Asian Journal of Chemistry; Vol. 23, No. 9 (2011), 4093-4097

ASIAN JOURNAL OF CHEMISTRY

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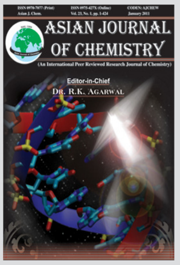

Hydrothermal Treatment of Magnesium Hydroxide Nanoparticles in the Presence of PEG6000

LINSHENG TANG[1,*], MINGYANG SU[1], JINGWEI YANG[2] and KAI YU[1]

[1]College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, P.R. China
[2]College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao 266042, P.R. China

*Corresponding author: E-mail: linshengt62@163.com

(*Received*: 10 December 2010; *Accepted*: 20 May 2011) AJC-9974

The effect of hydrothermal treatment on $Mg(OH)_2$ nanoparticles in the presence of polyethylene glycol (PEG6000) was investigated in this work. The resultant product was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and thermogravimetry-differential thermal analysis (TG-DTA). The experimental results indicate that the hydrothermal treatment in presence of the nonionic surfactant, PEG6000 can effectively control particle growth and improve the crystallinity and dispersivity of the product due to the adsorption of PEG6000 on the surface of $Mg(OH)_2$ throgh steric stabilization. Well-dispersed regular hexagonal flakes of $Mg(OH)_2$ with a mean size of 61 nm and specific surface area (BET) of 62.1 m^2/g were obtained by treating amorphous $Mg(OH)_2$ particles in presence of 4.4 wt % PEG6000 at 180 °C for 5 h.

Key Words: Hydrothermal treatment, $Mg(OH)_2$ nanoparticle, PEG6000.

INTRODUCTION

Nanoscale magnesium hydroxide, $Mg(OH)_2$ is an exceptionally important inorganic material for use in flame retardation, ceramics and catalysis and has attracted attention for both fundamental and application studies[1-10]. However, $Mg(OH)_2$ particles prepared under atmospheric pressure are apt to aggregate with each other and usually exhibit irregular morphology, poor crystallinity and bad filtration performance, which are disadvantageous for their use in the applications. One of the most effective methods to solve the above problems is hydrothermal treatment of the products under certain temperature in presence of aqueous solvent[11-14]. For example, Xiang *et al.*[11], obtained well-defined hexagonal flakes with an average particle size of 0.87 μm after hydrothermal treatment of irregular lamellar $Mg(OH)_2$ crystals in 5 mol/L NaOH solution at 200 °C for 5 h, accompanying with a decrease in specific surface area (BET) from 35-6.3 m^2. Furthermore, the influence of other hydrothermal solvents on hydrothermal treatment of $Mg(OH)_2$ has been investigated. Hong *et al.*[12], prepared well-dispersed particles of $Mg(OH)_2$ with a mean size of 0.4 μm and a thickness of 60 nm in the presence of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) at 150 °C for 6 h with Mg^{2+}/CTAB mol ratio of 80. Wu *et al.*[13], indicated that hydrothermal treatment of $Mg(OH)_2$ agglomerates in dilute $CaCl_2$ solution increased the particle size from 0.1-0.3 μm to 0.3-1.5 μm and decreased the BET surface area from 28.5-10.5 m^2. The common disadvantage of these hydrothermal processes is that $Mg(OH)_2$ crystals grow so fast that it is difficult to prepare nanoscale $Mg(OH)_2$ particles with perfect crystallinity using such processes.

During preparation of $Mg(OH)_2$ nanoparticles by direct precipitation, dispersants such as polyethylene glycol (PEG) and sodium stearate are often used to coat particle surfaces and thus sterically prevent particle agglomeration and hinder crystal growth[15-17]. Based on this observation, in the present work, PEG6000 was selected to control the growth and to prevent the agglomeration of $Mg(OH)_2$ particles during hydrothermal treatment.

EXPERIMENTAL

Sodium hydroxide and magnesium chloride hexahydrate were supplied from Sinopharm Chemical Reagent Co. Ltd., China and PEG6000 was provided by Tianjin Standard Science and Technology Co. Ltd., China. All chemicals used in this study were of analytical grade and were used without further purification.

