Materials Letters 170 (2016) 147–150

Contents lists available at ScienceDirect

Materials Letters

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

Rapid and microthermal synthesis of centimetre-sized mesoporous silica aerogel sphere by using DMSO-CO_2 as solvent

Huijun Yu [a,b], Xiaofeng Liang [a,b,*], Junxia Wang [a], Minmin Wang [a], Shiyuan Yang [a]

[a] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China
[b] Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, PR China

ARTICLE INFO

Article history:
Received 21 August 2015
Received in revised form
19 January 2016
Accepted 30 January 2016
Available online 1 February 2016

Keywords:
Porous materials
Sol-gel preparation
Silica aerogel sphere
DMSO-CO_2
Microthermal synthesis

ABSTRACT

Centimetre-sized mesoporous silica aerogel sphere (SAS) was synthesized via sol-gel technology by one-step aging/solvent exchange at 2 MPa and using DMSO-CO_2 as solvent. DMSO-CO_2 solvent was obtained at 7.5 MPa with CO_2 fluid in autoclave. The influence of an important factor, temperature, on the SASs' performance is briefly discussed and the optimal temperature is 4 °C. Low temperature is an effective way to overcome the fragility and shrinkage of SASs. Investigations by bulk density, FTIR, BET and FE-SEM indicate that the SAS has a typical three-dimensional porous structure with pore diameter about 25.4 nm, minimum bulk density 0.12 g/cm^3 and specific surface area as high as 1078 m^2/g. Due to the good properties of mesoporous, the SAS could be a promising candidate of filling materials.

1. Introduction

Silica aerogels (SA) synthesized by sol-gel process and supercritical drying method are materials exhibited extraordinary properties like large surface area, high porosity, low density, low thermal conductivity and low index of refraction [1–3]. However, SA products in the market were block or powder with different sizes due to their rigid skeletons, and failure to satisfy the requirement of the special filling material, such as spherical SA applied to recycling explosive ejecta and adsorbing toxic substance. Generally, flexible SA column [4,5], micrometer-sized SA beads [6,7], SA microparticles [8], and silica hollow spheres [9], are developed to expand the application area. Unfortunately, centimetre-sized SASs as outstanding filling material have not been reported. Recently, the majority of technological improvements for rapid process like one-pot synthesis [10,11], solvent-exchange-free [11], and rapid supercritical extraction [12,13], have been high-profile. Nonetheless, SASs are more sensitive to preparation temperature for their integrity and mechanical properties.

In this paper, the new rapid methods were combined to explore centimetre-sized mesoporous SASs via the sol-gel process, one-step aging/solvent exchange method at 2 MPa and CO_2 supercritical drying by using DMSO-CO_2 as solvent at low temperature.

2. Experimental

2.1. Preparation of DMSO-CO_2 solvent

0.3 L Dimethyl sulfoxide (DMSO, Kelong, AR) was placed in the autoclave within a vessel, and the autoclave was pressurized to 7.5 MPa with CO_2 fluid using plunger pump (HUALI: 2JX10/50). The autoclave was then kept at 7.5 MPa for 24 h until the CO_2 was dissolved in DMSO.

2.2. Preparation of SASs

Tetraethoxysilane (TEOS, Kelong, AR) and methyltrimethoxysilane (MTMS) were hydrolyzed in ethanol (EtOH, Kelong, AR) by mixing with hydrochloric acid (HCl, Kelong, AR) and deionized water (H_2O) with pH value of 5 at. a molar ratio of TEOS:MTMS:EtOH:H_2O of 0.8:0.2:2:4. After stirred for 30 min, the sol was maintained at 4 °C for 36 h. DMSO mixed ammonium hydroxide (NH_4OH, Kelong, AR) was dropped in sol to adjust the pH value to 8 with stirring for 2 min. The final molar ratio of TEOS: MTMS: EtOH: DMSO: H_2O is 0.8:0.2:2:2:4. Then the homogeneous sol was respectively injected into three teflon-based moulds of 4 cm inner diameter with syringe. After gelation at 4, 10 and 25 °C respectively, wet gel spheres were removed from the moulds and immediately immersed in DMSO-CO_2 solvent, which placed in the autoclave at 2 MPa with CO_2 for ageing/solvent exchange in order to strengthen network structure and remove excess water. After

* Corresponding author at: Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, PR China.
E-mail address: XFLiang@swust.edu.cn (X. Liang).

