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A Novel Preparation of Nano-sized hexagonal Mg(OH)$_2$

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Abstract

Nano-sized dispersive hexagonal magnesium hydroxide (Mg(OH)$_2$) was prepared by an ammonia-hydrothermal method. To improve the crystalline and dispersivity of magnesium hydroxide, citric acid was introduced into the reaction system at ammonia precipitation process and monoethanolamine (MEA) was introduced at hydrothermal process, respectively. In this study, the optimal parameters of nano-sized Mg(OH)$_2$ preparation were obtained. The as-prepared Mg(OH)$_2$ was characterized by SEM, XRD, TGA and etc. The results showed that the sample was hexagonal plates and had the mean diameter of 246 nm.

Keywords: Nano-sized; Mg(OH)$_2$; Hydrothermal process; Dispersity

1. Introduction

Nowadays, the requirements for flame retardants have put magnesium hydroxide to a more important position because of its environmental friendliness and relatively high decomposition temperature. However, magnesium hydroxide particles prepared under general condition are not qualified as flame retardants. Their granularity, agglomeration and morphology may seriously affect the properties of matrix when loaded. Magnesium hydroxide nanocrystals can be synthesized with three structural morphologies, needle-, lamellar- and rod-like [1-4]. Actually, it

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is found out that $Mg(OH)_2$ tend to grow in the (101) plane direction in the crystallization process [5, 6]. Crystals then can show high surface activity and a large strain.

Re-crystallization under hydrothermal conditions is an effective solution available to restrain the intention of growth in the (101) plane direction. Thus, $Mg(OH)_2$ nanocrystallines with different morphologies can be obtained. Adopting a hydrothermal reaction, $Mg(OH)_2$ nanocrystallines with controlled size, shape, and structure were successfully synthesized by choosing different solvents and reaction conditions [3]. To synthesize lamella-like hexagonal $Mg(OH)_2$ nano-particles, researchers put forward a simple hydrothermal process in which hydrazine hydrate was selected as an alkali source. The lamella particle was about 40 nm in thickness [6]. A new method of hydrothermal treatment of $Mg(OH)_2$ precipitates in dilute $CaCl_2$ solution was developed. After the hydrothermal modification, dispersive $Mg(OH)_2$ particles with an average size of about 0.3-0.7 µm, an average agglomerate size of 1.2 µm and BET surface area of 10.5 m^2/g were obtained. Results show that the hydrothermal treatment can improve the crystallinity and inhibit the growth of the (101) polar plane [7]. It is found that the presence of a minor amount of CTAB in the hydrothermal modification of $Mg(OH)_2$ can accelerate the dissolution-precipitation process. Dispersive $Mg(OH)_2$ particles with the mean agglomerate size of 1.071 µm were obtained after hydrothermal treatment in CTAB aqueous solution at 150 °C for 6 h at pH=11 [8]. Fang et al [9] synthesized nano-sized hexagonal magnesium hydroxide ($Mg(OH)_2$) with good dispersibility by a novel double injection-hydrothermal method.

Herein, an ammonia-hydrothermal method was designed to prepare dispersive hexagonal $Mg(OH)_2$ nano-particles. According to the oxygen affinity properties of Mg^{2+} ion, citric acid was introduced into the reaction system as templates and dispersant at ammonia precipitation process to promote the crystallization of magnesium hydroxide and improve dispersion of the crystal particles, respectively. To promote the dissolution–recrystallization process of magnesium hydroxide crystal and the growth in 001 plane (non polar), monoethanolamine (MEA) was employed at the hydrothermal process due to the complex action of neovaricaine towards Mg^{2+}.