Experimental procedure

Preparation of $Mg(OH)_2$ precipitate slurry: The preparation of the $Mg(OH)_2$ precipitate slurry was performed in a four-neck 250 mL flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and two dropping funnels. The stirring rate was kept at 250 rpm throughout the preparation.

The reaction temperature was controlled using a thermostatted water bath. 27 mL deionized water was taken into the flask and preheated to 70 -80 ºC under adequate stirring. 30.0 mL of 6 mol/L NaOH solution and 28.5 mL of 3 mol/L $MgCl_2$ solution were then added dropwise from separate dropping funnels into the reactor at a temperature of 70-80 ºC over a period of 15-30 min. After addition of all the ingredients, the reaction temperature of 70-80 ºC was maintained for an additional 3 h. The obtained slurry, which contained 5 % wt $Mg(OH)_2$ and 0.11 mol/L NaOH, was used as the starting material for the study of various hydrothermal treatment. As can be seen from Fig. 1(a), the sample consisted of irregular flakes with a diameter of 17-193 nm, mean size of 57 nm and BET of 91.6 m^2/g.

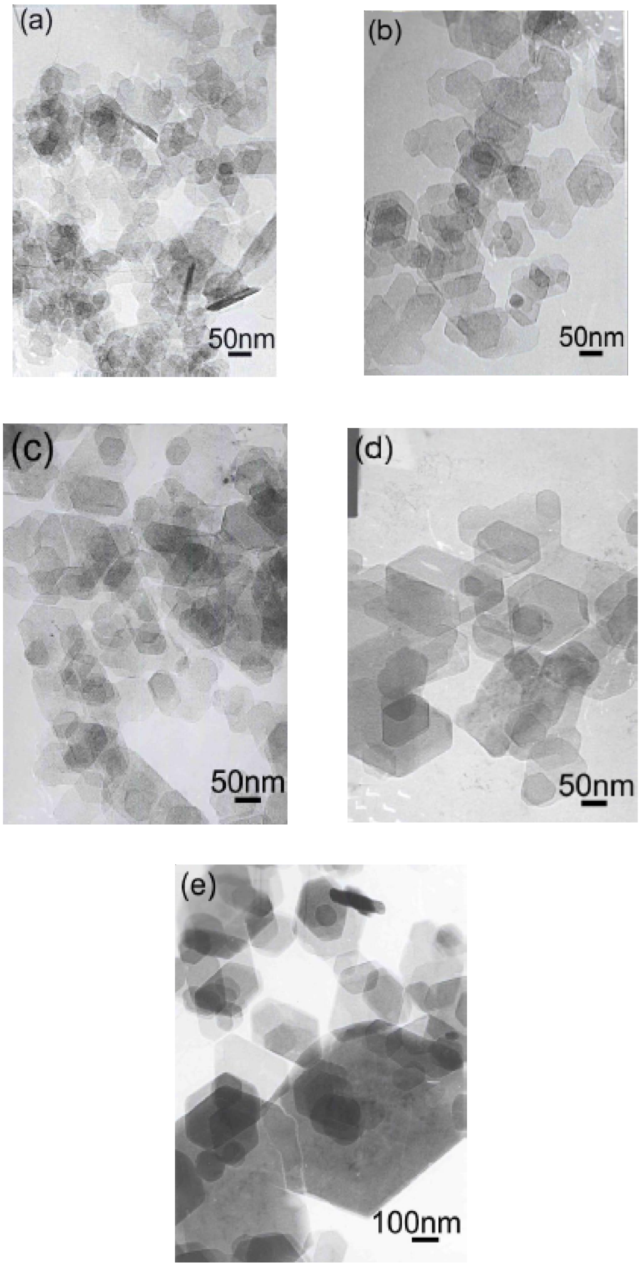

Fig. 1. Morphology variation of $Mg(OH)_2$ particles under different NaOH concentration hydrothermal condition: (a) the material particles used for hydrothermal treatment, (b) --- 0.11 mol/L NaOH, 180 ºC, 5 h; (c) --- 1 mol/L NaOH, 180 ºC, 5 h; (d) --- 2 mol/L NaOH, 180 ºC, 5 h; (e) --- 4 mol/L NaOH, 180 ºC, 5 h

