

Preparation of Active Porous Mg(OH)₂ Via Sintering-hydration Route

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Abstract

Active Mg(OH)₂ plates with a specific surface area (BET) of 250.7m²•g⁻¹ were produced via a facile sintering-hydration route, using Mg(OH)₂ micro-agglomerates with a BET of 13.2 m²•g⁻¹ as the raw material. The raw material were consisted of the un-regular plates with a diameter of 0.5-3.0μm. The sintering of the raw material at 500°C for 4.0 h led to the formation of the MgO porous plates with a diameter of 0.5~2.5μm and a BET of 95.3 m²•g⁻¹. The hydration of the porous MgO at 80 °C in water and 1.0 mol•L⁻¹ NaOH aqueous solution produced the active Mg(OH)₂ plates with a BET of 85.0 m²•g⁻¹ and 250.7 m²•g⁻¹, respectively. The quick hydration in NaOH solution was considered as one of the major reasons for the formation of Mg(OH)₂ plates with high BET.

Keywords

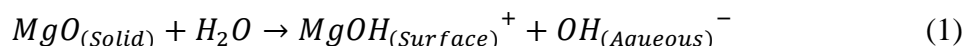
Mg(OH)₂; Sintering and Hydration; BET; NaOH.

1. Introduction

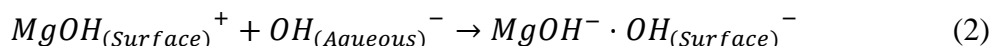
Magnesium hydroxide as an ecological and environment-friendly material, has attracted much interest because of its excellent performance applications[1-4]. Among them , porous Mg(OH)₂ has a high specific surface area and high adsorption capacity in comparison to general Mg(OH)₂. It's a promising functional materials for many applications such as wastewater treatment, the removal of harmful elements, adsorption and the catalysis field, etc[5-11]. Extensive works have been carried out on the preparation of nano-sized hexagonal Mg(OH)₂ with low specific surface area, but the porous Mg(OH)₂ with high specific surface area is less reported.

Jose Antonio Mejias[12] and L.F. Amaral[13] have reported many on the mechanism of MgO hydration. The mechanism based on the dissolution and precipitation of MgO particles is well accepted in the literature, although different kinetic models and intermediate steps for the reaction have been proposed. A short compilation of the proposed stages in this mechanism is presented below.

(1) MgO-alkaline oxide plays an electron donator role in water:



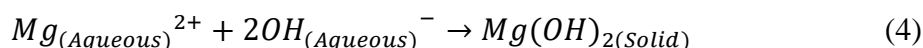
(2) OH⁻ anions are adsorbed in the positively charged surface:



(3) OH⁻ anions are desorbed from the surface, releasing magnesium ions into the solution:



(4) Ions concentration reaches the solution supersaturation, at which point the hydroxide starts to precipitate on the oxide surface:



In this paper, a facile sintering-hydration method was developed to synthesis the active porous $\text{Mg}(\text{OH})_2$ with a high BET (more than $200 \text{ m}^2 \cdot \text{g}^{-1}$) from micro-agglomerate $\text{Mg}(\text{OH})_2$ with a low BET ($13.2 \text{ m}^2 \cdot \text{g}^{-1}$). The micro-agglomerate $\text{Mg}(\text{OH})_2$ was sintered into porous active MgO particles and the sintering product was hydrated to produce porous $\text{Mg}(\text{OH})_2$ with a high BET. The influence of NaOH on the conversion of MgO to $\text{Mg}(\text{OH})_2$ nanoplates was investigated experimentally, and the detailed mechanism was revealed by the thermodynamic calculation method.

2. Experimental

2.1 Synthesis

The raw material of $\text{Mg}(\text{OH})_2$ was obtained from a domestic chemical industrial company. In a typical procedure, the raw material was sintered at 500°C for 4 h led to the formation of MgO , and the 3 g MgO of the sintering product was slowly added into 40 mL NaOH aqueous solution ($1.0 \text{ mol} \cdot \text{L}^{-1}$) and water at 80°C under stirring ($800 \text{ r} \cdot \text{min}^{-1}$), and kept thermostatic at 80°C for 1 h. Then, the hydration product was filtrated, washed with deionized water for three times, and finally dried at 105°C for 6 h.

