Powder Technology 320 (2017) 80–88

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Fabrication of tubular magnesium oxide nanocrystals via combining ammonium sulfate leaching and precipitation method and it's crystal growth behavior

Chunhui Huang, Jun Zong *, Jiaxin Xu, Fenge Yan

Department of Chemistry, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, PR China

ARTICLE INFO

Article history:
Received 28 November 2016
Received in revised form 9 July 2017
Accepted 12 July 2017
Available online 14 July 2017

Keywords:
Calcined dolomite
Ammonium sulfate leaching
MgO nanocrystal
Activation energy

ABSTRACT

Tubular magnesium oxide (MgO) nanocrystals were fabricated via combining ammonium sulfate leaching and precipitation method with calcined dolomite ($CaCO_3 \cdot MgO$) as magnesium source. The relationship between $(NH_4)_2SO_4$/MgO molar ratio, volume of distilled ammonia and dosage of calcined dolomite and the leaching rate of magnesium were investigated, and the highest value of 96.81% for leaching rate was obtained by optimizing leaching conditions. The tubular MgO nanocrystals were synthesized by precipitation and calcination process, which were characterized by XRD, FT-IR, SEM and TEM. After calcination process, the crystallite size of MgO nanocrystals varies from 12.4 nm to 42.2 nm with the calcination temperature increases from 500 °C to 1000 °C. The activation energy for crystal growth of MgO nanocrystals is about 10.69 ± 1.13 kJ/mol before 650 °C, while it increases to about 27.02 ± 0.95 kJ/mol after 650 °C.

1. Introduction

Due to excellent optical, thermodynamic, mechanical, electronic and special chemical properties, MgO nanopowders have been widely used as refractory materials [1], antibacterial materials [1–4], catalysts [5–7], toxic waste adsorbents [8], superconductor materials, paints, polymer reinforcement agents, and agricultural products. In recent years, several methods have been explored to fabricate MgO nanocrystallite, including chemical precipitation [3,6,7,9–12], sol-gel process [1,4,13–16], hydrothermal method [2,8,17], chemical vapor deposition [18,19], self-propagating combustion reaction method [20], and laser ablation method [21]. Among these methods, chemical precipitation is a simple, low-cost and high-yield method to produce MgO nanopowders with high purity. Therefore, direct precipitation method is chosen to synthesize MgO nanopowders in the research.

Dolomite is a kind of natural mineral with main composition of $CaMg(CO_3)_2$, which becomes the raw materials of magnesium and calcium resources. However, the important problem is how to separate calcium and magnesium effectively. Usually, the magnesium was obtained from dolomite via acid leaching method [22–25] or calcination at different temperatures [25,26]. As reported in the references [27–33], the chemical compositions of final products were different by calcining dolomite at different conditions, which was strongly dependent on calcination temperature. As shown in the previous studies, after calcination at high temperature, a powder mixture consisting of MgO and CaO was obtained, while the powder mixture with MgO and $CaCO_3$ could be obtained by low-temperature calcination process [27–33]. From some references, the magnesium was leached from solid materials containing magnesium compounds, and the influences of experiment factors on the leaching rate of magnesium were investigated, including lixiviant concentration, lixiviant type, solid to liquid ratio, reaction temperature, particle size and stirring speed, etc. [34–42]. Relatively, few researches are focused on magnesium leaching from dolomite with ammonium sulfate solution as the lixiviant. As shown in previous researches [25,26], MgO powders were prepared by calcining the dolomite at high temperature, while less investigation regarding the production of MgO from dolomite by calcination at low temperature was reported. Therefore, in this work, the calcined dolomite at low temperature was chosen as the raw material, and ammonium sulfate solution was employed as the lixiviant to obtain magnesium sulfate solution and ammonia solution, which were further used to prepare MgO nanocrystals.

In this study, magnesium sulfate solution and ammonia solution were produced from the calcined dolomite at low temperature by using ammonium sulfate leaching method, and the relationship between $(NH_4)_2SO_4$/MgO molar ratio (MgO is one of composition of calcined dolomite), volume of distilled ammonia and dosage of calcined dolomite and the leaching rate of magnesium were investigated. Subsequently, MgO powders were prepared with magnesium sulfate solution and ammonia solution obtained from the leaching process as the reactants via direct precipitation and calcination process. Based on

* Corresponding author.
E-mail address: jzong@chem.ecnu.edu.cn (J. Zong).

http://dx.doi.org/10.1016/j.powtec.2017.07.035
0032-5910/

phase structure and microstructure analysis, the crystal growth behavior of MgO nanocrystals was also analyzed.

2. Experimental

The MgO powders were fabricated from the calcined dolomite via combining ammonium sulfate leaching and precipitation method, including magnesium leaching process and preparation of MgO powders, as shown in Fig. 1:

2.1. Magnesium leaching process

Dolomite was crushed and calcined in a muffle furnace at different temperatures for 1 h, and then the calcined dolomite powders were obtained after cooling and grinding. A certain content of calcined dolomite powders were mixed with 200 mL of deionized water in a beaker, following by stirring in a water bath at 50 °C for 30 min, and then a slurry was obtained. Subsequently, a certain amount of ammonium sulfate was dissolved in 300 mL of deionized water, and it was injected in the slurry. After that, the mixture was transferred to a 1000 mL tri-mouth flask, and then it was stirred at 180 °C to obtain magnesium sulfate solution and ammonia solution. The magnesium leaching process was investigated by several parameters, and their values are given in Table 1. In this part, the distilling apparatus was used to accelerate the leaching reaction and ammonia distillation. Fe^{3+}, Fe^{2+} and Al^{3+} ions as impurities in magnesium sulfate solution were removed by adding 10 mL of 30% hydrogen peroxide as oxidant and regulating the solution pH to 7 with ammonia solution. Purified magnesium sulfate solution was obtained after filtration, and the contents of Mg^{2+} and Ca^{2+} ions in the solution were determined by EDTA complex titration method. The leaching rate of magnesium was calculated by Formula (1) [43]:

Table 1
The parameters and values in the magnesium leaching experiments.