Hydrothermal treatment: The above $Mg(OH)_2$ slurry and a small amount of hydrothermal modifiers were taken into a 200 mL stainless steel autoclave equipped with a magnetic stirrer and a thermometer. The reaction temperature was controlled using a thermostatted oil bath. The contents were treated hydrothermally at a certain temperature for a certain period. Then, the contents were cooled to ambient temperature and filtered. The filter cake was washed successively with 50 mL × 4 deionized water for 4 times and 50 mL ethanol for one time and dried until constant weight at 120-130 ºC in an oven.

Characterization: The morphology of the particles was observed by transmission electron microscopy (TEM, Model JEM-2000EX, Jeol, Japan). The mean size and size distribution of the particles in the dry powder was determined on 200-300 particles from the analysis of TEM micrographs. Samples for transmission electron microscopy (TEM) were prepared by placing a drop of the water suspension of the nanoparticles on a carbon coated Cu grid. The phase and crystallographic characterization of the samples was performed with a powder X-ray diffractometer (XRD, Model D/max-2500, Nigaku, Japan) with CuK_α radiation ($\lambda = 1.5406$ Å) with an accelerating voltage of 40 kV. BET analysis was performed on a Model ST-2000 instrument (Beifen, China). The TG-DTA analysis was carried out on a thermoanalyzer (Model STA449C, Netzsch, Germany) at a heating rate of 10 ºC/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Influence of NaOH concentration: TEM images of the products before and after hydrothermal treatment are presented in Fig. 1 which clearly revealed that hydrothermal treatment could improve crystalline morphology and dispersion of $Mg(OH)_2$ particles. The irregular flakes were transformed to regular hexagonal lamellae through hydrothermal treatment. Increasing NaOH concentration led to the formation of products with bigger mean size and wider particle size distribution. The lamellae formed in the 0.11 mol/L NaOH solution had diameter of 25-290 nm and mean size of 70 nm, but the lamellae formed in the 4.0 mol/L NaOH solution had average size of 200 nm and size distribution of 58-557 nm. Moreover, the BET of the samples decreased sharply from the untreated value of 91.6 to 50.5 m^2/g and 11.7 m^2/g by hydrothermal treatment, respectively in 0.11 and 4 mol/L NaOH. According to the Pauling rule and theoretical model of anionic coordination polyhedron, $Mg(OH)_6^{4-}$ is the growth unit of $Mg(OH)_2$ crystals. Therefore, the high OH^- concentration could favor the formation of basic units and the growth of $Mg(OH)_2$ crystals[11], making it difficult to maintain particle sizes in the nanometer scale during hydrothermal treatment.

The XRD patterns of hydrothermal samples and the sample without hydrothermal treatment are presented in Fig. 2. As can be observed, the diffraction peaks of each sample can be indexed to the hexagonal structure of $Mg(OH)_2$ with lattice constants comparable to the values reported in JCPDS 7-239. The absence of peaks arising from impurities such as NaCl and MgO indicated that the synthesized products had higher purity. According to the Debye-Scherrer formula, the observation of sharper diffraction peaks with increasing NaOH concentration indicated the growth of $Mg(OH)_2$ nanocrystals.

