Microporous and Mesoporous Materials 223 (2016) 27–34

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Fabrication synthesis of porous Al_2O_3 hollow microspheres and its superior adsorption performance for organic dye

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ARTICLE INFO

Article history:
Received 25 June 2015
Received in revised form
21 September 2015
Accepted 29 September 2015
Available online 28 October 2015

Keywords:
Alumina
Hollow microspheres
Sacrificial templates method
Adsorption

ABSTRACT

Al_2O_3 hollow microspheres with hierarchical pores have been synthesized via a novel sacrificial template process with further calcinations, in which $CaMg(CO_3)_2$ microspheres were used as sacrificial templates, and $Al(NO_3)\cdot 9H_2O$ was used as aluminum source. The route is facile and promising to use in preparation of other metal oxides. The as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), thermogravimetry analysis (TGA), and N_2 adsorption/desorption. The Al_2O_3 hollow microspheres samples showed superior adsorption performance, including rapid adsorption rate, excellent adsorption capacity and good reusability for removal of Congo Red from aqueous solution, which made them attractive in environmental remediation.

1. Introduction

Al_2O_3 as one of the most important inorganic non-metallic materials is widely used as an electrical insulator, filler, adsorbent, catalytic and catalytic support, as well as raw material of the ceramic, gemstone and laser window [1–6]. In order to improve its structural performance in the fields of adsorbent, catalysis and some new function materials, Al_2O_3 with various structures, including hierarchical architecture, ordered mesoporous structure, hollow structure and nano-structure, has been widely investigated in previous works [5,7–15]. Among them, porous hollow microspheres owned both the outer and the interior void space, which can be used to accommodate a large amount of guest molecules or large-size species, making the Al_2O_3 hollow microspheres potential for adsorption, catalysis, and biomedical applications, such as drug delivery and controlled storage/release of guest molecules [16,17]. Therefore, the design and fabrication of the Al_2O_3 hollow microspheres have attracted extensive interest.

In the past decades, several methods, including hard template, soft template and template-free method, have been used to prepare Al_2O_3 hollow microspheres successfully [4,5,13–15,18–21]. Compared with the template-free method, template process limited less by the crystal habit of the precursors and can be applied in preparation of hollow microspheres with various sizes by adjusting the dimension of templates. Moreover, the hard template method was considered more effective than soft template method, because the synthesis condition of the soft template method was very strict and hard to control. As one kind of the hard template method, sacrificial template method was more attractive for the reason that the sacrificial template did not only directly determine the shape and approximate cavity size of the obtained hollow spheres in the process, but also acted as reactant to be consumed partially or completely during the shell-forming process. In this regard, sacrificial template process had some inherent advantages, including that generally no additional surface functionalization was needed and shell formation was guaranteed by chemical reaction [16]. In recent years, several hollow structures, including several kinds of noble metal, metal oxides and metal sulfides hollow spheres, have been prepared by sacrificial template method [22–29].

Recently, several metallic oxides with hierarchical and porous structure have been prepared successfully by magnesium carbonate hard template route in our studies depending on the versatile structure of magnesium carbonate template family [30–35]. The route is simple, facile and economical. In this present work, taking advantage of the reaction of magnesium carbonate template family

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http://dx.doi.org/10.1016/j.micromeso.2015.09.055
1387-1811/

and the $Al(NO_3)_3$ solution, the Al_2O_3 hollow microspheres (AHS) with hierarchical pores were synthesized by a sacrificial template process with further calcinations, in which $CaMg(CO_3)_2$ microspheres were used as sacrificial templates, and $Al(NO_3)\cdot 9H_2O$ was used as aluminum source. The route is promising to be applied in synthesis of other metal oxides. Furthermore, Congo Red (CR), a widely used azo anionic dye and a known human carcinogen, was used as a representative demonstration to investigate the dye removal ability of as-prepared AHS samples. The as-obtained AHS samples possessed a high adsorption capacity (690 mg g^{-1}) and good reusability. The properties of AHS samples, including the simple preparation, high adsorption rate, high adsorption capacity and good reusability, make it potential for application in environmental remediation.

2. Experimental

2.1. Preparation of $CaMg(CO_3)_2$ microspheres

All reagents used during the process were AR, unless otherwise noted. The route to synthesize $CaMg(CO_3)_2$ microspheres was shown in our previous work [32]. In a typical synthesis, 50 mL $MgCl_2\cdot 6H_2O$ solution (1 M) and 50 mL $Ca(NO_3)_2\cdot 4H_2O$ solution (1 M) were mixed homogeneously in a beaker. Then 100 mL Na_2CO_3 solution (1 M) was added with continuous stirring for 10 min to form a white suspension in the solution, thereby transferred into an oven at 60 °C for 24 h to form the $CaMg(CO_3)_2$ microspheres. Finally, the microspheres were collected, filtered off, washed with water and ethanol three times respectively, and dried in a blast drying oven at 60 °C for 8 h.

