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Hydrothermal formation of dispersive $Mg(OH)_2$ particles in NaOH solution①

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Abstract: The hydrothermal modification of $Mg(OH)_2$ crystals in NaOH solution was investigated. The aggregated $Mg(OH)_2$ particles with irregular shape are converted to regular $Mg(OH)_2$ hexagonal plates after hydrothermal treatment. The prolongation of reaction time from 1 - 4 h or the increase of temperature from 140 ℃ to 200 ℃ can promote the formation of $Mg(OH)_2$ plates with big particle size but small cluster size. The dispersion characteristics of the hydrothermal products are improved owing to the improvement of $Mg(OH)_2$ crystalline degree and the increase of $I_{(001)}/I_{(101)}$ ratio. The proper hydrothermal modification condition is as follows: solid content 0.075 g/mL, NaOH concentration 5.0 mol/L, temperature 200 ℃ and time 4 h. Thermodynamic analysis indicates that the increase of $MgOH^+$ concentration at elevated temperature or the increase of OH^- concentration in concentrated NaOH solution is favorable for the hydrothermal formation of $Mg(OH)_2$ particles.

Key words: magnesium hydroxide; hydrothermal treatment; sodium hydroxide; structure; dispersion
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1 INTRODUCTION

Inorganic hydrates are commonly used in flame-retardant composites due to their ability to undergo endothermic dehydration in fire conditions. There is a growing interest in magnesium hydroxide ($Mg(OH)_2$) as a flame retardant filler that does not produce toxic and corrosive substances upon combustion. $Mg(OH)_2$ decomposes to MgO with release of H_2O. The decomposition starts at about 300 ℃ and the associated endotherm is about 1 450 J/g, which has a good match for many polymer systems. Since flame retardant fillers are usually used at high loadings, close to the maximum values that polymers can tolerate, $Mg(OH)_2$ particles with regular shape and high dispersion degree are expected if acceptable composites are to be obtained[1-3].

$Mg(OH)_2$ can be obtained by several methods, i.e. hydration of MgO, precipitation of a magnesium salt with an alkaline solution, and electrolysis of an aqueous magnesium salt solution. Industrial production of magnesium salt solution is mainly driven by the two former methods. However, $Mg(OH)_2$ particles synthesized at room temperature are easy to aggregate with each other, causing a lack of compatibility and the decrease of mechanical properties of composite[4, 5]. The normal $Mg(OH)_2$ particles usually have a predominant growth in (101) direction, which makes the surface of $Mg(OH)_2$ quite active since the crystal lattices in (101) direction often show a big strain[6]. One effective approach to improve the dispersion of $Mg(OH)_2$ is to re-crystallize the particles at hydrothermal conditions to inhibit the growth of $Mg(OH)_2$ along (101) direction. It was reported that the specific surface area (BET) or the cluster sizes of $Mg(OH)_2$ particles decreased obviously after treating the normal $Mg(OH)_2$ in $CaCl_2$ or ammonium solutions at elevated temperature[7, 8]. The shortcomings of the former method were that the Ca content in the hydrothermal product was usually beyond the limitation of retardant and the morphology of $Mg(OH)_2$ particles was irregular.

The objective of this paper is to investigate the variation of morphology, structure and dispersion characteristics of $Mg(OH)_2$ particles under hydrothermal condition in NaOH solution. Hydrothermal method is developed to inhibit the growth along (101) direction and to promote the growth along (001) direction, yielding hexagonal plate formed with high dispersion degree.

2 EXPERIMENTAL

2.1 Raw material

$Mg(OH)_2$ powder provided by Nafine Chemical Industry Group Cooperation Limited was used in the experiments. The raw material was composed mainly

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of irregular thin plates with a diameter of 0.2 – 1.4 μm and a thickness of about 0.04 μm. Clumps of plate with a "blossom petal" structure were commonly observed in the scanning electron microscope (Fig. 1 (a)). XRD analysis indicated that the raw material were composed of the Mg(OH)$_2$ phase, with the strongest intensity at (101) plane (Fig. 1(b)). The average cluster size of the raw material was 14.5 μm.