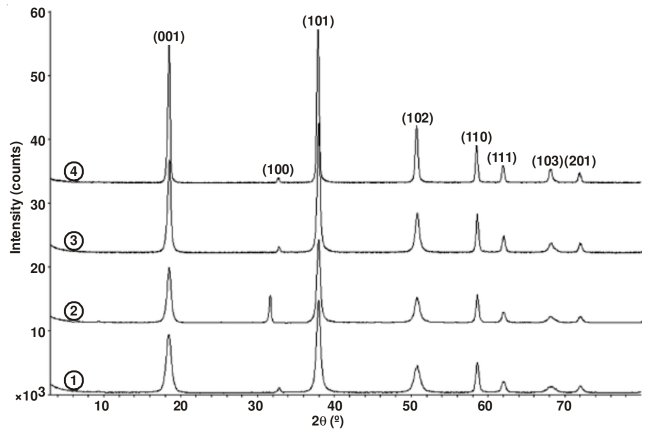

Fig. 2. Influence of NaOH concentration on the XRD spectras of hydrothermal products. Hydrothermal condition: ① the material particles used for hydrothermal treatment; ② --- 0.11 mol/L NaOH, 180 ºC, 5 h; ③ --- 1 mol/L NaOH, 180 ºC, 5 h; ④ --- 4 mol/L NaOH, 180 ºC, 5 h

This can be confirmed by Table-1. The intensity ratios and full width at half-maximum (FWHM) of diffraction peaks and crystal domain size along the various directions were given in Table-1. At higher NaOH concentration, the values of I_{001}/I_{101} and I_{001}/I_{110} increased after hydrothermal treatment and this tendency became more obvious due to improvement of the crystallinity along the (001) direction.

TABLE-1
INFLUENCE OF THE CONCENTRATION OF NaOH ON THE CRYSTAL DATA OF $Mg(OH)_2$ PARTICLES

NaOH conc. (mol/L)	Crystal facet	FWHM (ºC)	Grain size (nm)	I_{001}/I_{101}	I_{001}/I_{110}
0.11*	001	0.687	11.585	0.625	1.83
	101	0.575	14.449		
	110	0.437	20.622		
0.11	001	0.569	13.989	0.699	1.911
	101	0.502	16.552		
	110	0.380	23.711		
1.0	001	0.459	17.343	0.719	2.397
	101	0.426	19.053		
	110	0.365	24.685		
4.0	001	0.338	23.549	0.911	3.796
	101	0.344	24.145		
	110	0.323	27.881		

*Without hydrothermal treatment.

Influence of PEG6000 loading: Hydrothermal treatment in concentrated NaOH solution does not appear to be well-suited to the preservation of nanoscale particle size in $Mg(OH)_2$ slurries; additionally, this approach could prove uneconomical, *e.g.*, due to requiring corrosion-resistant equipment. As mentioned in the introduction, in preparing $Mg(OH)_2$ nanoparticles by precipitation, dispersants such as PEG and sodium stearate are often used to prevent particle agglomeration and hinder crystal growth. Therefore, hydrothermal treatment in the presence of PEG6000 without adding extra NaOH was studied.

Fig. 3 presents the TEM images of hydrothermal products obtained in the presence of different loading of PEG6000, revealing clearly that PEG6000 loading has significant effects on the morphology and dispersion of products. The particles obtained in the presence of 4.4 wt % of PEG6000 had more regular shapes and excellent dispersivity compared with others. The average flake diameter of hydrothermal products was about 60 nm without adding dispersant. The data were 69, 71 and 61 nm in the cases of 3.0, 3.7 and 4.4 wt % of PEG6000 (Fig. 2b-d), respectively. It was clearly observed that mean size of the resultant nanoparticles after hydrothermal treatment in the presence of PEG6000 increased by a relatively small amount in comparison to the growth observed in NaOH solution. Moreover, the average size decreased slightly when the loading of PEG6000 increase up to 4.4 %. This trend was confirmed by the variation of specific surface area. The BET surface area was 85.3, 53.4 and 62.1 m^2/g, respectively, for hydrothermal treatment in 0, 3, 4.4 % PEG6000.