http://dx.doi.org/10.1016/j.matlet.2016.01.136
0167-577X/

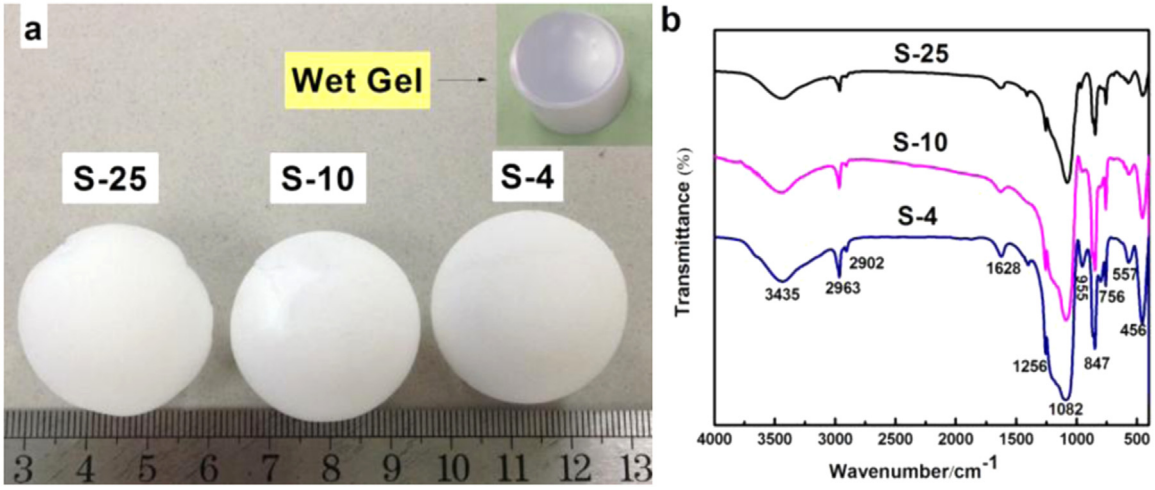

Fig. 1. The wet gel and SASs (a) and FTIR spectra (b) of SASs prepared at 4 °C (S-4), 10 °C (S-10) and 25 °C (S-25).

Table 1
Physical and textural properties of the SASs.

Sample	Bulk density ± 0.01 (g/cm^3)	Volume shrinkage ± 0.5 (%)	Surface area ± 5 (m^2/g)	Pore volume ± 0.1 (cm^3/g)	Average pore size ± 0.2 (nm)
S-4	0.12	16.8	1078	5.2	25.4
S-10	0.25	23.6	980	5.1	22.2
S-25	0.28	24.3	893	4.3	23.7

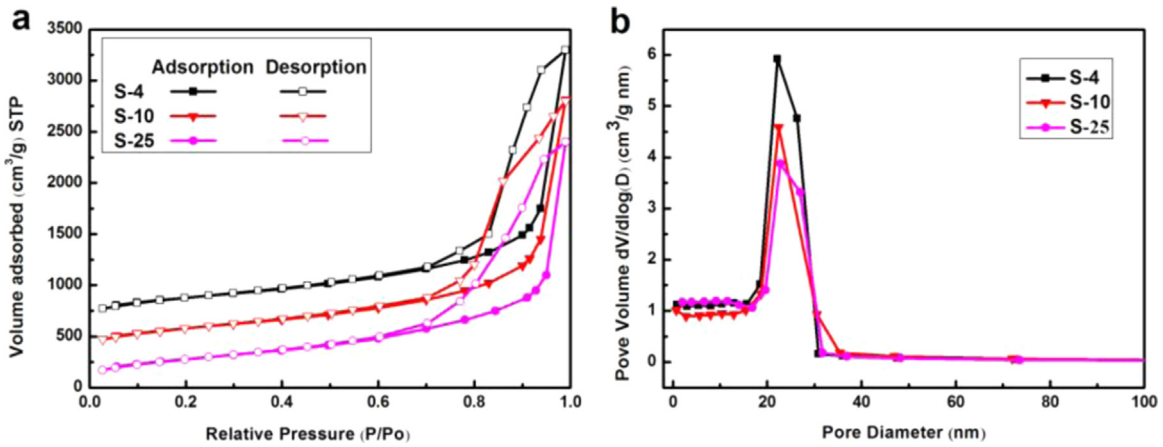

Fig. 2. Nitrogen adsorption/desorption isotherms at 77 K (a) and BJH analysis of pore size distribution (b).

ageing, the spheres were kept in autoclave with supercritical CO_2 above 12 MPa for 24 h, and depressurized to 8 MPa several times. Finally, the autoclave's temperature was slowly ramped to 40 °C to extract CO_2 from the skeleton, and SASs named S-4, S-10 and S-25 were obtained.

2.3. Characterization

Apparent densities were calculated from mass to volume ratios. Percentage of volume shrinkage (V_s %) and porosity were determined through the formulae [4]:

$$V_s\% = (1 - V_a/V_g) \times 100 \quad (1)$$

where V_a and V_g are the volumes of the SAS and wet gel respectively. Fourier transform infrared (FT-IR) spectra were recorded with the Spectrum One FT-IR spectrometer (USA). The specific surface areas and pore volume were commonly measured by the multipoint BET method on the basis of nitrogen adsorption-desorption isotherms at 77 K with the NOVA3000 instrument (USA). Pore size distributions were evaluated using the BJH method. Microstructural studies were carried out by a Ultra 55 Field Emission Scanning Electron Microscopy (FE-SEM) (Germany).

3. Results and discussion

The wet gel and SASs prepared at 4, 10, and 25 °C are shown in Fig. 1a, and the bulk densities and volume shrinkage are listed in Table 1. All samples based on TEOS/MTMS using DMSO-CO_2 as solvent and one-step aging/solvent exchange at 2 MPa maintain their overall spherical shape. Compared with volume shrinkage of S-25 (24.3%) and S-10 (23.6%), S-4 presents the minimum volume shrinkage (16.8%) and the minimum bulk density (0.12 g/cm^3). Further, S-4 sphere is intact without cracking. It can be due to network strengthen in DMSO-CO_2 solvent at lower temperature, which results in less dimensional shrinkage of the silica skeleton and less collapse of the pores. Fig. 1b shows FTIR spectra of SASs