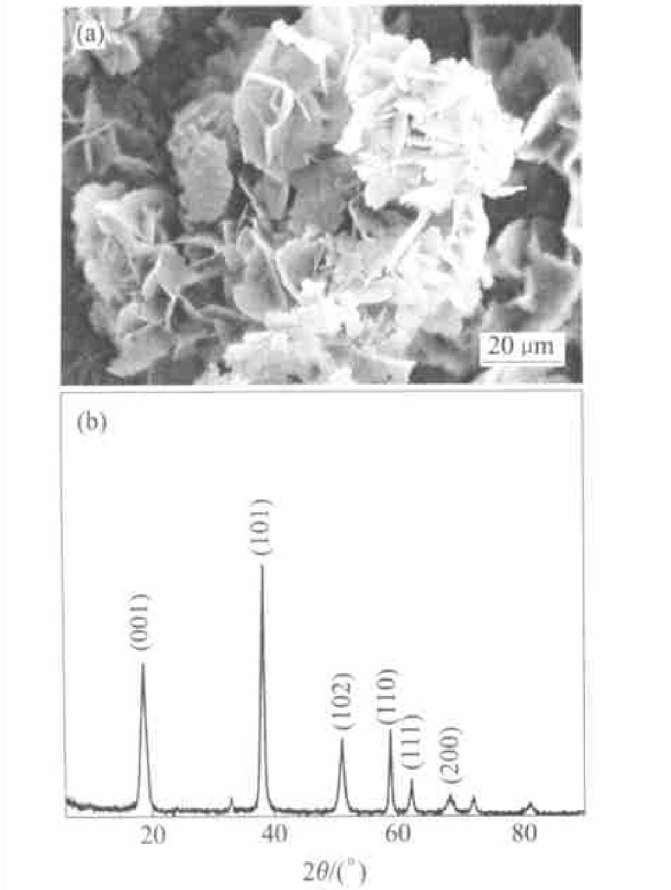

Fig. 1 Morphology (a) and XRD pattern (b) of as-received Mg(OH)$_2$ powder

2.2 Experimental procedure

3.0 g Mg(OH)$_2$ powder and 40 mL 3.0 – 5.0 mol/L NaOH solution were placed in a small polytetrafluoroethylen lined stainless steel autoclave with an inner volume of 80 cm^3. The autoclave was then heated (5 ℃/min) to 140 – 200 ℃ and kept for 1 – 4 h under stirring condition (770 r/min). After hydrothermal treatment, the autoclave was cooled down to room temperature in air, and the product was washed with distilled water, filtrated and dried at 105 ℃ for 12 h.

2.3 Analysis

Samples of Mg(OH)$_2$ powder were re-dispersed in water and a micro-drop was allowed to dry on a carbon substrate for FSEM examination. The structure of powder was characterized by powder X-ray diffractometry (XRD). The cluster size was investigated with a laser particle size analyzer. The average diameter of the Mg(OH)$_2$ particles for each sample are estimated roughly by directly measuring that of about 200 particles from the typical FSEM images.

3 RESULTS AND DISCUSSION

3.1 Morphological variation of Mg(OH)$_2$ particles with hydrothermal condition

Fig. 2 shows the morphologies of Mg(OH)$_2$ particles at different hydrothermal conditions. The hydrothermal treatment made at the temperature below 180 ℃ or for a time shorter than 3 h gives rise to the small plate-shaped particles with a more or less circular contour, as displayed in Fig. 2(a), (b), (e) and (f). Larger, more regular hexagonal plates form with the prolongation of reaction time to 3 – 4 h or the rise of temperature to 180 – 200 ℃. Water at high temperature shows a low viscosity and a high dissociation constant, which favors the electrolytic interactions, lowers kinetic barriers and accelerates the ripening processes, leading to the improvements in the morphology of the Mg(OH)$_2$ samples[9-11].