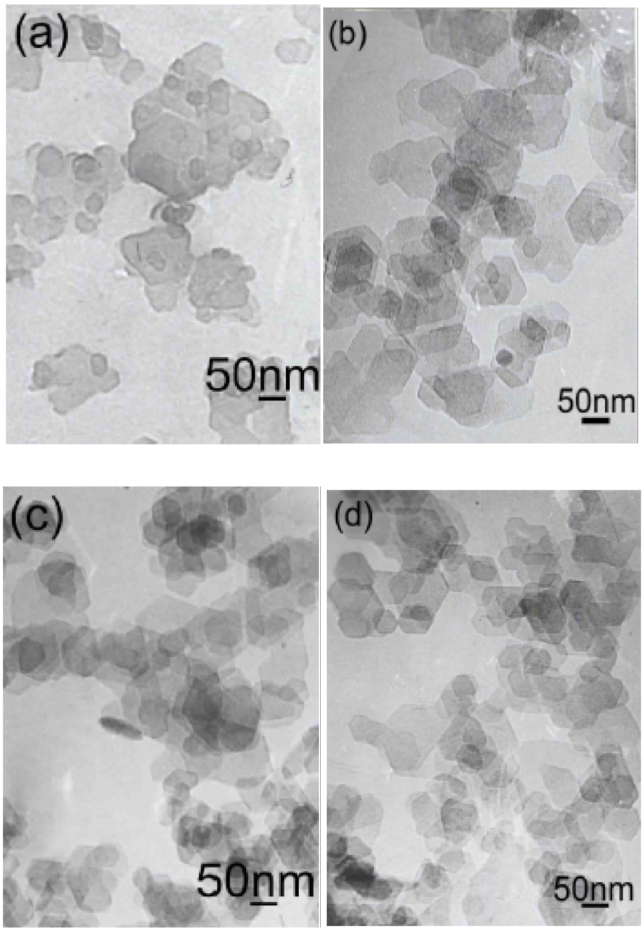

Fig. 3. Morphology variation of $Mg(OH)_2$ particles under different PEG6000 loading hydrothermal condition: (a) --- 0 % PEG6000, 180 ºC, 5 h; (b) --- 3 % PEG6000, 180 ºC, 5 h; (c) --- 3.7 % PEG6000, 180 ºC, 5 h; (d) --- 4.4 % PEG6000, 180 ºC, 5 h

XRD patterns of the hydrothermal samples obtained in the presence of different dosage of PEG6000 were shown in Fig. 4. The intensity ratios and full width at half-maximum (FWHM) of diffraction peaks and crystal domain size were given in Table-2. Especially, by comparison of the intensity ratio I_{001}/I_{101} and I_{001}/I_{110}, respectively at different loading of PEG6000, the intensity of (001) crystal plane increased more than the plane of (101) and (110) with PEG6000 loading, the changes in XRD are mostly due to improved crystallinity, which can be convinced by the growth of crystal domain size based on the Debye-Scherrer formula and the change of particle diameter.

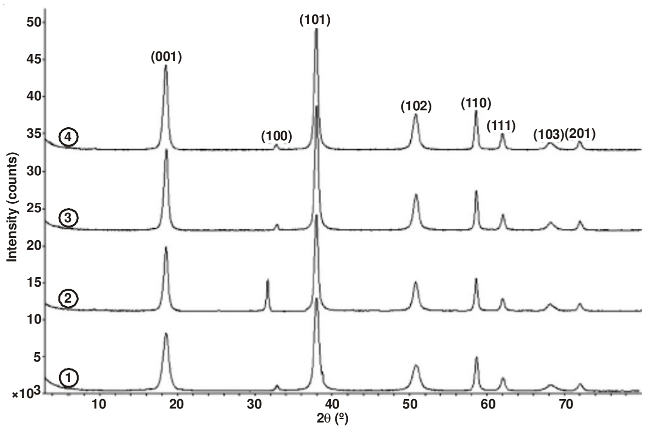

Fig. 4. Influence of PEG6000 loading on the XRD spectras of hydrothermal products. Hydrothermal condition: (a) --- 0 % PEG6000, 180 ºC, 5 h; (b) --- 3 % PEG6000, 180 ºC, 5 h; (c) --- 3.7 % PEG6000, 180 ºC, 5 h; (d) --- 4.4 % PEG6000, 180 ºC, 5 h