2. Experimental

A minor amount of citric acid (3.0 wt% of $Mg(OH)_2$ precipitation yield) was dissolved ultrasonically in 50 mL $MgCl_2$ solution of 3.0 mol/L. Then, the solution was transferred into a three-neck flask in which the temperature is kept at 60 °C. After that, aqueous ammonia was injected into the above mixture solution by a peristaltic pump with a constant flow rate of 1 mL/min with vigorous stirring (300 rpm). An aging process of suspension for 1.0 h was followed after the injection. The precipitation should be washed with de-ionized water for three times and dried at 120 °C for 5.0 h. Dispersive and white $Mg(OH)_2$ precursor were then ready for hydrothermal treatment. The hydrothermal process was conducted in a Teflon-lined stainless steel autoclave at a constant temperature. To promote the dissolution-recrystallization process of precursor, monoethanolamine (MEA) or diethanolamine (DEA) or triethanolamine (TEA) was employed during the hydrothermal process. After cooling down to room temperature naturally, $Mg(OH)_2$ sample should be washed and dried again. The preparation parameters of $Mg(OH)_2$ sample such as concentration of substrate, injection rate and treating temperature were optimized by single-factor testing.

The purity of $Mg(OH)_2$ precipitation was measured according to GB 9857-88. The average particle size and D_{50} of $Mg(OH)_2$ samples prepared under optimal conditions was detected with a laser particle size analyzer (MS-2000, UK). The phase and crystallinity of $Mg(OH)_2$ samples were characterized with XRD (Simens D500). The morphology and structure of $Mg(OH)_2$ crystals were observed with a SEM (JEOL S4800). Thermogravimetric analysis of the as-prepared $Mg(OH)_2$ samples was carried out under nitrogen at a heating rate of 10 °C/min with a thermogravimetric analyzer (METTLER, TGA/DSC-1).

3. Results and discussion

3.1. Dispersant

At the precipitation process, citric acid was introduced into the reaction system as dispersant. The obtained powders were then characterized by XRD. As illustrated in Fig. 1, the diffraction peaks of XRD pattern correspond to hexagonal structure of $Mg(OH)_2$ very well according to JCPDS Card No. 7-239. In the pattern, no extraneous

peaks were observed indicating the high purity of the precursor. It can be inferred that a moderate addition of citric acid can promote the formation of element layer (001 plane) of $Mg(OH)_2$ crystal during the initial precipitation process effectively. According to the oxygen affinity properties of Mg^{2+} ion, citric acid could be remarkable templates forming magnesium hydroxide with their polydentate ligands [10-12]. On the other hand, the hydroxy group of citric acid can be dispersed well in aqueous solution contributing to the improvement of $Mg(OH)_2$ precipitation dispersibility. The possible mechanism of the promotion is described in Fig. 2.
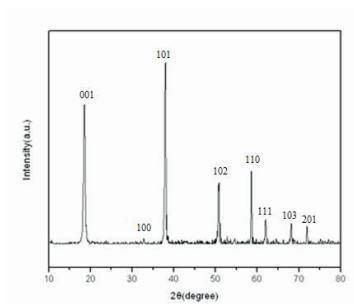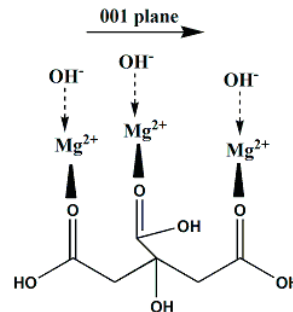
Fig. 1 XRD pattern of $Mg(OH)_2$ precursor   Fig. 2 The possible mechanism of the promotion of crystallization by citric acid
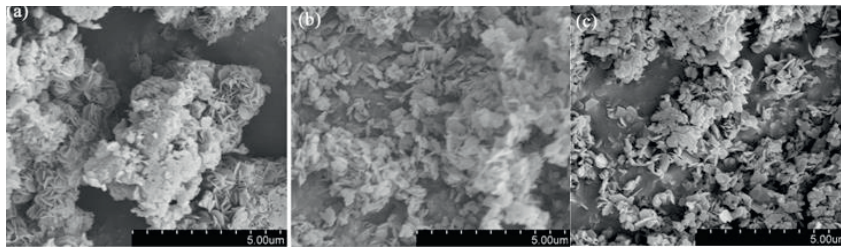
Fig. 3 SEM images of Mg(OH)2 particles treated with different modifier (a) TEA, (b) DEA, (c) MEA

3.2. Modifier

In the present work, TEA or DEA or MEA was employed as modifier of $Mg(OH)_2$ precursor at the hydrothermal treatment process. Fig. 3 shows the morphologies of $Mg(OH)_2$ samples obtained by hydrothermal treatment for 6 h under 453 K adopting different modifier. Comparing to sample (a) and (b), sample (c) shows a better morphology of regular hexagonal nano-plates and better dispersivity. It can be inferred that MEA has a stronger complexing effect towards Mg^{2+}. Actually, the hydrothermal method is a process of dissolution-recrystallization. Thus, the ability of modifier to chelate Mg^{2+} is a key factor to promote the dissolution process which can directly affect the morphology of hydrothermal treated $Mg(OH)_2$ samples.

