

Synthesis of cubic MgO nanostructure by an easy hydrothermal-calcinations method

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Cubic MgO micro-particles with approximately 5-10 μm dimensions were synthesized indirectly from magnesium salt solutions through three consecutive steps, namely: wet chemical precipitation, hydrothermal and thermal dissociation. In wet chemical precipitation step $\text{Mg}(\text{OH})_2$ uniform lamellar hexagonal nano-structure with about 30 nm in thickness were synthesized from 0.2 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution, subsequent hydrothermal processing of synthesized $\text{Mg}(\text{OH})_2$ lamellar hexagonal nano-structure in 10, 20, 30, 60, 120 and 180 min produced 5-10 μm MgCO_3 micro-cubes which calcinations of these particles leads to production of the same size MgO micro-cubes. Most pure MgCO_3 micro-cubes were synthesized after 120 min of hydrothermal processing. STA analysis revealed that the best temperature for calcinations is about 700 $^\circ\text{C}$.

Key words: MgO, Nano structure, Cubic morphology, Hydrothermal, Calcinations.

Introduction

Magnesium oxide (MgO) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) structures recently have attracted a great deal of interest, mostly because of their high biocompatibility and surface area [1]. This makes them applicable in various industrial and technological areas such as catalysts [2], water treating [3], as additive in refractories [4], painting industry [5] and super conductors [6]. Endothermic dehydration of $\text{Mg}(\text{OH})_2$ enables it to have application as fire retardant [7], it is also a suitable precursor for MgO synthesis [1].

There are numerous methods to produce MgO and $\text{Mg}(\text{OH})_2$ structures such as electrical precipitation [8], sol-gel [9], chemical precipitation [10], hydrothermal [11-17], laser [18] and microwave fabrication [19]. Sol-gel is a convenient method and has attracted a lot of attention. In this method alkoxides are used as precursors which after heating at elevated temperatures, small organic or inorganic molecules are disappeared. Heating at elevated temperatures emits toxic gases, and it restricts industrial use of this method. Prolonged operation time is another drawback of sol-gel method [20]. Microwave and laser fabrication methods are delicate and require obscure, elaborated apparatus and precise control systems [18, 19]. Hydrothermal processing is a versatile and widely accepted method in metal oxide synthesis. Homogenous powder synthesis, low crystalline temperature, reduced agglomeration, narrow particle size

distribution, homogenous phase, smooth composition, high purity and controlled particle morphology are among various merits of hydrothermal method [21-24].

In this paper cubic MgO micro-particles are indirectly synthesized from 0.2 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. First, 30 nm $\text{Mg}(\text{OH})_2$ lamellar hexagonal nano-structure were synthesized from 0.2 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ through a wet chemical precipitation method. Synthesized $\text{Mg}(\text{OH})_2$ nano-plates were converted to cubic MgCO_3 micro-particles via hydrothermal processing at various temperatures. Finally calcinations of MgCO_3 particles lead to production of cubic MgO micro-particles of the same size.

Experimental Procedures

Mg(OH)₂ synthesis

0.2 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck. Art No: 105853) and 0.2 M NaOH (Merck. Art No: 6498) solutions were used as precursor and pH adjuster, respectively. $\text{Mg}(\text{OH})_2$ nano-plates were synthesized by slow addition of 0.2 M NaOH solution to the stirring 0.2M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. pH was monitored by means of a pH meter (Metrohm). At $\text{pH} \approx 9.5$ a white material precipitates in the solution. After washing with distilled water, the white precipitate dried at 70 $^\circ\text{C}$ for 24 hours.

Hydrothermal processing of Mg(OH)₂

Hydrothermal process was performed in an autoclave. 0.5 g of synthesized $\text{Mg}(\text{OH})_2$ was dissolved in 35 mL distilled water. Subsequently 5 g urea ($\text{CH}_4\text{N}_2\text{O}$ - Merck, Art No: 8486) was added to the solution. After pouring the solutions in a Pyrex beaker and locating into the autoclave, solutions were heated at constant temperature

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and pressure (200 °C and 12 kg/cm² respectively) for 10, 20, 30, 60, 120 and 180 min. After cooling to room temperature, solutions were washed with ethanol which produced a white precipitate. The precipitates were dried at 70 °C for 24 hours.