TABLE-2
INFLUENCE OF THE DOSAGE OF PEG6000 ON THE CRYSTAL DATA OF $Mg(OH)_2$ PARTICLES

PEG6000 dosage (%)	Crystal facet	FWHM (ºC)	Grain size (nm)	I_{001}/I_{101}	I_{001}/I_{110}
0	001	0.569	11.585	0.625	1.833
	101	0.502	14.449		
	110	0.380	20.622		
3.0	001	0.569	13.989	0.699	1.911
	101	0.502	16.552		
	110	0.380	23.711		
3.7	001	0.563	14.319	0.661	2.053
	101	0.496	16.753		
	110	0.394	22.873		
4.4	001	0.585	13.606	0.694	2.103
	101	0.512	16.225		
	110	0.383	23.520		

According to the hybrid orbital theory and coordination theory, Mg^{2+} possesses unoccupied hybrid orbita and can accept an isolated electron pair from O atom in the PEG molecule[7,18]; thus PEG6000 can adsorb onto the crystal facet of $Mg(OH)_2$ resulting in steric stabilization against particle agglomeration and hinder crystal growth.

The TG and DTA measurements were carried out to analyze the thermal behavior and decomposition process of the hydrothermal product obtained at 180 ºC for 5 h in the presence of 4.4 wt % of PEG6000. One of the main applications of magnesium hydroxide is flame retardation. The thermal behavior and decompositon of the $Mg(OH)_2$ have influence on flame resistance. A typical TG-DTA profile was shown in Fig. 5. As seen in TG curve, a pronounced weight loss step was found in the temperature range of 291-453 ºC with 32.23 % weight loss and a corresponding well-defined endothermic peak was observed at 385.4 ºC in the DTA curve that could be attributed to the decomposition of $Mg(OH)_2$ and PEG6000.