Parameters	Values
$(NH_4)_2SO_4$/MgO molar ratio	1.0:1; 1.1:1; 1.2:1; 1.3:1; 1.4:1; 1.5:1; 1.6:1;1.7:1; 1.8:1*; 1.9:1; 2.0:1
Volume of distilled ammonia (mL)	100; 150; 200; 250; 300; 350*; 400
Dosage of calcined dolomite (g)	20*; 40; 60; 80; 100

* The constant values used when other parameters were investigated.

$$\alpha(Mg) = w(Mg)/w_0(Mg) \times 100\% \quad (1)$$

where $\alpha(Mg)$ is the leaching rate of magnesium, $w_0(Mg)$ and $w(Mg)$ are the content of Mg in calcined dolomite ($w_0(Mg) = 16.28\%$) and that leached from the calcined dolomite, respectively.

2.2. Preparation of MgO powders

The ammonia solution collected during distillation was added dropwise to the purified magnesium sulfate solution, and it was stirred in water-bath at 50 °C for 30 min, then the reaction was continued for 1 h and the white precipitates were obtained finally after they were aged at room temperature for 30 min. Subsequently, the precipitates were filtered, and washed with the deionized water and absolute

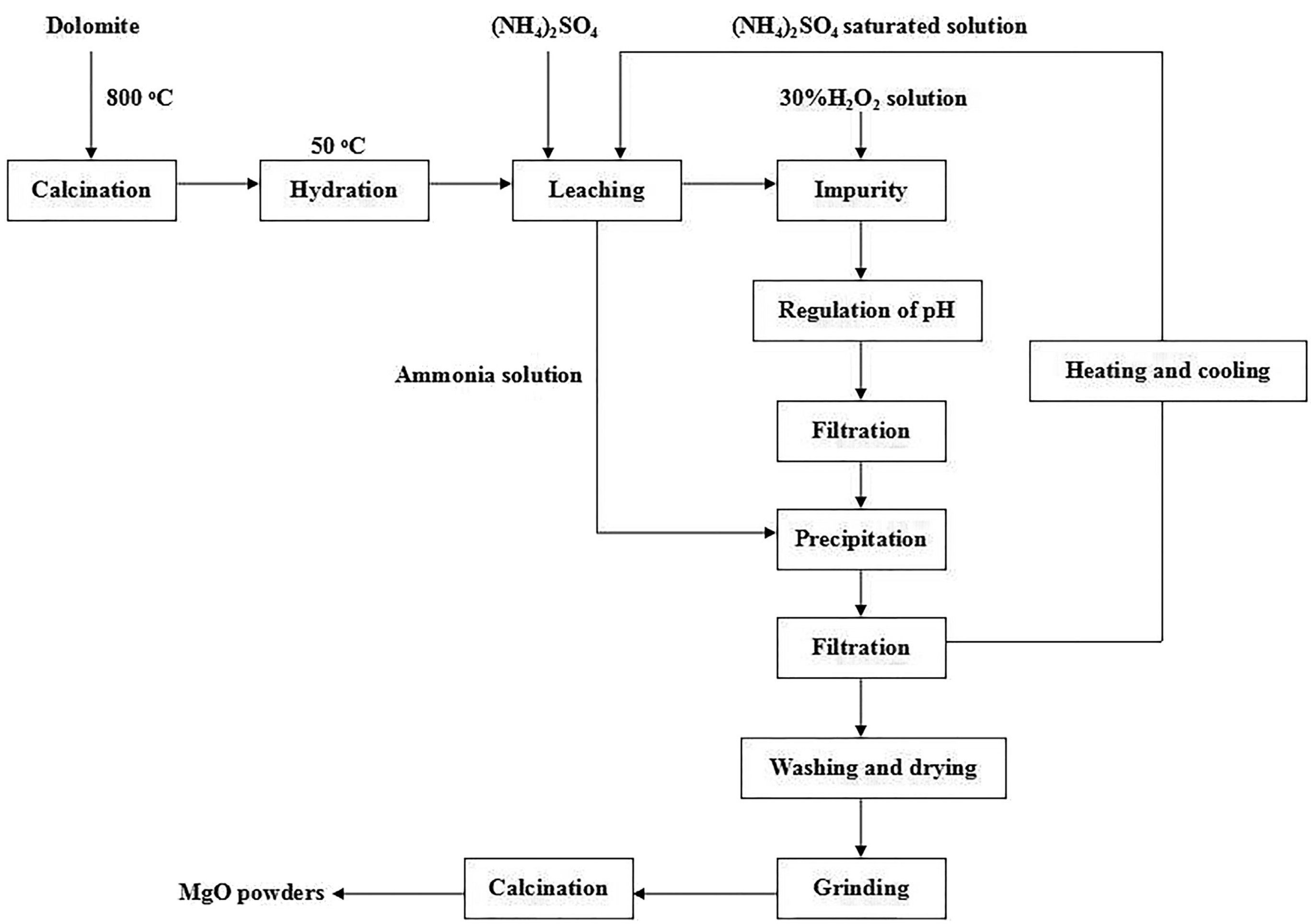

Fig. 1. Process flow diagram of preparing MgO powders from calcined dolomite.