3.2 Structural variation of Mg(OH)$_2$ particles with hydrothermal condition

Fig. 3 shows the XRD patterns of the Mg(OH)$_2$ samples after hydrothermal treatment in NaOH solution at 140 – 200 ℃ for 1 – 4 h. Compared with the raw material (Fig. 1(b)), the hydrothermal products show an obvious increase of XRD intensities (Fig. 3), indicating an overall enhancement of the crystalline after hydrothermal treatment. Moreover, the fact that the predominant peak changes from (101) to (001) imply that the growth direction of Mg(OH)$_2$ crystals alter at elevated temperatures, producing crystals with less (101) plane exposing. Table 1 lists the variation of $I_{(001)}/I_{(101)}$ with reaction time and temperature.

The $I_{(001)}/I_{(101)}$ ratios of the hydrothermal samples, which are much higher than those of the raw

Table 1 Variation of $I_{(001)}/I_{(101)}$ with reaction time and temperature

Time/h	Temperature/℃	$I_{(001)}/I_{(101)}$
1		1.3
2		1.6
3		4.8
4		5.8
	140	2.1
	160	3.6
	180	4.0
	200	5.0

$I_{(001)}/I_{(101)}$ (raw material) = 0.58

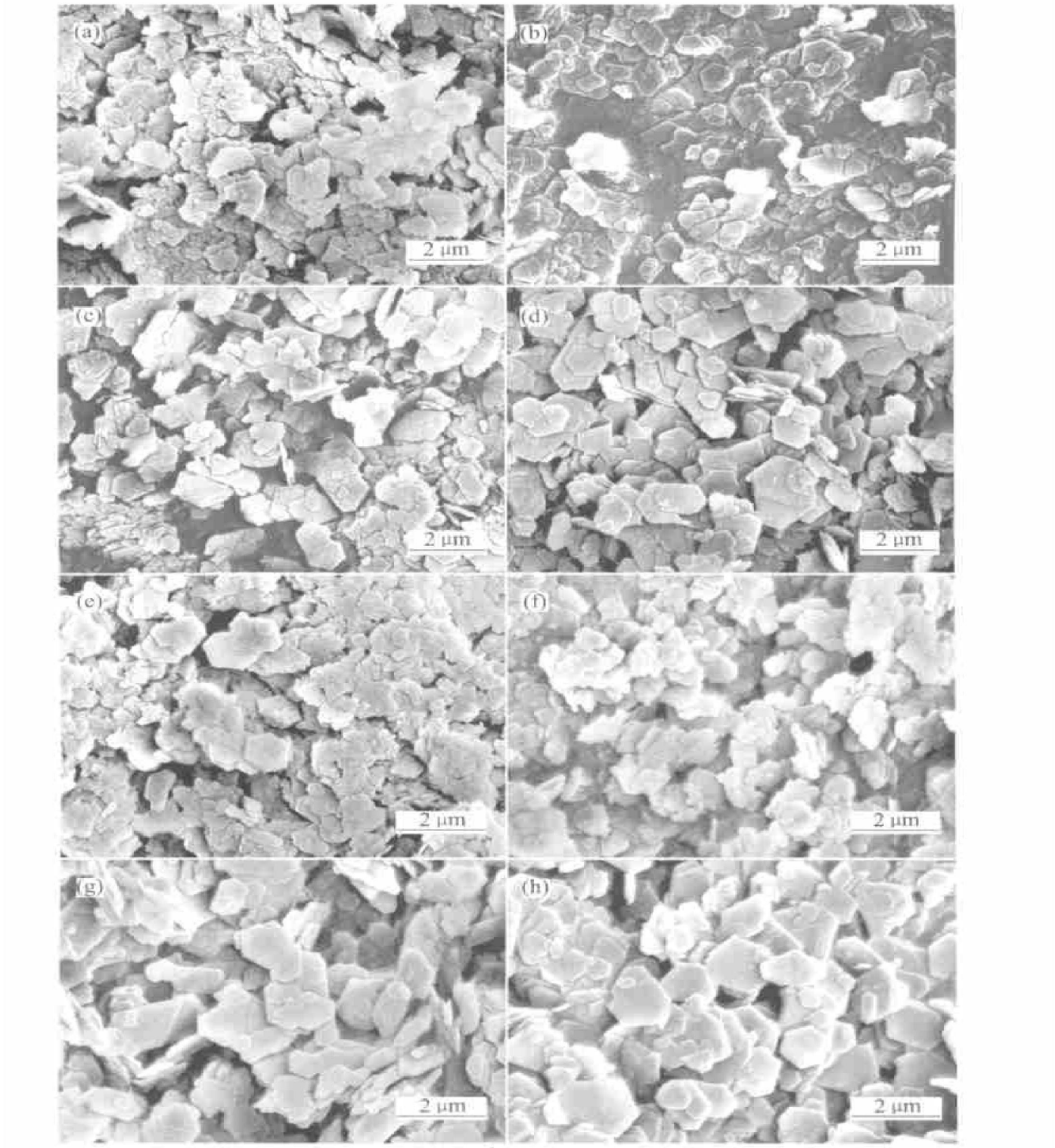

Fig. 2 Morphology variation of $Mg(OH)_2$ under hydrothermal condition