3.3. Hydrothermal temperature

Fig. 4 illustrates XRD patterns of $Mg(OH)_2$ samples obtained by hydrothermal treatment under different temperatures. The diffraction peaks can correspond with hexagonal structure of $Mg(OH)_2$ very well according to JCPDS Card No. 7-239. It indicates that no apparent impurities are detected. Comparing with the untreated $Mg(OH)_2$ precursor, the increase of peak intensities and narrowing of peak width of hydrothermal treated samples show better crystallinity of $Mg(OH)_2$. Table 1 shows the crystal data of hydrothermal treatment samples under different temperatures of 423K, 453K and 483K. It can be seen from Table 1 that the intensity ratio of I_{001}/I_{101} increases from 0.697 to 0.737 and I_{001}/I_{110} from 2.560 to 3.016 with increasing the temperature of the hydrothermal treatment. Moreover, the particle sizes increase in each plane (001, 101 and 110). Actually, the growth of 001 plane (non polar) represents the extension of $Mg(OH)_2$ crystal element layer, which needs more activation

energy [13]. Thus, a higher treating temperature is reasonable for hydrothermal process. Taking energy efficiency into consideration, 453 K is selected as the temperature of the hydrothermal treatment.
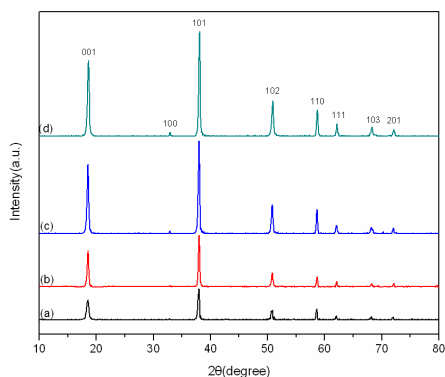

Fig. 4 XRD patterns of Mg(OH)₂ samples hydrothermal treated under different temperatures (a) untreated, (b) 423K, (c) 453K, (d) 483K
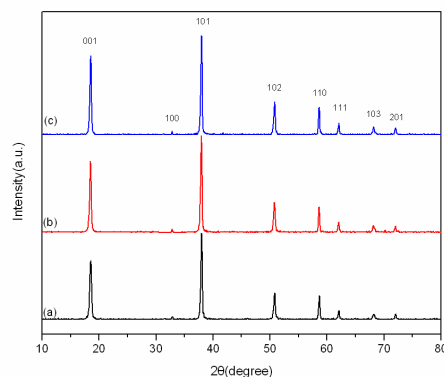
Fig. 5 XRD patterns of Mg(OH)₂ samples with different hydrothermal treatment duration (a) 3 h, (b) 6 h, (c) 9 h

Table 1. Crystal data and crystalline size information from XRD patterns

temperature (K)	Miller index (hkl)	FWHM (deg)	Grain size (nm)	I001/I101	I001/I110
	001	0.413	19.273		
Untreated sample	101	0.279	29.777	0.630	1.971
	110	0.275	32.771		
	001	0.387	20.568		
423	101	0.275	30.211	0.697	2.560
	110	0.265	34.008		
	001	0.320	24.876		
453	101	0.230	36.124	0.724	2.730
	110	0.256	35.202		
	001	0.299	26.624		
483	101	0.250	33.238	0.737	3.016
	110	0.200	45.057		

*The grain size was estimated by applying Debye-Scherrer formula

3.4. Hydrothermal duration

In order to improve the crystallinity of Mg(OH)₂ and help producing more feature-regular particles, a fully understanding for the dissolution–recrystallization process is necessary. Fig. 5 and Table 2 illustrate the correlation between the hydrothermal treatment time and crystal parameters of Mg(OH)₂. It can be seen that the intensity ratios (I001/I101, I001/I110) increase observably with increasing the hydrothermal treatment time. Apparently, a prolonged treating time implies a relatively adequate dissolution–recrystallization process in the hydrothermal treatment. Theoretically, it would be more reasonable to set the time as long as possible, as is shown in Table 2. However, to lower the synthesis cost of flame retardant is also a factor which should not be neglected. Thus, 6 h can be regarded as an optimal hydrothermal treatment time.