Thermal analysis

In order to determine appropriate calcination temperature for hydrothermally processed materials, Simultaneous Thermal Analysis (STA- PLSTA 1940, England) was utilized in air atmosphere at a rate of 10 °C/min.

Characterization

Morphology of the Mg(OH)₂, MgCO₃ and MgO particles was analyzed with a field emission scanning electron microscope (FESEM, Hitachi, S-4162, Vacc = LSKV) operated at an accelerating voltage of 15 kV. Crystal structure analysis was carried out by employing an X-ray diffractometer (XRD-Philips PW 3710) equipped with a CuKα radiation source (λ = 1.5406 Å) and a two-dimensional area detector. The XRD patterns were checked by X'Pert HighScore software, 2006 (PANalytical B.V., Almelo, Netherland). From XRD data, the crystallite size of particles was calculated with the aid of Scherrer equation:

$$t = 0.9\lambda / \beta \cos\theta \quad (1)$$

where β is the integral breadth that depends on the width of the particular plane, λ = 1.5406 Å, the wavelength of the CuKα source and θ is the Bragg's angle of the reflection [25].

Also, the amounts of MgCO₃ phase was determined using semi-quantitative XRD by comparing the peak of MgCO₃ (104) and Mg₄(OH)₂ (CO₃)₃ · 3H₂O (-601) from XRD patterns [26].

$$\text{MgCO}_3 = (I_{\text{MgCO}_3}) / (I_{\text{Mg}(\text{CO}_3)} + I_{\text{Mg}_4(\text{OH})_2 (\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}}) \quad (2)$$

Results and Discussion

XRD spectrum of the white powder produced after the wet chemical precipitation process is presented in Fig. 1. Consequently, white deposits formed after addition of NaOH to Mg(NO₃)₂ solution are Mg(OH)₂. The depicted spectrum can be indexed as hexagonal Brucite phase of Mg(OH)₂, which would correspond to JCPDS card No of 084-2164 (a = 3.15 Å, c = 4.74 Å). Using Scherrer equation, the estimated crystallite size of the synthesized Mg(OH)₂ from the line broadening of (101) diffraction peak, which is the most preferentially oriented crystal plane, is approximately 12 nm.

Synthesized Mg(OH)₂ powders were heated at fixed temperature (200 °C) and pressure (12 kg/cm²) in an autoclave in order to conduct the hydrothermal process. Fig. 2 represents XRD spectrum of the powders after

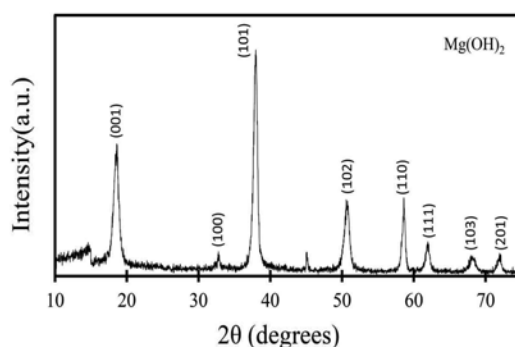


Fig. 1. XRD pattern of Mg(OH)₂ prepared by the chemically precipitation method.

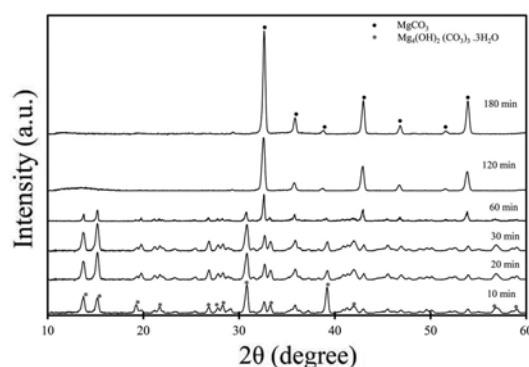


Fig. 2. XRD patterns of hydrothermal processing products in different reaction times: 10 min, 20 min, 30 min, 60 min, 120 min and 180 min.