2.2 Analysis

The composition and crystallographic structure of the $\text{Mg}(\text{OH})_2$ was identified by an X-ray powder diffractometer (XRD, Bruker-AXS D8 Advance, Germany). The morphology of the samples was observed using a field emission scanning electron microscopy (FESEM, JSM 7401F, JEOL, Japan) and a high resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL, Japan). The BET surface area of the samples was measured with nitrogen monosorb adsorption equipment (Autosorb-IQ, Quantachrome, America). The thermal behavior of the $\text{Mg}(\text{OH})_2$ powders was studied through thermogravimetric analysis (TGA) with a TGA/DSC⁻¹ thermoanalyzer (STARE, METTLER-TOLEDO, America). The agglomerate particle size of the samples was determined with a laser particle size analyzer (Mastersizer 3000, Malvern, UK).

3. Result and discussion

3.1 Formation of active $\text{Mg}(\text{OH})_2$ via sintering-hydration route

Figure 1 shows the morphology of the raw material $\text{Mg}(\text{OH})_2$ (a), sintering MgO (b) and product $\text{Mg}(\text{OH})_2$ (c). The $\text{Mg}(\text{OH})_2$ raw material was composed of the un-regular plates with a diameter of $0.5\text{--}3.0 \mu\text{m}$. After the sintering treatment at 500°C for 4.0 h, the $\text{Mg}(\text{OH})_2$ raw material was converted to the MgO porous plates with a diameter of $0.5\text{--}2.5 \mu\text{m}$. The hydration of the porous MgO at 80°C in water and $1.0 \text{ mol} \cdot \text{L}^{-1}$ NaOH aqueous solution produced the active $\text{Mg}(\text{OH})_2$ plates, respectively.

Figure 2 shows the XRD patterns of the hydration product in water (a), the hydration product in NaOH (b). The XRD peaks in curve a is weaker than curve b, revealing that the sintering-hydration treatment in NaOH promotes $\text{Mg}(\text{OH})_2$ to form a better crystal structure.

Figure 3 shows the BET mesurment of the raw material, the sintering MgO , the hydration product in water and the hydration product in NaOH . The BET were $13.5 \text{ m}^2 \cdot \text{g}^{-1}$, $95.3 \text{ m}^2 \cdot \text{g}^{-1}$, $85.0 \text{ m}^2 \cdot \text{g}^{-1}$ for the hydration product in water, $250.7 \text{ m}^2 \cdot \text{g}^{-1}$ for the hydration product in NaOH , revealing the higher BET the produc $\text{Mg}(\text{OH})_2$ after sintering and hydration treatment in NaOH aqueous solution.

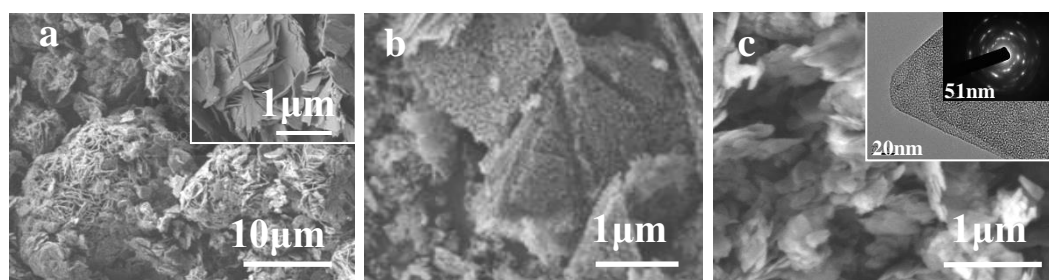


Figure 1. Morphology: (a) raw material $\text{Mg}(\text{OH})_2$; (b) sintering MgO ; (c) product $\text{Mg}(\text{OH})_2$

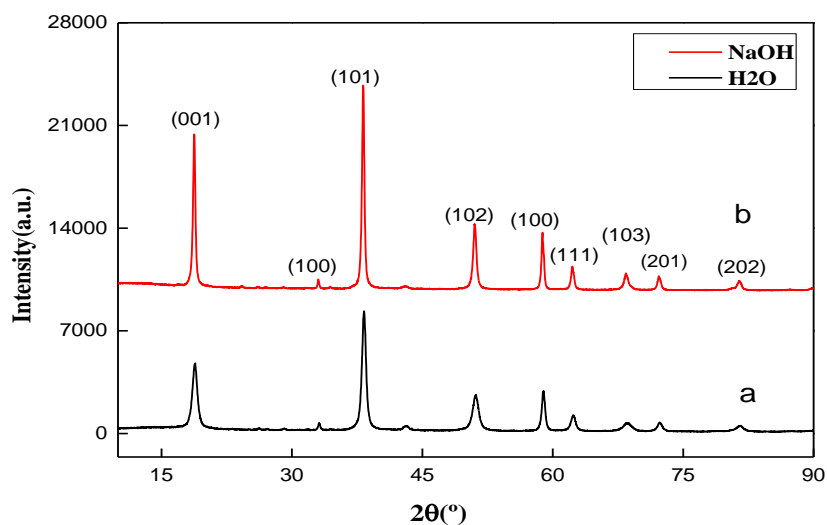


Figure 2. The X-ray patterns of the hydration Mg(OH)₂ in pure water (a); the hydration Mg(OH)₂ in NaOH solution(b)

