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Original Research Paper

Additive-free and time-saving microwave hydrothermal synthesis of hollow microspheres structured boehmite

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ABSTRACT

In this study, by using $Al_2(SO_4)_3$ aqueous solution and urea as raw materials, hollow microspheres structured boehmite was successfully synthesized only after 30 min reaction time at 180 °C via an additive-free and time-saving microwave hydrothermal route. The final products were characterized by techniques of X-ray diffraction (XRD), transmission electronic microscope (TEM), scanning electron microscope (SEM) and Fourier transform infrared spectrometry (FTIR). To investigate its crystal form and morphology evolution process, samples subjected to different reaction durations were prepared and characterized. The pivotal influence factors on boehmite morphology, such as reaction temperature, dosage of urea and microwave power range were discussed based on the experiment facts.

1. Introduction

Because the morphology of most inorganic micro/nanostructures has a great effect on their chemical and physical properties, there is a growing interest in the fabrication of inorganic materials with desired morphologies and properties due to their close relationship [1]. Hollow microspheres with nanometer or micrometer size often exhibit special physical and chemical properties, owing to their low density, larger specific surface area, hollow structure and nanostructured wall [2]. Therefore, many attempts have been focused on the synthesis of inorganic materials with hollow spheres architectures, such as Fe_3O_4 [1], ZrO_2 [3], TiO_2 [4,5], hydroxyapatite [6–8], calcium phosphates [9], and SnO_2 [10].

As an important target material, boehmite can be considered as partly dehydrated aluminum hydroxides. In addition, boehmite can transform into alumina after being heated between 400 and 700 °C without altering its original morphology, which is a suitable precursor for the preparation of alumina and alumina-derived ceramics [11–14]. Therefore, many efforts have been made to synthesize of boehmite with different morphologies, especially for hollow microspheres architectures, as well as their potential application in advanced catalysts, catalysts supports, coatings, membranes and water treatment [14–17].

Generally, fabrication of uniform hollow microspheres with dimenstions from nanometer to micrometer require additives (template materials [2–4] or other accessory ingredients [1,5–8,14–16])to build sphere architectures, and these additives need to be removed later. However, the introduction of additives into the syntetic routes usually suffers from disadvantages related to high cost and troublesome synthetic procedures, and the relevant removal process might compromise the structural integrity of the final products or cause environmental pollution, which may prevent them from being used in large-scale applications [16–18]. It is obvious that the additive-free procedure to obtain inorganic materials with hollow-sphere structure will be greatly simplified if only the essential reactants are used in the reaction process, with no need for additives [17,18].

On account that less reaction time usually means less energy consumption or better eco-friendly and energy efficient, it is also an unremitting pursuit to develop time-saving boehmite fabrication routes, which will greatly facilitate their future industrial applications. It is known that microwave methods are based on interactions of the bipolar momentum of molecules with a radiation frequency. Collisions and friction between the moving molecules result in heating. In a broad sense, the more polar a molecule is, the more effectively it will couple with and be influenced by the microwave field [19]. Compared with conventional hydrothermal method which usually needs to maintain the reaction temperature for 3–24 h [11–17], microwave-assisted heating is generally faster and energy efficient. Such a combination is termed as the microwave hydrothermal (M-H) method [19–24].

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As the extension and improvement of our previous work [21], in this study, we report an additive-free and time-saving microwave hydrothermal route to gain hollow microspheres structured boehmite only after 30 min at 180 °C.

2. Experimental procedure

Firstly, 10 mL of 0.1 mol L^{-1} $Al_2(SO_4)_3$ aqueous solution and 30 mL distilled water were added to a double-walled Teflon-lined digestion vessel of ~50 mL capacity. After 0.364 g urea (accounted for 200% theoretical dosage) was added, the vessel was sealed and placed on a turntable for uniform heating using a MDS-6 microwave hydrothermal system (Sineo, China) [20,21]. Temperature-controlled mode M-H treatments were conducted at 180 °C by non-pulsed heating type for 6–40 min, using 2.45 GHz microwave radiation under power range of 0–1000 W (full power). Afterwards, the vessel was immersed in water to cool to room temperature rapidly. The samples were collected by centrifugation and washed with distilled water and absolute ethanol respectively for several times.

The phase purity and phase structure of the microwave hydrothermal synthetic products were characterized by X-ray powder diffraction (XRD) using Japan Rigaku D/max r-A X-ray diffractometer (40 kV, 40 mA) equipped with graphite monochromatized Cu Kα radiation (λ = 0.154, 18 nm). The step size of 0.02° and scan rate of 4° min^{-1} were applied, and the patterns were recorded in the 2θ range of 10–80°. Fourier transform infrared spectrometry (FTIR) measurements were performed on a Thermo Nicolet 380 Fourier-transform spectrometer using KBr pellets. Scanning electron microscope (SEM) images were performed on JEOL JSM-6610LV microscope operating at 15 kV. Transmission electron microscope (TEM) images were obtained on a Hitachi H-7650 microscope with an accelerating voltage of 80 kV.