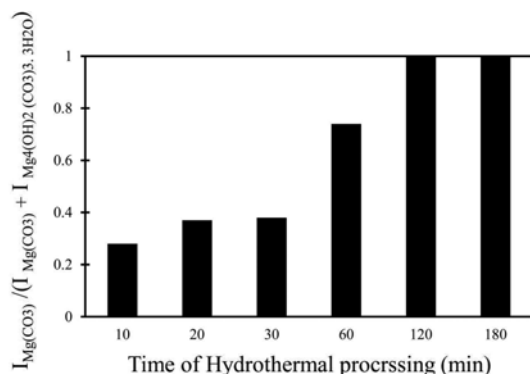
hydrothermal processing for 10, 20, 30, 60, 120 and 180 min.

For 10, 20 and 30 minutes of hydrothermal processing, Hydromagnesite (Mg₄(OH)₂ (CO₃)₃ · 3H₂O) is the dominant phase (according to JCPDS 008-0179), but as thermal processing temperature increases, Hydromagnesite gradually dissipates and is replaced (specifically after 60 min) with rhombohedral MgCO₃. MgCO₃ peaks are evident in 2θ = 32 °, 36 °, 38 °, 42 °, 46 °, 52 °, 55 ° related to (104), (006), (110), (113), (202), (024) and (116) crystalloplanes respectively, which would correspond to JCPDS card No of 084-2164 (a = 4.64 Å, c = 5.02 Å). These peaks are intensified as hydrothermal processing temperature increases (Fig. 2). This suggests that among increasing processing temperature, MgCO₃ crystallinity is increased. As it is evident from Fig. 2, hydrothermal processing for 120 min leads to complete replacement of Hydromagnesite with MgCO₃.

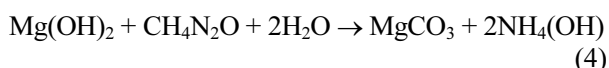
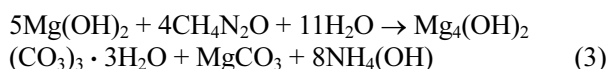
Dependency of crystallite size of Hydromagnesite and MgCO₃ on hydrothermal processing time and relative quantity of MgCO₃, estimated by semi-quantitative XRD, is given in table 1. Given the third column of table 1, relative quantity of MgCO₃ is less than 0.5 until 60 minutes but after that persistently increases to 1 until 120 minutes. Also, relative amount of MgCO₃ to Hydromagnesite versus time was used as the degree of reaction (Fig. 3).

Table 1. Crystallite size of Hydromagnesite and $\text{Mg}(\text{CO}_3)$ on hydrothermal processing time.

Time	$\text{Mg}(\text{CO}_3)$	$\text{Mg}_4(\text{OH})_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$
10 min	31.05	23.70
20 min	27.30	20.80
30 min	26.60	22.90
60 min	25.80	21.80
120 min	21.90	—
180 min	26.40	—

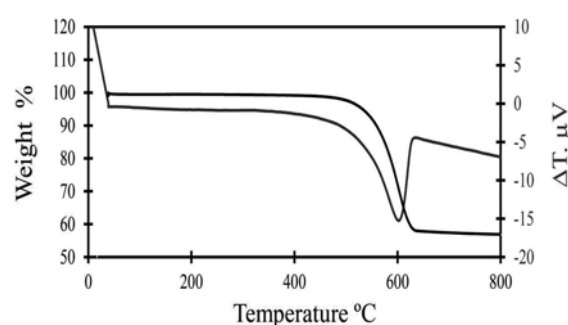
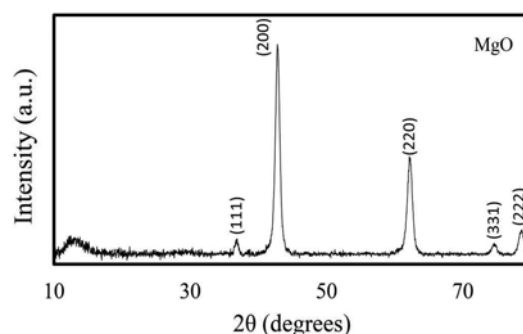
**Fig. 3.** Relative amounts of MgCO_3 to Hydromagnesite deduced from the XRD patterns, indicating reaction progress.

The degree of reaction between the $\text{Mg}(\text{OH})_2$ and urea was estimated from the amounts of MgCO_3 produced (Fig. 3). The relative amount of MgCO_3 to Hydromagnesite was derived from the intensities of MgCO_3 and Hydromagnesite peaks. Although XRD analyses is not sufficient for determining the exact amounts of the existing phases present in a sample, but it is still useful to recognize the relative differences between the specimens with similar processing conditions. Eq (3) and (4), resulted from XRD analysis, are suggested relations for hydrothermal process respectively for less and more than 60 minutes.