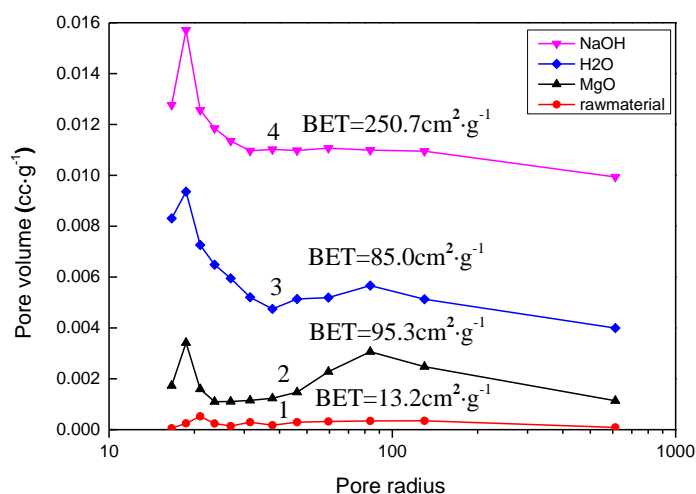


Figure 3. BET of raw material(1), MgO(2), Mg(OH)₂ formed in water(3) and 1.0 mol.L⁻¹ NaOH(4)

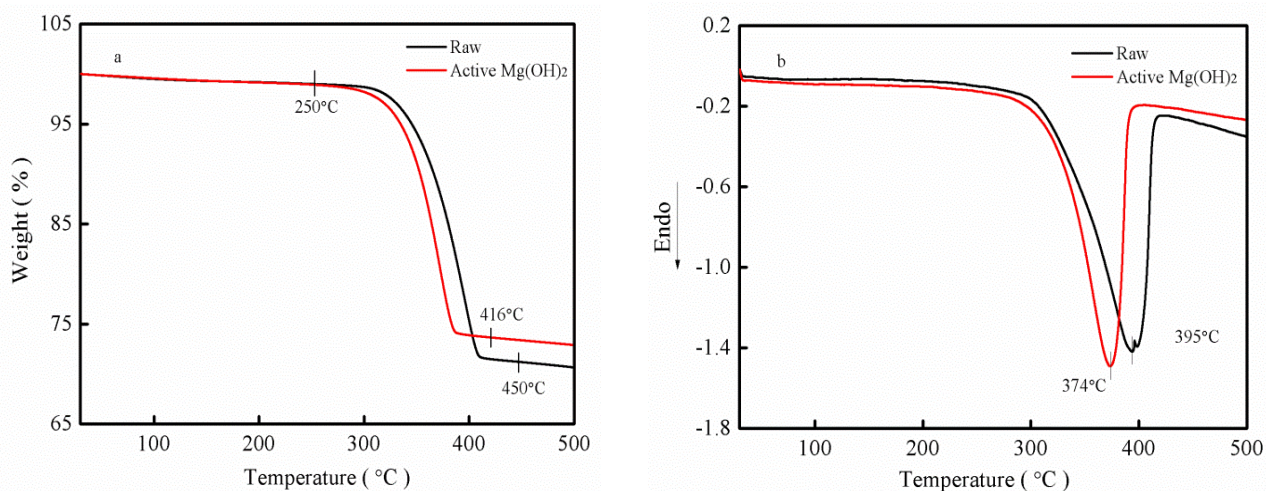
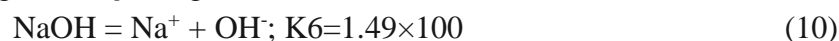
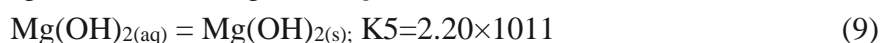
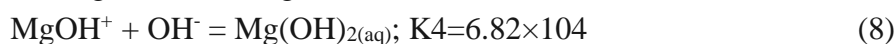
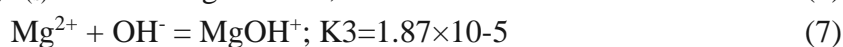
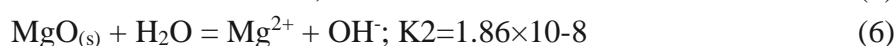
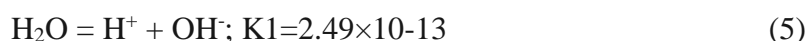


