzer (SSA-4300). The concentrations of soluble Mg^{2+} were analyzed by EDTA titration.

Table 1
D₅₀ and D₉₀ of MH at different reaction temperatures.

Samples no.	Reaction temperature/°C	D ₅₀ /μm	D ₉₀ /μm
1	40	0.50	0.95
2	75	0.60	1.07
3	100	0.82	1.40
4	120	0.86	1.41
5	140	0.94	1.57

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