Chemical Engineering Science 135 (2015) 285–293

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Effect of the drying process on the preparation of porous silica microspheres

Huisheng Lv [a,b,c], Fanmei Meng [a,b,c], Minhua Zhang [a,b,c,*], Zhongfeng Geng [a,b,c], Yanpeng Sun [a,b,c]

[a] Key Laboratory for Green Chemical Technology of Ministry of Education, Tianjin University, Tianjin 300072, China
[b] R&D Collaborative Innovative Centre of Chemical Science and Engineering, Tianjin 300072, China
[c] R&D Center for Petrochemical Technology, Tianjin 300072, China

HIGHLIGHTS

- Silica microspheres: silica microspheres are of great interest in several areas.
- Sol–gel process: four uncertain and important parameters are investigated.
- Drying process: three drying methods are used and their feasibility are investigated.
- All experiments led to a successful precipitation of silica microspheres, in the micrometer range.

ARTICLE INFO

Article history:
Received 27 November 2014
Received in revised form
2 March 2015
Accepted 29 March 2015
Available online 4 April 2015

Keywords:
Silica microspheres
Sol–gel process
Intermittent Supercritical Fluid drying
Continuous Supercritical Fluid drying
Vacuum drying

ABSTRACT

Silica microspheres are of much interest in several areas, such as liquid chromatography, medicine, biochemistry, colloidal chemistry and aerosol research. In this study, the sol–gel method was used to prepare these microparticles followed by three different drying processes. The first process involved intermittent supercritical fluid drying (SCF-I) using intermittent supercritical carbon dioxide ($scCO_2$) at a low temperature. The second approach involved continuous supercritical fluid drying (SCF-C) using continuous $scCO_2$ at low temperature, as well. The third approach involved vacuum drying (WO), which is a high temperature process. All of the experiments led to the successful precipitation of silica microparticles in the micrometre range. In all of the cases, a spherical morphology and no agglomeration were observed. The optimum preparation conditions were determined as follows: stirring speed is 200 r/min; continuous phase/dispersed phase is 2/1; Span® 80/ Tween® 20 is 5/2; the ratio of surfactant is 17%. In addition, the primary textural characteristics of these microspheres were investigated by nitrogen physisorption experiments. The results indicated that the size of the pore volume is as follows: $V_{SCF\text{-}C} > V_{SCF\text{-}I} > V_{WO}$. The BET data indicate that the specific surface area of the porous silica microspheres is as follows: $S_{SCF\text{-}C} > S_{SCF\text{-}I} > S_{WO}$.

1. Introduction

Porous silica microspheres have external pores on the surface or internal pores in the core (usually interconnectivity), and active substances can be dissolved or dispersed on the surface or in the core of the microspheres (Cai et al., 2013; Chang and Jang, 2014). Due to their enhanced physicochemical properties (Ge et al., 2009), porous particles have received substantial attention and have a wide range of potential applications including drug delivery (Rigby et al., 2008), aerosol research (Chang and Jang, 2014), thin films (Chen et al., 2008; Nadargi et al., 2010), biochemistry (Zhao et al., 2011), colloidal chemistry, medicine, proteins encapsulations and high performance liquid chromatography (Hayes et al., 2014; Li et al., 2014).

Microspheres are primarily produced using various well-known techniques, such as a two-step sol–gel process (Bhagat and Rao, 2006), polymerisation method (Yan et al., 2012) and spray drying method (Beitollahi et al., 2010). However, due to the sensitivity of microspheres, there are many challenges in the preparation technology, such as less specific surface area, uneven particle size, and serious adhesions. It is necessary to modify the employed processes to meet the demands of porous silica microsphere production. One major challenge in the preparation of microspheres involves eliminating the liquid solvent from the gel

* Corresponding author. Tel./fax: +86 22 27406119.
E-mail address: mhzhang@tju.edu.cn (M. Zhang).

http://dx.doi.org/10.1016/j.ces.2015.03.050
0009-2509/

without collapsing the already existing nanoporous structure, which prevents subsequent shrinkage and cracking during the dry process (Garcia-Gonzalez et al., 2012). The drying of the gel–oil dispersion is critical for obtaining a material in the dry form while preserving the original nanostructure of the wet gel. A potential drying method for use with a gel–oil dispersion includes air-drying in a desiccator. This drying procedure is not able to avoid the subsequent shrinkage and cracking of the dried gel. Therefore, it is impossible to preserve the gel structure leading to porous microspheres (Valentin et al., 2005). Upon solvent removal, the surface tension of the liquid contained in the gel nanopores generates a high capillary pressure gradient in the pore walls that is capable of collapsing the pores of the existing gel nanostructure. Freeze-drying is a more gentle drying method where the primary structure of the product can be preserved. However, structural damage to the original gel pore structure and the formation of large cracks due to thermal shock and solvent expansion during freezing have been reported using this drying method for gels (Job et al., 2005). The supercritical drying process is an alternative drying technique assisted by the use of supercritical fluids (e.g., $scCO_2$). Because the supercritical fluid drying process is implemented in the homogenous phase region, which eliminates the effect of surface tension and avoids the capillary force that damages the gel structure, supercritical fluid drying is required to overcome this challenge.

