Chinese Journal of Chemical Engineering 22 (2014) 1352–1356

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

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

Materials and Product Engineering

Preparation of Silica–Alumina Hollow Spheres with a Single Surface Hole by Co-axial Microchannel☆

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ARTICLE INFO

Article history:
Received 17 December 2012
Received in revised form 26 February 2013
Accepted 18 March 2013
Available online 16 September 2014

Keywords:
Silica-alumina
Hollow
Single surface hole
Sphere
Microchannel

ABSTRACT

Si/Al composite hollow spheres with a surface hole were prepared with the co-axial microchannel in a one-step method. It is easy to use the technique for size control and continuous operation. At Si/Al ratio between 4 and 5, a hole forms on the surface, due to the fast gelation process and high viscosity of the sol. Scanning electron microscopy, nitrogen adsorption–desorption isotherms, and mercury intrusion method are used to characterize the samples. The hole size is 40–150 μm and the particle size is 450–600 μm. The size can be adjusted by the flow rate of the oil phase.

1. Introduction

Hollow spheres attract considerable interest because of their potential applications in drug delivery, controlled release, biomolecular separation, catalyst support, *etc.* [1–4]. Compared with other material types, hollow spheres are characterised by a high surface-to-volume ratio, low density, and low coefficient of thermal expansion [5,6]. Recently, a new type of hollow microsphere with a single hole in the shell has received much attention. These microspheres are classified as a new category of particles on account of their higher effective diffusivity and available surface area compared with microporous spheres of the same size [7,8]. However, the controllable preparation of single-hole microspheres faces significant challenges [9]. A few studies in the field have been performed but most are focused on organic materials. Luo *et al.* [10] reported a method for preparing poly(3,4-ethylenedioxythiophene)-coated polystyrene spheres with a single hole. The PS core was removed using toluene at room temperature to form the hole. Lysozymes in phosphate buffer solutions were effectively removed by these spheres. Minami *et al.* [11] found that such hollow polymer particles can be synthesised through the self-assembly of phase-separated polymers. Lim *et al.* [12] synthesised silica capsules with a single surface hole fabricated by evaporating emulsion droplets in a single-step emulsion process. The silica capsules were successfully used for *in vitro* cell labelling and *in vivo* molecular imaging. However, few reports are for inorganic materials. In recent years, the microfluidic device for preparing particles has been developed rapidly because of some advantages, such as easy control, continuous operation, and uniform flow [13,14]. Zhai *et al.* [15,16] developed a method for synthesising uniform silica spheres with large pore structures combined with microfluidic flows. Several flow patterns exist in the microflow because of the differences in viscosity and interfacial tension. Aluminium chloride is a common flocculants, which can significantly increase the silica sol viscosity and improve the rate of gelation. In a highly viscous system, a small tail forms on the droplet. At sufficiently high gel rate, the surface will be a solid and the tail detaches from the surface, forming a hole. This method may be a new and *in situ* way for preparing hollow microspheres with a single hole on the surface. In this paper, we present a one-step method for preparing single-hole Si/Al composite hollow spheres with a co-axial microfluidic device.

2. Experimental

2.1. Materials and equipment

Tetraethyl orthosili-cate (TEOS) was obtained by Xilong Chemical Co. (Shantou, China). Liquid paraffin was purchased from Bodi Chemicals Co. (Tianjin, China). Trioctylamine (TOA) was produced by Feixiang Chemicals Co. (Zhangjiagang, China). Sorbi-tan trioleate (Span 85) was obtained from China Medicine (Group) Shanghai

☆ Supported by the National Basic Research Foundation of China (2013CB733600), the National Natural Science Foundation (20976096, 21036002), and the Innovative Science and Technology Foundation of PetroChina (2011D-5006-0407).
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http://dx.doi.org/10.1016/j.cjche.2014.09.017
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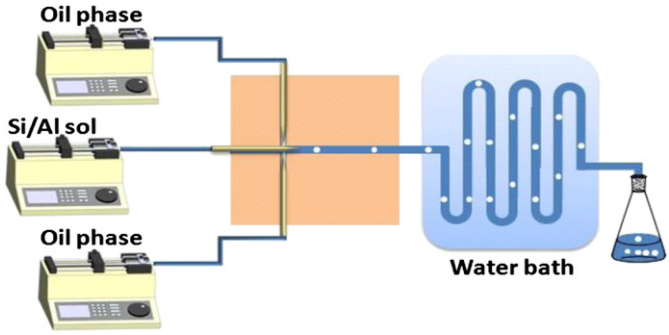

Fig. 1. Schematic of the microfluidic device.

Chemical Reagent Corporation (Shanghai, China). Poly(eth-ylene glycol) (PEG 20000) was obtained from Yili Fine Chemical Co. (Beijing, China).