(a) —200 ℃, 1 h, 3 mol/L NaOH; (b) —200 ℃, 2 h, 3 mol/L NaOH; (c) —200 ℃, 3 h, 3 mol/L NaOH; (d) —200 ℃, 4 h, 3 mol/L NaOH; (e) —140 ℃, 4 h, 5 mol/L NaOH; (f) —160 ℃, 4 h, 5 mol/L NaOH; (g) —180 ℃, 4 h, 5 mol/L NaOH; (h) —200 ℃, 4 h, 5 mol/L NaOH

material, increase with the prolongation of the reaction time or the increase of temperature.

3.3 Variation of sizes of particles and clusters with hydrothermal condition

Table 2 shows the variation of the particle and cluster sizes of $Mg(OH)_2$ with reaction time and temperature. The prolongation of reaction time from 1 h to 4 h or the increase of temperature from 140 ℃ to 200 ℃ promotes the formation of $Mg(OH)_2$ plates with big particle size but small cluster size, indicating the obvious improvement in dispersion properties of $Mg(OH)_2$ particles after hydrothermal treatment.

Fig. 4 shows the detailed size distribution of the $Mg(OH)_2$ particles treated for different time. Small particles with diameter lower than 0.2 μm occupy about 60% of the hydrothermal product af-

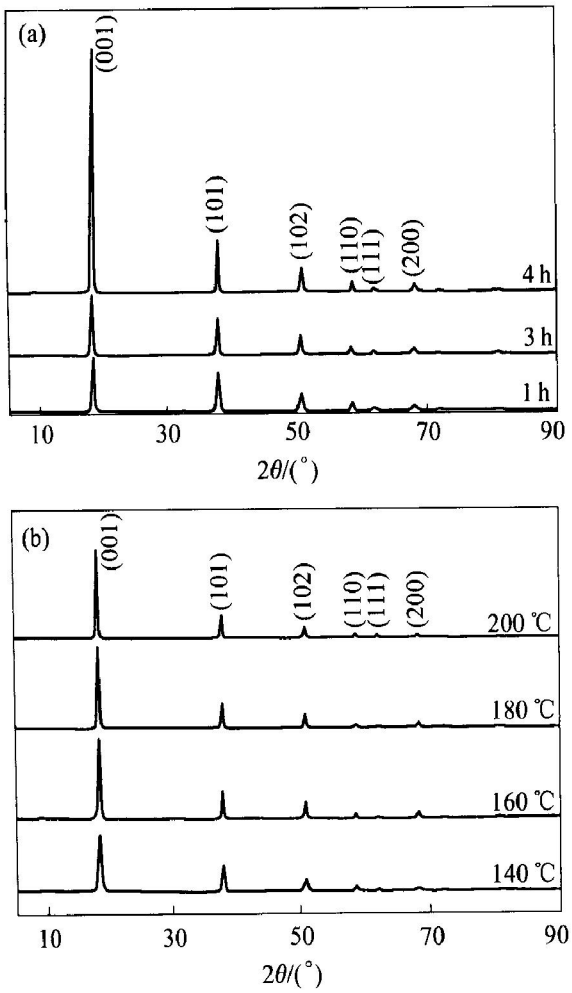

Fig. 3 XRD patterns of Mg(OH)$_2$ at different hydrothermal conditions
(a) —Change of reaction time(3 mol/L NaOH, 200 ℃);
(b) —Change of reaction temperature(5 mol/L NaOH, 4 h)