As equation shows (3), $\text{Mg}(\text{OH})_2$ and urea transform into Hydromagnesite and MgCO_3 together with evolving ammonia gas. For time period of above 60 minutes (Eq (4)), Hydromagnesite phase is unstable and transforms into MgCO_3 . Dependency of crystallite size of Hydromagnesite and $\text{Mg}(\text{CO}_3)$ on hydrothermal processing time is given in table 1.

In order to determine appropriate calcination temperature, STA on a fixed scan rate ($10^\circ\text{C}/\text{min}$) was utilized. Results of the STA which comprises of simultaneous DTA and TG, are depicted in Fig. 4. As it can be observed from DTA data an endothermic peak

**Fig. 4.** Simultaneous thermal analysis (simultaneous DTA and TG) curve, for a 120 minute hydrothermally processed MgCO_3 powder sample.**Fig. 5.** XRD pattern of MgO obtained from the calcination process of MgCO_3 at 700°C .

is evident in $500\text{--}660^\circ\text{C}$ range, accompanied by a substantial weight loss ($\sim 43\%$) in TG curve. During $500\text{--}660^\circ\text{C}$ temperature interval, CO_2 escapes and emits out of the sample and results in the above mentioned weight loss:



$$\Delta G^\circ = 117600 - 170T \quad (25\text{--}727^\circ\text{C}) \quad (6)$$

Equation (6) corresponds to the free Gibbs energy of reaction (5) as a function of temperature in $25\text{--}727^\circ\text{C}$ range. Although STA curves suggests 630°C as the appropriate temperature for calcination, by solving equation (6) for $\Delta G^\circ = 0$, calcination temperature would be 691°C [27]. The underlying reason for this discrepancy might be attributed to size of particles and thermodynamic conditions [28].

According to simultaneous DTA and TG results (STA), proper calcination temperature was determined at $\sim 700^\circ\text{C}$. After calcination at 700°C , acquired powder was characterized with XRD. The results are presented in Fig. 5. According to JCPDS 071-1176, all peaks are characteristics of cubic MgO Pericclass ($a = 4.22 \text{ \AA}$). There is not any other conspicuous phase in the XRD pattern which implies high purity of the acquired MgO particles. Crystallite size of the synthesized MgO particles from the line broadening of (200) diffraction peak, which is the most preferentially

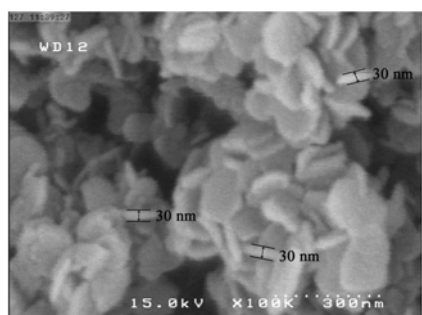


Fig. 6. FESEM image of chemically precipitated $\text{Mg}(\text{OH})_2$ nano-plates.

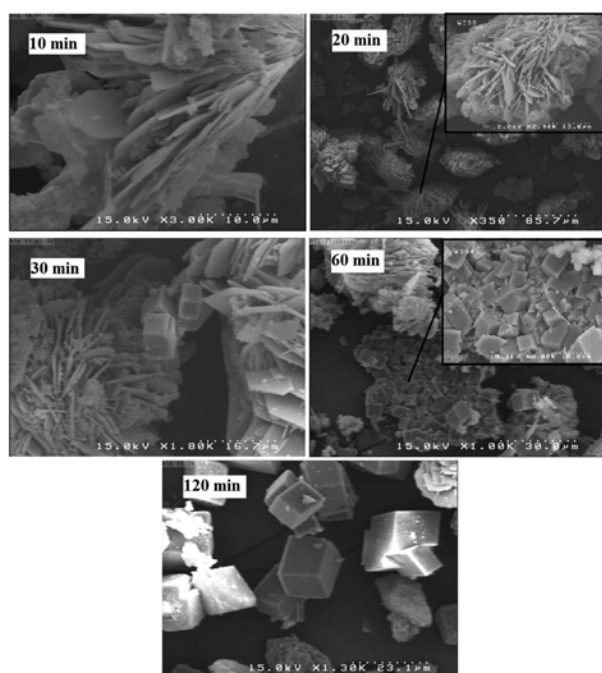


Fig. 7. FESEM micrographs of hydrothermally processed products at 200 °C for 10 min, 20 min, 30 min, 60 min, and 120 min respectively.

oriented crystal plane, is approximately 12 nm.