In this work, SiO_2 particles were prepared using a two-step sol–gel process followed by three drying processes including intermittent supercritical fluid drying (SCF-I), continuous supercritical fluid drying (SCF-C) and vacuum drying (WO). Particle size, particle size distribution and textural parameters were investigated to assess the drying processes and their feasibility.

2. Materials and methods

2.1. Material

Carbon dioxide with a purity of 99.9% was purchased from the Tianjin Liufang Factory (Tianjin, China). Tetraethoxysilane (TEOS, AR), anhydrous ethanol (AR), 25% ammonia water and 36% hydrochloric acid were purchased from Tianjin Jiangtian Chemical Engineering Co. Ltd. (Tianjin, China). Castor oil (AR), Span® 80 (CP) and Tween® 20 (CP) were purchased from Tianjin Guangfu Chemical Engineering Co. Ltd. (Tianjin, China). All of the chemicals were used as provided without any further processing.

2.2. Methods

2.2.1. Preparation of silica gel microspheres

The silica sol was produced according to a two-step sol–gel process (Smirnova and Arlt, 2003; Smirnova et al., 2003). In the first step, tetraethoxysilane (TEOS), ethanol, water and hydrochloric acid were mixed together in a molar ratio of 1 mol TEOS: 2.4 mol EtOH: 1.3 mol H_2O: 10^{-5} mol HCl.

The mixture was stirred at room temperature for 30 min. Next, the mixture was diluted with ethanol to obtain the desired density of the aerogels. Then, additional water and ammonia solutions were added to obtain the following molar ratio: 1 mol TEOS: 2.4 mol EtOH: 4 mol H_2O: 10^{-5} mol HCl: 10^{-2} mol NH_4OH.

Finally, the sol solution was stirred for 3 additional minutes.

2.2.2. Emulsification of the silica sol in an oil phase

Castor oil (continuous phase) and two different surfactants (Span® 80 and Tween® 20) were placed in a beaker and mixed using a stirrer with a constant stirring rate. Then, the sol (dispersed phase) was poured into the oil phase all at once. Next, droplets of the dispersed phase formed under continuous stirring. After 30 min of stirring, the dispersed phase formed. At this stage, the stirring was terminated because the emulsion was converted to a dispersion consisting of spherical gel particles in an oil phase. Finally, the emulsion was aged for different amounts of time.

Different process parameters were investigated to obtain the desired particle size and shape.

2.2.3. Three different drying methods for the gel–oil dispersion

In this part, three different drying methods were used to obtain desirable porous silica microspheres.

2.2.3.1. Intermittent supercritical fluid drying of the gel-oil dispersion. One of the methods applied involves intermittent supercritical fluid drying, which is a low temperature process that uses supercritical carbon dioxide ($scCO_2$).

The oil was separated from the gel phase by filtration prior to the intermittent supercritical fluid drying. A process flow diagram of the intermittent supercritical fluid drying is shown in Fig. 1. In a typical experiment, the gel was placed into a cylindrical stainless steel vessel. A predetermined amount of CO_2 was delivered into the vessel via a mass meter and pump system (P-50, Thar Technologies Inc., USA). Then, the vessel was heated to the target temperature. After one hour, the drying was complete, and the microspheres were removed from the vessel.

The drying conditions in this study are listed in Table 1. Table 1 also lists the ratio of the removed solvent. All of the conditions were in the homogenous phase region above the critical temperature and pressure for CO_2+ethanol (Zhu et al., 2002).

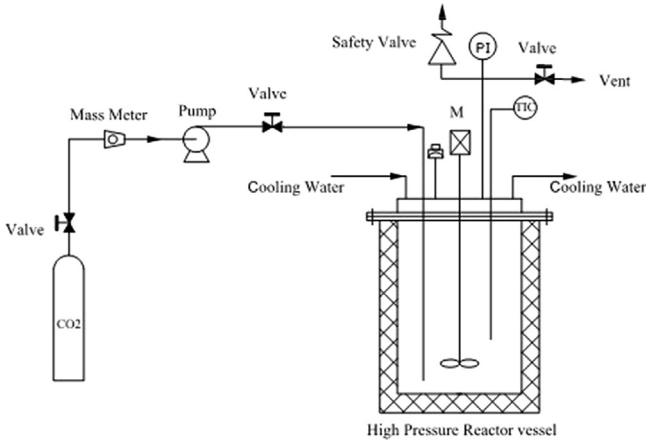

Fig. 1. Experimental flow sheet of intermittent supercritical fluid drying.

Table1
The operating conditions of intermittent supercritical fluid drying process.

Run	Temperature (°C)	Pressure (MPa)	The amount of CO_2 (g)	The ratio of the removed solvent (%)	Weight-loss ratio at 180 °C (%)
1	50	10	198	76.04	6.67
2	50	11	240	79.83	4.09
3	50	12	267	82.30	2.49
4	55	10	170	74.13	8.81
5	55	11	210	76.36	5.23
6	55	12	240	80.33	3.38
7	60	10	150	71.88	9.05
8	60	12.5	230	79.11	4.18
9	60	13.5	255	81.24	3.16