Fig. 1 shows the microfluidic device. It includes a long polytetrafluoroethylene tube (3 m in length, 1.5 mm ID, and 2.0 mm OD) embedded in the main channel. A polypropylene needle (0.25 mm ID and 0.51 mm OD) is inserted into the tube immersed in a water bath to guide the dispersed aqueous phase into the continuous oil phase. Two stainless steel needles (1.3 mm ID and 1.6 mm OD) are embedded in the side channels to serve as the inlets for the oil phase.

2.2. Synthesis of silica–alumina spheres

The dispersed phase, Si/Al sol, was prepared as follows: 1 g of PEG20000, 0.5 g of methyl cellulose, and a certain amount of $AlCl_3 \cdot 6H_2O$ were added to 10 g of 0.01 $mol \cdot L^{-1}$ HCl aqueous solution. The mixture was stirred until it became clear, and 5 g of tetraethylorthosilicate was added dropwise to the mixture. Then, the solution was stirred at room temperature for 6 h to obtain a clear Si/Al sol. The continuous phase consisted of 68 % (by mass) liquid paraffin, 2 % (by mass) span 85, and 30 % (by mass) of TOA.

The experiments were performed at 60 °C. The spheres were collected at the outlet of the tube and then treated at 100 °C for 24 h in an autoclave. Finally, the product was washed with water and ethanol for a few times, dried at 80 °C for 12 h, and calcined at 550 °C for 6 h.

2.3. Characterization of samples

A scanning electron microscope (SEM) (JEOL JSM7401F) operating at 1.0 kV was used to characterize the samples. Nitrogen adsorption–desorption isotherms were measured at 77 K using a Quantachrome Autosorb-1-C Chemisorption–Physisorption Analyzer. Intrusion volume and pore size distribution of macropores were measured with a Micromeritics Auto-pore IV 9510 porosimeter using the mercury intrusion method. The droplet-forming process was observed using a microscope (MVC300SAM-GE200), and the viscosity of samples with different Si/Al ratios was measured on a Model NDJ-5S viscometer (Shanghai Jingtian Co. Ltd., China).

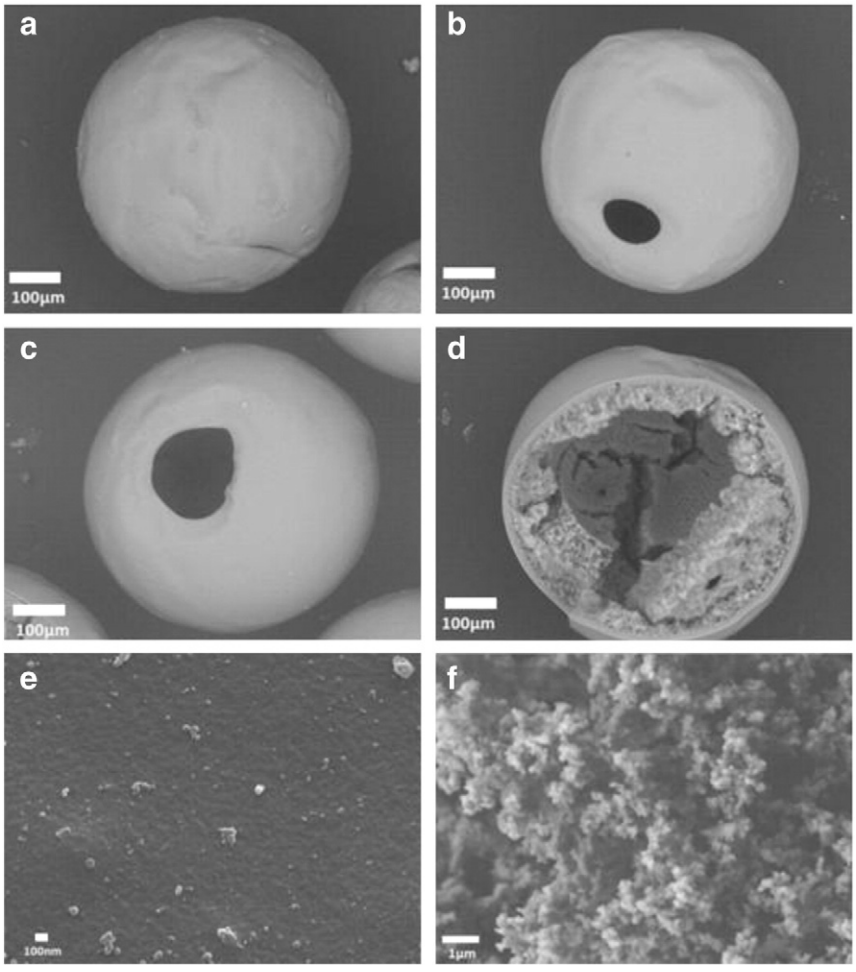

Fig. 2. SEM images of samples S1 (a), S2 (b), S3 (c), section of S2 (d), surface of S2 (e), and internal structure of S2 (f). (Mole ratio Si/Al: 10 for S1, 5 for S2, 4 for S3; flow rate: 5 μm for dispersed phase, 200 μm for continuous phase).