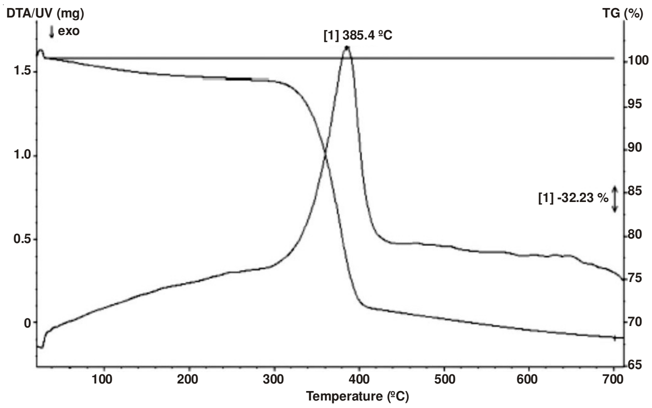

Fig. 5. TG and DTA curves of hydrothermal product

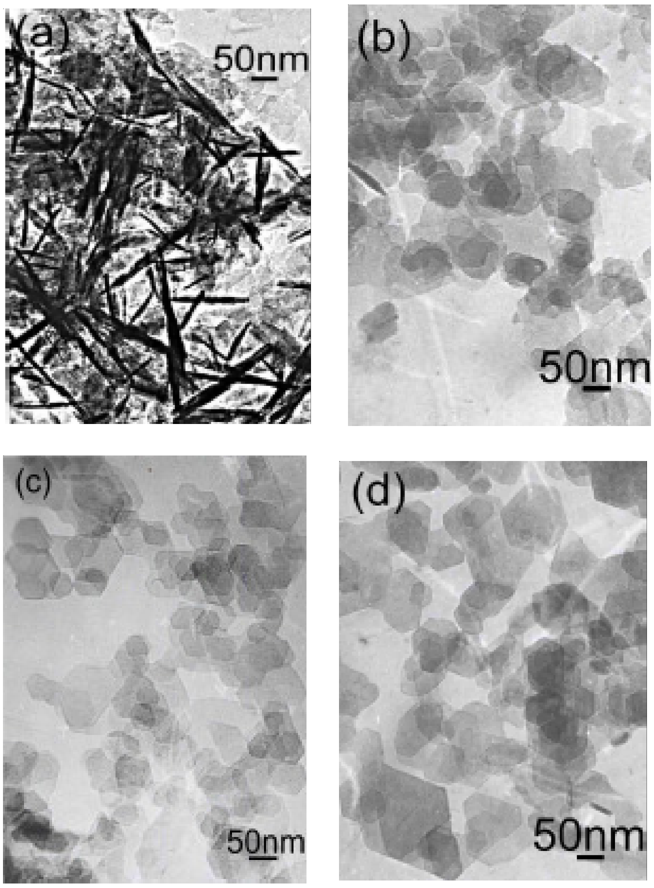

Fig. 6. Morphology variation of $Mg(OH)_2$ particles under different hydrothermal temperature hydrothermal condition: (a)--- 140 ºC, 5 h, 4.4 % PEG6000; (b) --- 160 ºC, 5 h, 4.4 % PEG6000; (c) --- 180 ºC, 5 h, 4.4 % PEG6000; (d) --- 200 ºC, 5 h, 4.4 % PEG6000

Effect of hydrothermal temperature: Fig. 6 showed the influence of hydrothermal temperature on the morphology of products. As seen in Fig. 6, the crystals obtained at 140 ºC displayed needle-like morphology, but the ratio of the plate-shaped crystals to the needle-like increased rapidly when temperature was raised and almost completely plate-shaped hexagonal nanocrystals with good dispersivity were obtained at 180 ºC. The reasons for this phenomenon is still not clear, needs further study. The product prepared at 200 ºC had bigger particle size in comparison with others and some platelets appeared to be agglomerated or fused. The XRD spectras in Fig. 7 indicated that the position, intensity and FWHM of characteristic diffraction peaks varied slightly with the increase of the temperature. Based on the above results, 180 ºC was thought to be optimal hydrothermal temperature.

Effect of hydrothermal period: Fig. 8(a)-(c) showed TEM images of the products obtained by hydrothermal treatment for 3.5, 5, 6.5 h, respectively. As seen in Fig. 8, the product obtained for 3.5 h appeared some needle-like or irregular

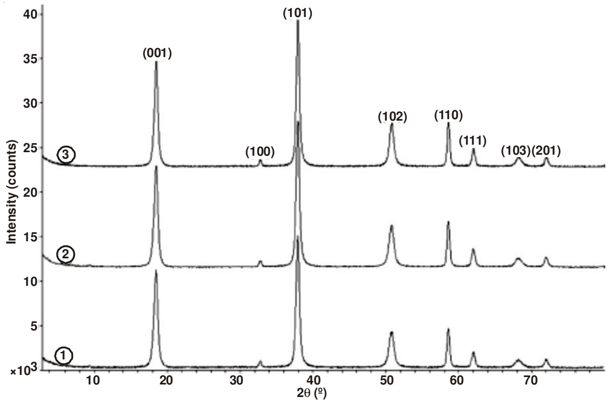

Fig. 7. Influence of hydrothermal temperature on the XRD spectras of hydrothermal products. Hydrothermal condition: (a) --- 140 ºC, 5 h, 4.4 % PEG6000; (b) --- 160 ºC, 5 h, 4.4 % PEG6000; (c) --- 180 ºC, 5 h, 4.4 % PEG6000; (d) --- 200 ºC, 5 h, 4.4 % PEG6000