2.2. Preparation of Al_2O_3 hollow microspheres

In a typical process, 0.553 g $CaMg(CO_3)_2$ microspheres were dispersed in 100 mL industrial alcohol, then 20 mL $Al(NO_3)_3\cdot 9H_2O$ solution (0.2 M) was added to the liquid dropwise under vigorous stirring at room temperature. The formed product was collected, centrifugated, washed with water and ethanol three times respectively, and dried in a blast drying oven at 60 °C for 8 h, resulting the precursors. The precursors were calcined in air at temperature of 550 °C, 650 °C, 750 °C, 850 °C and 1150 °C, for 3 h, to obtain the Al_2O_3 hollow microspheres (marked as AHS-550, AHS-650, AHS-750, AHS-850 and AHS-1150, respectively).

2.3. Characterization

The crystalline phases of the as-prepared samples were identified by X-ray powder diffraction (XRD, Rigaku-DMax 2400) in reflection mode (Cu-Kα radiation) at scanning rate of 0.02 S^{-1} in the 2θ from 5° to 80°. The morphologies and structures of the as-prepared samples were observed by a scanning electron microscope (SEM, QUANTA 450, operated at 20 kV). Furthermore, energy dispersive X-ray (EDX) analysis was conducted during SEM. A Mettler TG/SDTA851e thermogravimetric analyzer was employed to accomplish the thermogravimetry analysis (TGA) of samples at a heating rate of 10 °C min^{-1} in air. An ASAP 2020 physisorption apparatus was used to measure adsorption/desorption isotherms of the samples at 77 K (temperature of liquid nitrogen). The specific surface area and the total specific volume of the pores were calculated by the BET method and BJH method, respectively.

2.4. Evaluation of adsorptive property

For adsorption tests, 0.1 g of as-obtained Al_2O_3 hollow microsphere powder was added to 200 mL of the aqueous solution of Congo Red (CR) at different initial concentrations. The samples used were AHS-550 and the initial pH was natural value, unless they were explored as condition variable, respectively. Then the mixture was stirred continuously at room temperature. At different adsorption times, 8.0 mL of the mixture was collected and separated. The absorbance of the CR solutions was measured by UV–visible spectrophotometer (Hitachi, U-4100), and the concentrations of the solutions were evaluated by the Beer's law equation. The relationship between the CR concentration and absorbance at $\lambda = 490$ nm was explored in our previous work [34], and the unknown concentration was calculated from the corresponding equations. Detail information of the CR was listed in the Table S1.

After adsorption, the adsorbent was collected, filtered off, washed with ethanol two times, and dried in a blast drying oven at 60 °C for 8 h. Then, the adsorbent was calcined in air at temperature of 550 °C for 1 h, to obtain the regeneration samples (marked 2-AHS). This process was conducted again on the 2-AHS samples to obtain the second regeneration samples (marked 3-AHS). The crystalline phases and the surface areas of as-obtained Al_2O_3, 2-Al_2O_3 and 3-Al_2O_3 samples were compared. Additionally, adsorptive property of them was evaluated and compared.

3. Results and discussion

3.1. Crystalline phase and composition

XRD was used to monitor the changes in the crystalline phases of the as-prepared samples. The XRD patterns of the precursor and the AHS samples calcined at different temperatures are shown in Figs. 1 and S1. As can be seen in Fig. 1, the precursor, AHS-550 and AHS-650 samples were amorphous. The diffraction peaks of γ-Al_2O_3 can be observed after calcined at 750 °C, and the crystallization of the γ-Al_2O_3 phase was more clearly at 850 °C. The absence of characteristic peaks from other crystalline impurities was presented in Fig. S1, indicating purity stable α-Al_2O_3 phase can be obtained at 1150 °C. The EDX pattern of as-prepared AHS-550 sample shown in Fig. S2 revealed that the chemical composition of as-prepared sample was consistent with the Al_2O_3.

3.2. Morphology

Fig. 2 shows the SEM images of the precursor (a, b), AHS-550 (c, d) and AHS-1150 (e, f) samples. As can be seen, the morphology of

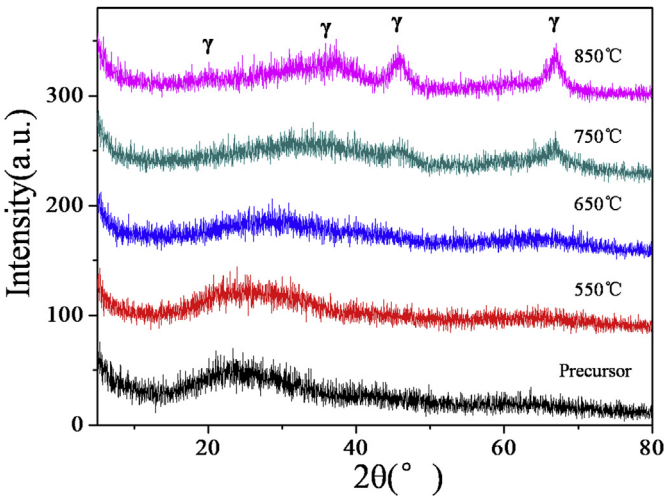

Fig. 1. XRD patterns of precursor and Al_2O_3 hollow microspheres calcined at 550–850 °C.