Figure 4. TG(a) and DTG(b) curve of Mg(OH)₂

Figure 4 shows the TG and DTG information, compared to the $\text{Mg}(\text{OH})_2$ raw material, the thermal decomposition temperature of the hydration product $\text{Mg}(\text{OH})_2$ decreases from $250^\circ\text{C}\sim 450^\circ\text{C}$ to $250^\circ\text{C}\sim 416^\circ\text{C}$, and the fastest decomposition temperature decreases from 395°C to 374°C . Thus indicates that the thermal stability of hydrated product $\text{Mg}(\text{OH})_2$ is decreased. The above work show that the sintering-hydration treatment favors the formation of the $\text{Mg}(\text{OH})_2$ plates with high BET.

3.2 Formation of active $\text{Mg}(\text{OH})_2$ via sintering-hydration route

The hydration rate of MgO and the morphology of hydrated product were different from water and NaOH solution, it was considered that related to the components concentration of different solutions. Herein, the changes of the components in different systems of $\text{MgO-H}_2\text{O-Mg}(\text{OH})_2$ and $\text{MgO-NaOH-Mg}(\text{OH})_2$ were calculated by thermodynamic calculation to explain the influence of hydration mediums respectively. The following reactions were should be included.



All of the chemical reaction equilibrium constant were calculated by using the thermodynamic software HSC (80°C), the concentration was replaced by the activity.

According to above calculation of hydration of MgO at 80°C in water and $1.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution, the results of the equilibrium concentration of components in the Table 1. The hydration in water system using Eq 5-9, and NaOH solution using Eq 5-10.

Table 1. The equilibrium component concentration of different solutions

$\text{mol}\cdot\text{L}^{-1}$	OH^-	Mg^{2+}	MgOH^+	$\text{Mg}(\text{OH})_{2(aq)}$
H_2O	1.19×10^{-4}	1.31×10^{-5}	1.28×10^{-13}	4.55×10^{-12}
NaOH	6.27×10^{-1}	9.04×10^{-12}	1.06×10^{-16}	4.55×10^{-12}

From Table1, the concentration of OH^- in NaOH solution was much higher than water Therefore, we can speculate from the experimental results that the higher concentration of OH^- favors the formation of porous, better crystal morphology and regular plate $\text{Mg}(\text{OH})_2$, the higher concentration of Mg^{2+} and MgOH^+ did not favor the formation of porous of $\text{Mg}(\text{OH})_2$.

3.3 The formation of $\text{Mg}(\text{OH})_2$ pore-structure

The sintering MgO has a higher BET, which leads to a higher hydration reactivity, and the rapidly dissolve of MgO on its surface to form the Mg^{2+} , OH^- , the quick dissolution of the surface of MgO , which releases a large amount of Mg^{2+} , OH^- , and then the reaction of Mg^{2+} and OH^- leading to the formation of abundant $\text{Mg}(\text{OH})_2$ initial particles. However, the initial particles rapidly align simultaneously having a disorganized alignment direction, which finally forms the porous $\text{Mg}(\text{OH})_2$. Figure 5 shows the formation schematic diagram of pore-structure.

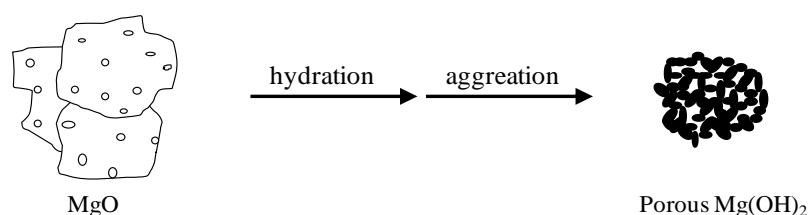


Figure 5. Formation of porous $\text{Mg}(\text{OH})_2$

4. Conclusion

The influence of NaOH on the hydration of MgO to synthesis the porous Mg(OH)₂ plates from agglomerate Mg(OH)₂ was investigated in this paper. The experimental results showed that the quick hydration in NaOH solution favored the formation of porous Mg(OH)₂ plates with high BET. The hydration of MgO to prepare porous Mg(OH)₂ with a high BET, because of pore-structure, the crystal lattice with disordered arrangement, and leading to the low thermal stability. Porous structure is not favored to prepare magnesium hydroxide flame retardant, however, porous Mg(OH)₂ has a high specific surface area and high adsorption capacity, it has a promising application in wastewater treatment, the removal of harmful elements, adsorption, and catalysis field.

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