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Preparation of mesoporous spherical magnesium hydroxide particles via the static self-assembled method

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ABSTRACT

As the original first time, the novel mesoporous spherical magnesium hydroxide (MH) particles were synthesized via static self-assembled method using magnesium sulfate, ammonia solution, ethanol and sodium hydroxide as raw materials. To control the structure of the mesoporous spherical material, the effects of reaction time, $MgSO_4$ concentration, reaction temperature, contacting area and volume ratio were comprehensively investigated. Structural characterizations of these products were analyzed by SEM, XRD, TEM, EDX, SAED, FT-IR, TG-DTG and BET. The optimal parameters of mesoporous spherical MH preparation were obtained as follows: the reaction time was 25 h, the $MgSO_4$ concentration was 1 −2 mol/L, the reaction temperature was 25−45 °C, the gas-liquid two-phase contacting area was 100 −150 m^2/m^3. The structural characterizations analysis indicated that the mesoporous spherical materials prepared under optimal conditions were polycrystalline particles with many properties, such as high specific surface area, slit porous channels and uniform particle size distribution.

1. Introduction

MH as an important inorganic chemical product and intermediate, has been widely used in many industries and fields for many years. MH has many advantage characteristics of non-toxic, non-polluting, smoke-free, flame retardant and others [1–3]. MH is used as the environmentally friendly material has been attracted much attention in recent years. It is usually as flame retardant additives, ceramic materials, wastewater purification materials, medicine and flue gas treatment materials [4–7]. MH granules could also be used as a precursor for the synthesis of magnesium oxide (MgO) particles [8], which as a significant material for use in catalysis, toxic waste remediation, or as additives in refractory, paint, superconductor products, batteries and supercapacitors [9–11]. As we know, the shapes, dispersibility, and size of nanoparticles play critical roles in determining their fundamental properties and application areas. Larger diameter ratio particles are good candidates for functional polymeric composites and fiber hybrid materials as reinforcing agents and flame retardants [12–14]. Wastewater purification materials and flue gas treatment materials are required that the MH particles have a more extensive specific surface area [15]. So it is of great interest to explore novel routes for fabricating individual morphological and ultrafine MH particles. During large-scale synthesis, MH nanoparticles may adopt various shapes. MH with versatile morphological structures [16–20] of needle-, lamellar-, fiber-, rod-, spherical- and flower-like nanocrystals have been obtained by different preparation methods, such as solution precipitation [21–23], hydrothermal route [24,25], sol-gel method [26], microwave or ultrasonic assisted synthesis techniques [27,28], gas-liquid contact method solvothermal techniques [29], high-gravity precipitation [30], electrodeposition [16], etc. Moreover, the morphology is controlled by different preparation conditions and process [31,32], such as amide-assisted oxidization metal, surfactant, complex dispersants, auxiliary and crystal form control agent. The preparation methods, conditions, and process have been used to prepare MH with controlled shape, size, and structure in the existing studies. Amongst these methods, the precipitation

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approaches are more usually employed in practice than others since it is easy-operated and economically acceptable. However, their main disadvantages are related to the limitations of the porous structure, specific surface area, and particle size distribution that the product prepared by the precipitation method. To improve the adsorption activity in the process of dye molecules, heavy metal ions and sulfur dioxide, there was a strong urgency requirement and great significance for synthesizing new materials with special structural characteristics and morphology of MH particles, which include high specific surface area, pore width, and uniform particle size distribution. As a result, it is still desired to develop a new method capable of generating MH in a moderate quantity with a well-controlled dimension and structural morphology.

In this work, a new route to synthesize the spherical structural MH particles with mesoporous, uniform size and the large specific surface area is developed. Both magnesium sulfate and ammonia water as raw materials, and the reactants are under the action of the crystal form control agent through self-assembled method to synthesize mesoporous spherical MH particles. The procedure is a mild condition, excellent treatment effect, ease of work-up and promising large-scale production. Mesoporous spherical structural MH, therefore, would have a wide range of applications in many fields, such as flue-gases (sulfur dioxide), heavy metal and dye wastewater treatment.

2. Experimental

2.1. Materials

We used magnesium sulfate, ammonia solution ($NH_3 \cdot H_2O$: 25%), ethanol and sodium hydroxide as raw materials in this study. All the above chemical agents used in the experiments were of A.R. grade without further purification.