Table 2 Effect of reaction time and temperature on sizes of particles and clusters

Time/h	Temperature/℃	Average particle size/μm	Average cluster size/μm
1		0.29	5.1
2		0.35	2.0
3		0.46	1.7
4		0.55	1.5
	140	0.40	2.4
	160	0.48	1.7
	180	0.74	1.6
	200	0.87	2.0

ter 2 h hydrothermal treatment. With the proceeding of hydrothermal treatment, the peak of the size distribution shafts toward the right side, indicating the gradual disappearance of the smaller grains and the increase of bigger particles. These phenomena imply that the hydrothermal modification process of

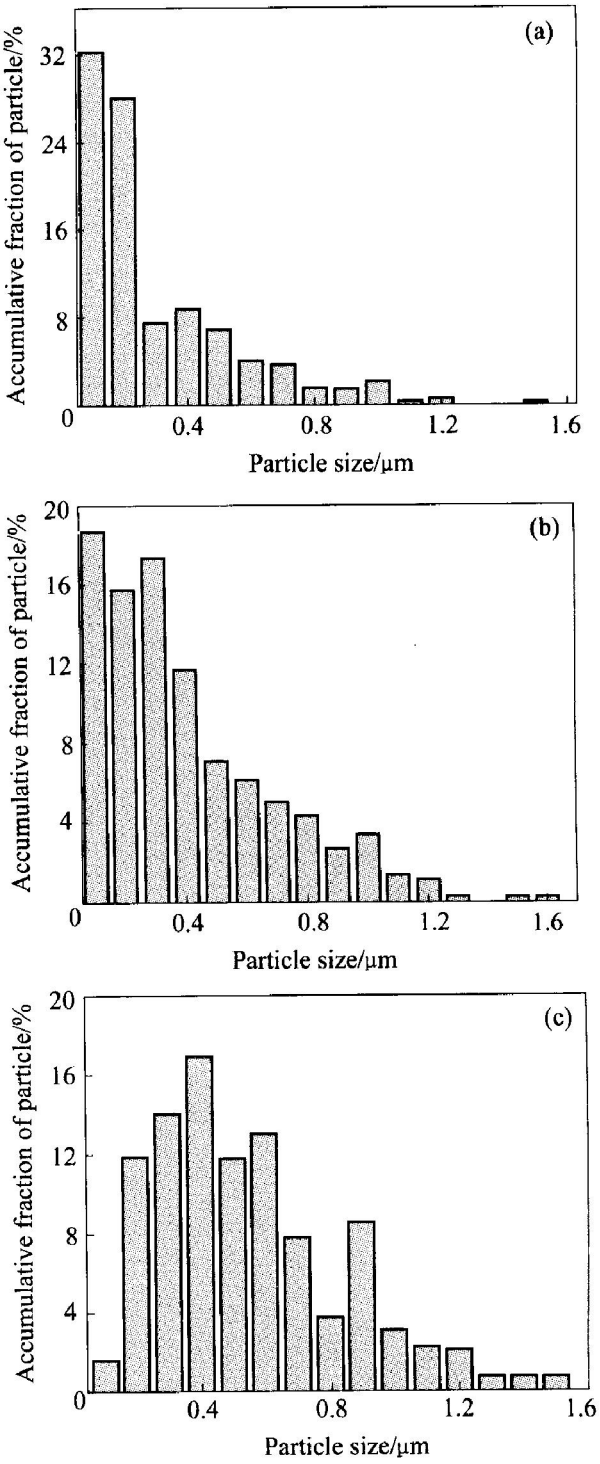

Fig. 4 Variation of Mg(OH)$_2$ particle size with reaction time
(3 mol/L NaOH, 200 ℃)
(a) —2 h; (b) —3 h; (c) —4 h

Mg(OH)$_2$ may occur via the dissolution-precipitation mechanism, that is, the smaller particles dissolve and then precipitate on the surface of bigger particles.