Table 2. Crystal data and crystalline size information from XRD patterns

Duration (h)	Miller index (hkl)	FWHM (deg)	Grain size (nm)	I001/I101	I001/I110
	001	0.335	23.762		
3	101	0.254	32.713	0.676	2.685
	110	0.260	34.662		
	001	0.320	24.876	0.724	2.730

6	101	0.230	36.124		
	110	0.256	35.202		
	001	0.297	26.801		
9	101	0.229	36.280	0.803	2.789
	110	0.202	44.611		

3.5. Monoethanolamine concentration

The addition of MEA was supposed to promote the dissolution process of $Mg(OH)_2$ precursor in order to improve the crystallinity. As we can see from Fig. 6 and Table 3, the particle sizes of $Mg(OH)_2$ and intensity ratios (I001/I101, I001/I110) intend to increase firstly and then decrease with increasing the concentration of MEA. Certainly, in dilute solution of MEA, an increasing concentration can promote the dissolution process which can affect the crystal parameters. However, excessive MEA (4 mol/L for example) would increase the viscosity of the aqueous solution. Namely, the mass transfer coefficient and complexing effect towards Mg^{2+} would decrease, which would restrict the dissolution–recrystallization process. On the other hand, relative sufficient aqueous phase in the solution was necessary for the dissolution of $Mg(OH)_2$ while the concentrated solution might not afford [14]. 2 mol/L is therefore selected as the optimal concentration of MEA.
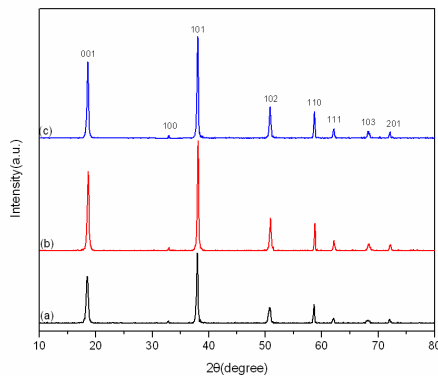

Fig. 6 XRD patterns of $Mg(OH)_2$ samples treated under different MEA concentrations (a) 1 mol/L, (b) 4mol/L, (c) 2mol/L
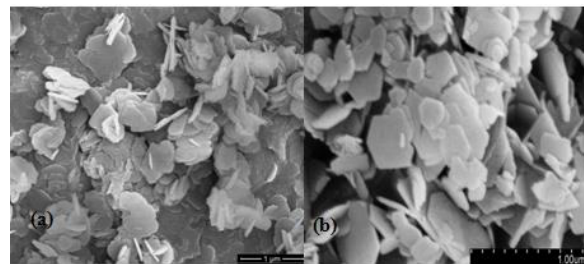
Fig. 7 SEM images of $Mg(OH)_2$ particles (a) $Mg(OH)_2$ precursor (b) hydrothermal treated samples under optimal conditions

Table 3. Crystal data and crystalline size information from XRD patterns

MEA concentration (mol/L)	Miller index (hkl)	FWHM (deg)	Grain size (nm)	I001/I101	I001/I110
1	001	0.387	20.568		
	101	0.275	30.211	0.671	2.500
	110	0.265	34.008		
2	001	0.300	26.534		
	101	0.256	32.456	0.740	2.881
	110	0.219	41.146		
4	001	0.320	24.876		
	101	0.230	36.124	0.724	2.730
	110	0.256	35.202		