2.2. Synthesis

Mesoporous spherical MH particles were prepared by two steps. The first step was to prepare crystal seeds. 200 ml of a certain concentration of magnesium sulfate solution was added into 500 ml beaker. And then 3–5 drops of 0.01 mol/L sodium hydroxide solution were added to the beaker under vigorous stirring. The second step was to prepare mesoporous spherical. The crystal seeds solution prepared, and 200 ml of concentrated ammonia water were placed in a sealed container without touching each other. Using the characteristics of volatile and readily soluble in water for ammonia, it provided a constant concentration of ammonia gas bath in a closed container. Nanocrystalline MH particles self-assembled into mesoporous spherical. Ammonia bath aging self-assembled reaction was completed with the setting time. The solutions in this group were filtered and washed until no sulfate ions presented in the filtrate. Moreover, MH particles were washed with anhydrous ethanol for four times. The products were dried for 24 h at 120 °C.

2.3. Characterization

The structural characterization of the as-synthesized material was investigated. The structures of the as-products were detected by Bruker D8 Advance X-ray diffractometer (XRD) using Cu Kα radiation ($\lambda = 0.15406$ nm). FT-IR spectrum (KBr disc) was recorded on a Bruker Vector 22 spectrometer. The dimension and morphology of MH sample were investigated by scanning electron microscopy (SEM) from a JEOL JSM-6700F electron microscope. The selected area electron diffraction (SAED), TEM images, and EDX analyses were taken with a JEOL JEM-2100 electron microscope. Sample particle diameter and size distribution were measured by a laser particle size analyzer. Thermo-gravimetric analyzer (TG-DTG) was used to identify the thermal behavior of the hydrothermal product. The sample was heated under the air from ambient to 1200 °C at a heating rate of 10 °C/min. The gas adsorption-desorption isotherms, pore size and specific surface area of the samples were measured by Beckman Coulter gas adsorption analyzer at −195.64 °C.

3. Results and discussion

3.1. Optimization of preparation conditions and process

3.1.1. Effect of reaction time for spherical growth

The effect of reaction time on the spherical growth of MH particles was examined with FESEM measurement when the $MgSO_4$ concentration was fixed at 1 mol/L, and the reaction temperature was fixed at 25 °C. Fig. 1 showed the product morphology structure prepared using different reaction times (5–35 h). A small number of spherical particles formed for the reaction time of 5 h (Fig. 1(a)). The amount of nano-particles clusters and some lamellar-MH products emerged in 5 h. Moreover, the diameter of spherical particles varied considerably. The number of nano-particles decreased, and the number of spherical particles increased with the increase of reaction time (Fig. 1(b)–d). After 25 h, less MH micro-agglomerates occurred in the spherical particles system than the agglomerated MH system, indicating that increasing the reaction time converted the active MH nano-particles to stable agglomerates MH, and favored the quick formation of spherical MH particles. Moreover, the spherical particle size distribution was becoming more uniform. Thus, the optimized reaction time is 25 h for the synthesis of the spherical MH particles.

3.1.2. Effect of $MgSO_4$ concentration on spherical growth

The effect of the concentration of the reactants on the morphology structure and particle size distribution of prepared MH samples for spherical growth was examined with FESEM measurement when the reaction time was fixed at 25 h, and the reaction temperature was fixed at 25 °C. The concentration of $MgSO_4$ with 0.05–2 mol/L had an obvious influence on the growth of MH pellets in Fig. 2(a–f). The morphologies structure of the particles changed from lamellar to spherical with the concentration of the $MgSO_4$ reactants increasing. Fig. 2 (a) showed that the microscopic topography structure was lamellar and globular-like particles. It clearly showed that MH crystallites piled up randomly. Lamellar particles were round or hexagonal with the diameter of 1–10 μm. The similar spherical particle was stacked together by nano-lamellar of MH. Compared with Fig. 2 (a), the number of spherical particles was increased with the decrease of lamellar particles in Fig. 2 (b). With the increasing of $MgSO_4$ concentration up to 0.5 mol/L, the morphology structure of the spherical particles became inconsistent in Fig. 2 (c). Further, with the concentration continues to increase from 1 to 2 mol/L, the morphologies of samples was more uniform in Fig. 2(d–f). Thus, the optimized $MgSO_4$ concentration of synthetic MH particles is 1–2 mol/L.

3.1.3. Effect of reaction temperature on spherical growth

Figs. S1(a–e) showed microscope images of the spherical particles produced by a typical temperature when the reaction time was fixed at 25 h, and the $MgSO_4$ concentration was fixed at 1 mol/L. We found that the particles were spherical without the lamellar and another shape appearing. When the temperature was between 25 °C and 45 °C, no significant effect was found. The similar morphology was found in Figs. S1(a–c). Moreover, small balls and their aggregates emerged. The average diameter of the spherical