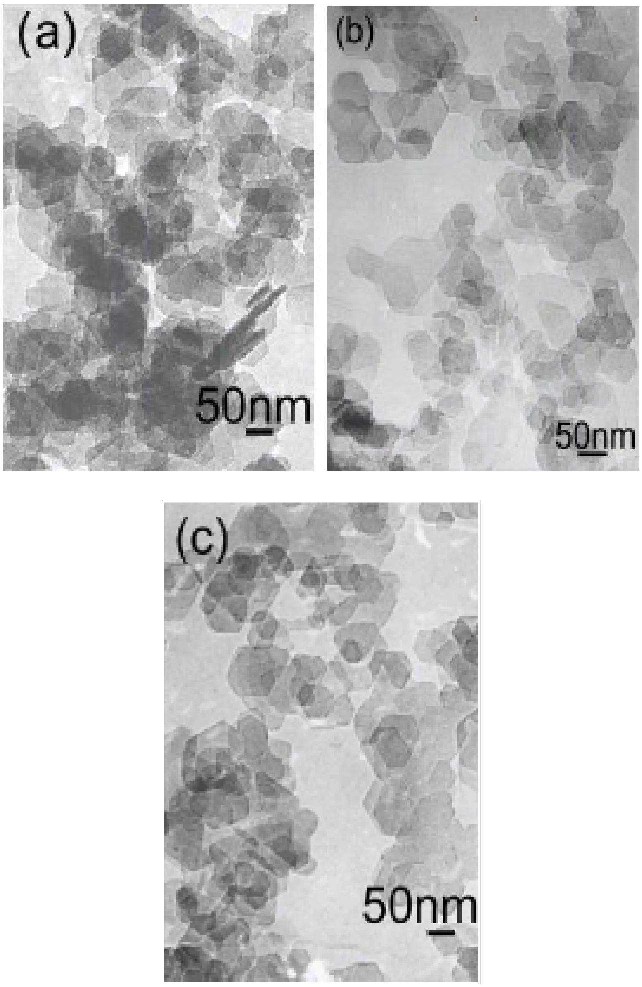

Fig. 8. Morphology variation of $Mg(OH)_2$ particles under different hydrothermal reaction time hydrothermal co dition: (a)--- 3.5 h, 180 ºC, 4.4 % PEG6000; (b) --- 5 h, 180 ºC, 4.4 % PEG6000; (c) --- 6.5 h, 180 ºC, 4.4 % PEG6000

crystals, but ones for 5 and 6.5 h appeared almost completely hexagonal nanocrystals.

From the XRD curves (Fig. 9), it was indicated that the hydrothermal periods had little influence on the crystal data. When the influence on morphology and structure was comprehensively considered, 5 h was thought to be the optimal reaction time.

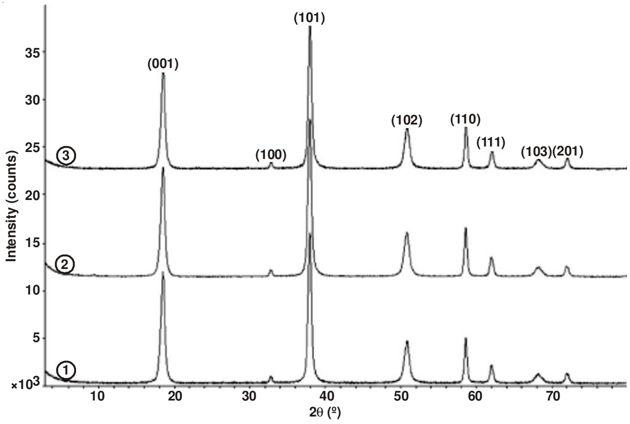

Fig. 9. Influence of hydrothermal reaction time on the XRD spectras of hydrothermal products. Hydrothermal condition: (a) --- 3.5 h, 180 ºC, 4.4 % PEG6000; (b) --- 5 h, 180 ºC, 4.4 % PEG6000; (c) --- 6.5 h, 180 ºC, 4.4 % PEG6000

Conclusion

PEG can be adsorbed on the surfaces of $Mg(OH)_2$ particles sterically stabilizing them against agglomeration and slowing crystal growth. Therefore, well-dispersed $Mg(OH)_2$ nanoparticles with regular shapes and high crystallinity can be obtained through hydrothermal treatment of irregular $Mg(OH)_2$ particles in the presence of PEG without adding extra NaOH. By contrast, it is difficult to maintain small particle size (*e.g.*, < 100 nm) through hydrothermal treatment in concentrated NaOH solution. Through optimizing our treatment conditions, we obtained regular hexagonal flakes with mean diameter of 61 nm and BET surface area of 62.1 m^2/g by treating irregular $Mg(OH)_2$ nanoparticles in the presence of 4.4 wt % PEG6000 at 180 ºC for 5 h.

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