The dispersive hexagonal $Mg(OH)_2$ nano-particles can be prepared under the conditions as following: the $MgCl_2$ concentration of 3.49 mol/L, reaction temperature of 333 K, the joining velocity of ammonia of 4 ml/min, the adding amount of citric acid of 4.5 wt.%, the mol ratio of $NH_3 \cdot H_2O$ to $MgCl_2$ of 4, hydrothermal temperature of 453 K,

hydrothermal treatment period of 6.0 h and MEA concentration of 2.0 mol/L. Fig. 7 clearly shows the difference of $Mg(OH)_2$ morphology between the $Mg(OH)_2$ precursor and hydrothermal treated $Mg(OH)_2$ particles. Comparing to $Mg(OH)_2$ precursor, $Mg(OH)_2$ particles obtained by the hydrothermal treatment show morphologies of regular hexagonal nano-plates and no obvious agglomeration is found. The $Mg(OH)_2$ particles disperse well with and the mean diameter is 246 nm.

Meanwhile, the particle size distribution after the hydrothermal treatment becomes narrow, as shown in Fig. 8. D_{50} of the particles decreased from 11.316 μm (Fig. 8a) to 4.395μm (Fig. 8b).

TGA and DSC curves are preformed to investigate the thermal stability of the as-prepared $Mg(OH)_2$ particles, as shown in Fig. 9. A weight loss stage of the $Mg(OH)_2$ samples begins at 553 K and ends at 814 K, with 29.05% weight loss, which is slight lower than the theoretical weight loss of 30.89%.
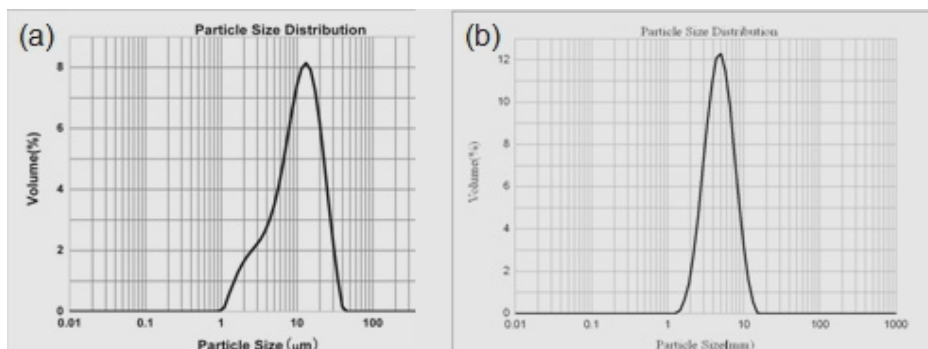

Fig. 8 Particle size distribution (a) $Mg(OH)_2$ precursor (b) hydrothermal

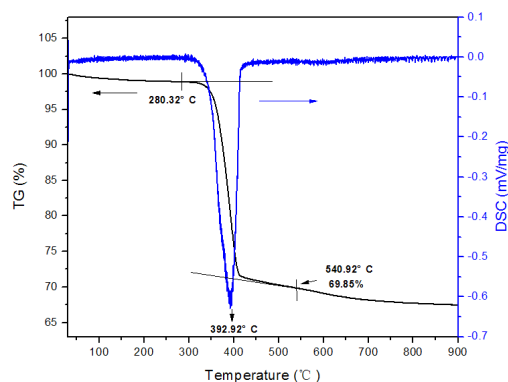Fig .9 TGA and DTG curves of the as-prepared $Mg(OH)_2$ particles treated samples under optimal conditions

4. Conclusion

In the research, an ammonia-hydrothermal method was used to synthesize dispersive hexagonal $Mg(OH)_2$ nano-particles for flame retardants. The introduction of citric acid successfully controlled the growth of $Mg(OH)_2$ crystallites at the initial stage of precipitation reaction. At the following hydrothermal treatment process, the presence of complex dispersant (MEA) promoted the dissolution process contributing the recrystallization of dispersive $Mg(OH)_2$ nano-particles with regular hexagonal morphological structure. Meanwhile, the preparation parameters of nano-sized $Mg(OH)_2$ were optimized by single-factor testing. Characterization of the product indicates that the magnesium hydroxide prepared can satisfy the requirement for the flame retardant.

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