3. Results and discussion

3.1. Phase structures

As shown in Fig. 1a, diffraction peaks corresponding to boehmite (PDF No. 21-1307) have been found for the final product which was synthesized at 180 °C with 30 min reaction time under full microwave power range of 0–1000 W. No obvious XRD peaks arising from other phases of alumina are found. In addition, the intensity of the peak corresponding to the (020) crystal plane is distinctly strong as compared to other peaks. Thus, it can be concluded that the relatively slower growth rate for the boehmite samples is (020) facets, which is in accordance with the well-known fact that the facets with a slower growth rate will be exposed more on the crystal surface and consequently exhibit relatively stronger diffraction intensity in the corresponding XRD patterns [24–26].

In order to further ascertain its chemical compositions, the Fourier transform infrared spectrometry (FTIR) spectra of the M-H product was verified. As shown in Fig. 1b, the intensive bands around 3310.6 and 3094.3 cm^{-1} can be assigned to ν_{as}(Al–O–H) and ν_s(Al –O–H) stretching vibrations. The shoulder around 1644.8 cm^{-1} was the feature of the bending mode of absorbed water. The band around 1067.5 cm^{-1} was assigned to the δ_s(Al–O–H) mode of boehmite. The three bands around 744.5, 615.5, 479.2 cm^{-1} represented the vibration mode of AlO_6. The above FT-IR analysis matches well with the XRD result, which confirms that the as-obtained products are pure-phase γ-AlOOH.

3.2. Morphology

Fig. 2a and b are the TEM images with different magnifications of the boehmite samples obtained after 30 min reaction time at 180 °C. As shown in Fig. 2a, a large amount of hollow microspheres particles with obvious contrast between the dark edge and pale center are revealed by TEM image. Enlarged TEM image shown in Fig. 2b manifests distinctly that these boehmite samples have uniform hollow microspheres morphology. SEM image shown in Fig. 2c with low magnification is recorded to state clearly the general view of the uniform hollow microspheres morphology. Fig. 2d is the enlarged SEM image of the center part of Fig. 2c, which is provided to demonstrate the superficial structure of boehmite with hollow microspheres morphology. Especially, as can be seen from the SEM images of some broken up boehmite ultra-fine particles, we could recognize that the detailed structure of hollow microspheres was composed of laminar morphology boehmite.

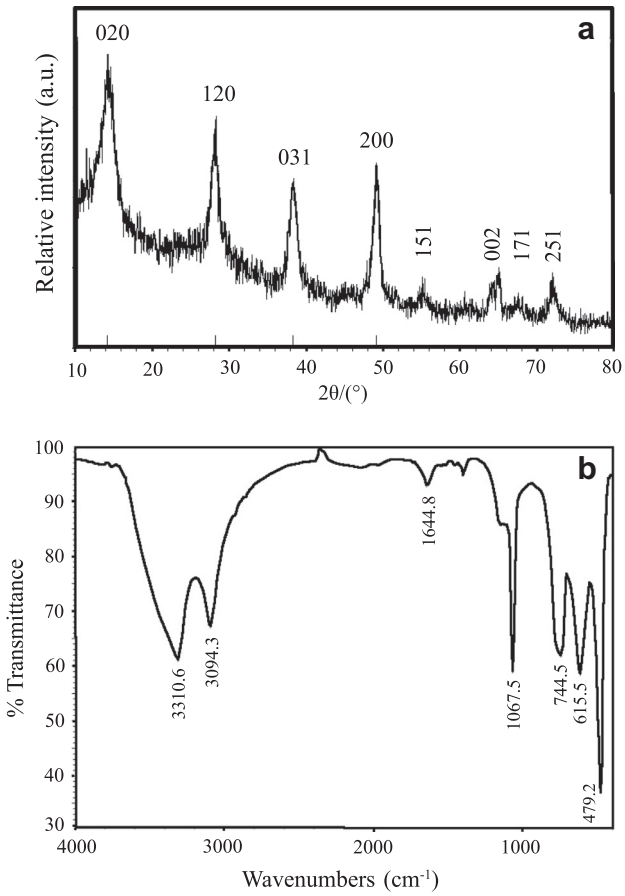

Fig. 1. XRD pattern (a) and FTIR spectra (b) of microwave hydrothermal products obtained after 30 min reaction time at 180 °C.

3.3. Influence factors on M-H reaction

Although a fixed microwave frequency of 2450 MHz (2.45 GHz) is preferred because it has the correct penetration depth required to interact with laboratory scale samples, its energy is not powerful enough to bring about any significant direct molecular activation [24]. Indeed, the advantage of the application of microwave to the synthesis of inorganic materials was the significant reduction in reaction time. Microwave appeared to be particularly effective as a means of inducing nucleation and might affect the crystallization [20]. Literature reported that the enhancement of crystallinity performed in short periods *via* microwave treatment could be attributed to fast heating of the precursor due to avoidance thermal gradients [19,23]. In this study, microwave power range of 0–1000 W (full power) was utilized to express the ultimate