FESEM image of $\text{Mg}(\text{OH})_2$ particles is shown in Fig. 6, which reveals uniform lamellar hexagonal structure with about 30 nm in thickness.

As previously mentioned, in order to shed more light on the effect of hydrothermal processing time on phase formation and morphology of the acquired powder, hydrothermal process was conducted in 10, 20, 30, 60, 120 and 180 min. Fig. 7, represents FESEM graphs of 10, 20, 30, 60 and 120 min hydrothermally processed $\text{Mg}(\text{OH})_2$. Clearly there is not any sign of MgCO_3 after 20 minutes of hydrothermal processing and the only dominant structural constituent is Hydromagnesit close packed plates (Fig. 7 (10 min, 20 min)). In the inset of Fig. 7 (20 min), close packed structure of Hydromagnesit plates is shown with greater magnification. Among increasing hydrothermal processing time (specifically after 30 minutes), nascent MgCO_3 cubic micro-plates start to emerge in the structure (Fig. 7 (30 min)). After

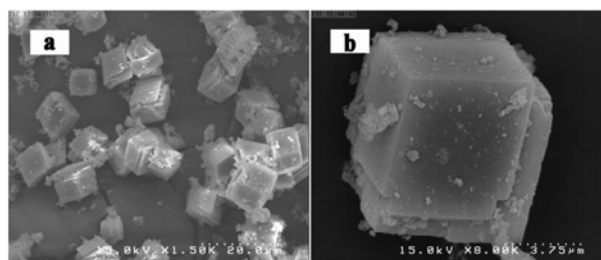


Fig. 8. FESEM images of calcinations processed MgO cubic micro-particles (a) low-magnification image and (b) high-magnification image.

60 minutes of hydrothermal processing, MgCO_3 cubic micro-plates presence becomes more dominant and Hydromagnesit close packed plates fade away in the structure (Fig. 7 (60 min)). As it is evident in the inset of Fig. 7 (120 min), MgCO_3 cubic micro-plates are relatively close packed, this is because of the fact that they are newborn and need more energy to detach each other, therefore, by increasing hydrothermal processing temperature, after 120 minutes, structure is solely composed of independent, detached 5-10 μm MgCO_3 cubic micro-plates (Fig. 7 (120 min)). FESEM images (Fig. 7) are in complete accordance with the results of X-ray diffractometry (Fig. 2). During hydrothermal processing of $\text{Mg}(\text{OH})_2$ nano-plates, these plates initially (before 60 minutes) react with urea and produce Hydromagnesit close packed structure, but as time passes Hydromagnesit loses its structural water and is converted to more stable cubic MgCO_3 micro-particles.

In Fig. 8a, b FESEM images of MgO cubic micro-particles which are produced after calcination processing at 700 °C are depicted. It can be observed that MgO particles are cubic with 5-10 μm dimensions. Same morphology and dimension of MgO and MgCO_3 particles infers that MgO is flourished in a MgCO_3 template during calcination, in other words heating has not devastated MgCO_3 cubic micro-particles, rather, MgO simply has grown in a single cubic MgCO_3 micro-particle and replaced it [13].

Conclusions

A morphologic study on MgO particles synthesized from $\text{Mg}(\text{NO}_3)_2$ precursor is presented in this paper. First, $\text{Mg}(\text{OH})_2$ nano-plates were chemically precipitated from 0.2 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and characterized with X-ray diffractometry and FESEM and secondly, in order to evaluate phase formation, synthesized $\text{Mg}(\text{OH})_2$ was hydrothermally processed at various processing times. It was concluded that before 30 minutes of hydrothermal processing, dominant phase is close packed Hydromagnesite, but after this time, it is gradually replaced by cubic MgCO_3 micro-particles, optimum hydrothermal processing time was determined as 120 minutes. Calcination of hydrothermal processed MgCO_3 at 700 °C produced homogeneous MgO micro-cubes.

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