3.4 Hydrothermal modification of Mg(OH)$_2$

The following reactions are considered in Mg(OH)$_2$-NaOH-H_2O system:

$$Mg(OH)_2(s) = Mg(OH)_2(aq) \quad (1)$$

$$Mg(OH)_2(aq) = MgOH^+ + OH^- \quad (2)$$

$$MgOH^+ = Mg^{2+} + OH^- \quad (3)$$

$$NaOH(aq) = Na^+ + OH^- \quad (4)$$

$$H_2O = H^+ + OH^- \quad (5)$$

The equilibrium constants of the above reactions at different temperatures are calculated automatically from the HSC software and listed in Table 3. Based on the simultaneous equilibrium principle, the equilibrium concentrations of the soluble ions at various temperatures can be calculated in a $Mg(OH)_2$ slurry solution containing knowing concentration of NaOH. The concentration instead of activity is adopted to simplify the calculation process.

Table 3 Equilibrium constants of reaction (1)~(5)

Temperature/ ℃	k_1	k_2	k_3
140	2.88×10^{-12}	0.0571	4.93
160	2.43×10^{-12}	0.133	1.44
180	2.03×10^{-12}	0.282	0.443
200	1.685×10^{-12}	0.552	0.144
220	1.39×10^{-12}	1.01	0.048 7

Temperature/ ℃	k_4	k_5
140	5.66×10^{-1}	1.77×10^{-12}
160	4.69×10^{-1}	2.66×10^{-12}
180	3.83×10^{-1}	3.66×10^{-12}
200	3.08×10^{-1}	4.64×10^{-12}
220	2.44×10^{-1}	5.48×10^{-12}

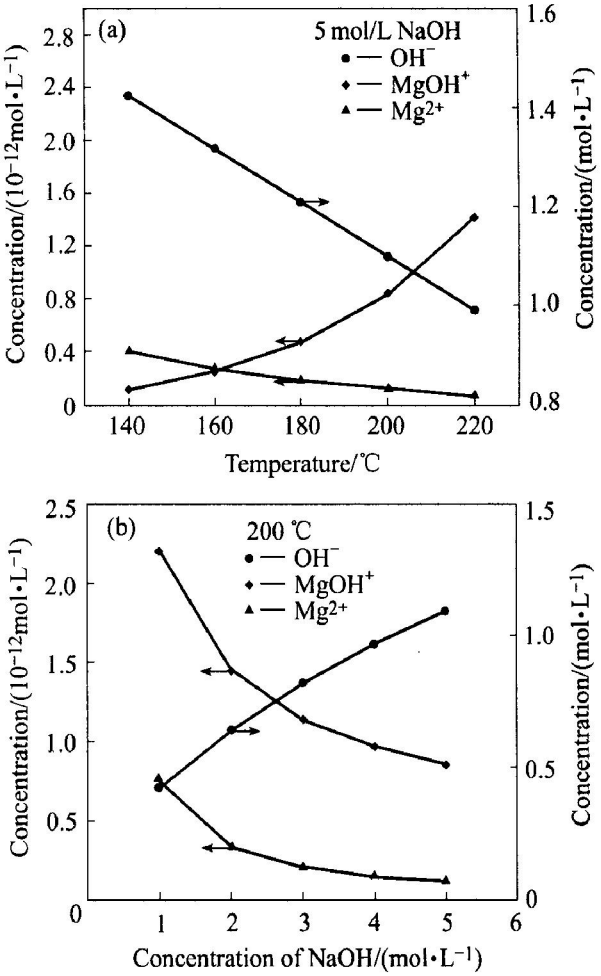

Fig. 5 Variation of equilibrium concentrations of OH^-, $MgOH^+$ and Mg^{2+} with temperature(a) and NaOH concentration(b)

Fig. 5 shows the variation of equilibrium concentrations of OH^-, $MgOH^+$ and Mg^{2+} ions with temperature and NaOH concentration. The hydrothermal modification of $Mg(OH)_2$ may occur via the dissolution of $Mg(OH)_2$ to soluble $MgOH^+$, Mg^{2+} and OH^-, and the combination of $MgOH^+$, Mg^{2+} and OH^- to form $Mg(OH)_2$ crystals. As shown in Fig. 5, the concentration of OH^- is almost 10^{12} times higher than that of the Mg^{2+}-bearing species, indicating an excess of OH^- environment for the formation of $Mg(OH)_2$ crystals. Fig. 5 also indicates that the rise of temperature is favorable for the formation of $MgOH^+$, and the increase of NaOH concentration results in the increase of OH^- concentration.

Crystalline $Mg(OH)_2$ belongs to the bivalent metal hydroxide group, whose crystal structure is a layered CdI_2-type arrangement. Successive hexagonal Mg^{2+} ion layers and OH^- ion layers are stacked one upon another. The Mg^{2+} is six-fold coordinated by OH^-, thus forming $Mg(OH)_6^{4-}$ octahedral—the growth unit for $Mg(OH)_2$ crystal. Such a layered crystal structure has an advantage for plate-shaped crystallization[5]. The excess concentration of OH^- ions will presumably affect the way in which ions are over laid and the growth rate in different directions, causing changes in the crystal shape and the dispersion properties. The increase of $MgOH^+$ concentration at elevated temperatures or the increase of OH^- concentration at concentrated NaOH solution is favorable for the formation of $Mg(OH)_6^{4-}$ octahedral, leading to the acceleration of the hydrothermal modification of $Mg(OH)_2$ particles.

4 CONCLUSIONS

Regular $Mg(OH)_2$ hexagonal plates with high dispersion degree are formed after the hydrothermal treatment of the irregular and aggregated raw materials in NaOH solution. The rise of temperature from 140 ℃ to 200 ℃ or the prolongation of time from 1 h to 4 h can improve the crystalline degree of $Mg(OH)_2$, resulting in the increase of $I_{(001)}/I_{(101)}$. The proper hydrothermal modification condition is as follows: solid content 0.075 g/mL, NaOH concentration 5.0 mol/L, temperature 200 ℃ and time 4 h. The thermodynamic analysis indicates that the increase of $MgOH^+$ concentration at elevated tempera-

tures or the increase of OH^- concentration at concentrated NaOH solution is favorable for the hydrothermal formation of $Mg(OH)_2$ particles.

REFERENCES

[1] Rothon R N, Horsby P R. Flame retardant effects of magnesium hydroxide[J]. Polymer Degradation and Stability, 1996, 54: 383 - 385.

[2] Ondrej G, Elena H, Olga B, et al. Flame retardant treated plywood[J]. Polymer Degradation and Stability, 1999, 64(3): 529 - 533.

[3] Camino G, Maffezzoli A, Braglia M, et al. Effect of hydroxides and hydroxycarbonate structure on fire retardant effectiveness and mechanical properties in ethylene-vinyl acetate copolymer[J]. Polymer Degradation and Stability, 2001, 74(3): 457 - 464.

[4] Phillips V. The gowth of $Mg(OH)_2$ crystals from $MgCl_2$ and $Ca(OH)_2$ in a bine environment[J]. Journal of Crystal Growth, 1977, 41: 228 - 234.

[5] Henrist C, Mathieu J P, Vogels C, et al. Morphological study of magnesium hydroxide nanoparticles precipitates in dilute aqueous solution[J]. Journal of CrystalGrowth, 2003, 249: 321 - 330.

[6] Nisiue W, Komatsu M. Fabrication of Magnesium Hydroxide[P]. JP 57100918, 1982.

[7] Miyada S, Kuroda M, Okada S, et al. Fabrication of Magnesium Hydroxide with High Dispersion[P]. JP 2111625, 1990.

[8] Miyada S, Kuroda M, Okada S, et al. Synthesis of Magnesium Hydroxide with New Structure[P]. JP 2199019, 1990.

[9] Byrappa K, Yoshimura M. Handbook of Hydrothermal Technology[M]. New Jersey: Noyes, 2001. 13 - 16.

[10] Mohmel S, Kurzawski I, Uecker D, et al. The influence of a hydrothermal treatment using microwave heating on the crystallinity of layered double hydroxides[J]. Crystal Research and Technology, 2002, 37(4): 359 - 369.

[11] Yan L, Zhuang J, Sun X M, et al. Formation of rod-like $Mg(OH)_2$ nanocrystallites under hydrothermal conditions and the conversion to MgO nanorods by thermal dehydration[J]. Materials Chemistry and Physics, 2002, 76(2): 119 - 122.

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