J. of Supercritical Fluids 57 (2011) 198–206

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Formation of porous glass via core/shell-structured poly(methyl methacrylate)/powder glass prepared by ultrasonic irradiation in liquid CO_2

Kiyoshi Matsuyama*, Kenji Mishima, Takafumi Kato, Kiyomi Ohara

Department of Chemical Engineering, Fukuoka University, 8-19-1 Nanakuma Jonan-ku, Fukuoka 814-0180, Japan

ARTICLE INFO

Article history:
Received 17 December 2010
Received in revised form 17 February 2011
Accepted 17 February 2011

Keywords:
Porous glass
Dry-powder coating
Liquid carbon dioxide
Ultrasonic irradiation
Cavitation

ABSTRACT

The formation of porous glass ceramic via core/shell-structured poly(methyl methacrylate)(PMMA)/powder glass was investigated. Core/shell structures were prepared via ultrasonic irradiation in high-pressure liquid carbon dioxide (CO_2) using PMMA microspheres as the core material and glass powder as the shell material. The mean particles sizes of PMMA template microspheres and glass powder were 9.8 μm and 0.9 μm, respectively. After removal of the PMMA template by calcination in air, porous glass was obtained. The products were characterized by scanning electronic microscopy (SEM) and thermogravimetric-differential thermal analysis (TG-DTA). The average pore diameter of porous glass was 4.3 μm. Compared with porous glass prepared by the other method, the porous glass prepared by ultrasonic irradiation of liquid CO_2 was achieved the narrow pore size distribution (CV = 35%) and the higher porosity (89%). The pores are not isolated and connected each other. Furthermore, the effects of experimental conditions, such as coating method, crosslink density of the template PMMA microspheres, ultrasonic intensity and calcination temperature, on the product morphology were investigated. The higher ultrasound intensity achieved the uniform coating of PMMA templates with powder glass. The calcination temperature and crosslinked density of PMMA template microspheres affect the pore structure.

1. Introduction

Porous glass ceramic materials have attracted considerable attention in catalysis [1,2], sensors [3], drug delivery [4], and chemical systems [5] because they have lower density, larger surface area, permeability, and distinct optical and electronic properties compared with bulk materials. Recently, porous glass ceramics have been used as 3D bioactive scaffolds in tissue engineering applications [6–8] owing to their controlled pore size and pore-size distributions as well as the simplicity of fabricating complex and bulk shapes.

Various approaches have been proposed for the preparation of porous glass materials with different morphologies. Numerous chemical and physicochemical approaches, such as self-assembly techniques based on the sol–gel method [9,10] and phase separation [11–13] as well as template-sacrificial [9] approaches, have been developed for the preparation of porous glass.

The template-based method is an effective and multifunctional strategy for fabricating ceramic materials with hollow and porous structures [9,10,14–17]. Recently, highly porous Al_2O_3 has been prepared by filling the opening of a poly(methyl methacrylate) (PMMA) template block with Al_2O_3 slurry [14]. The Al_2O_3 slurry was prepared by ball milling to produce a uniform slurry. After calcination to remove the PMMA template, the porous Al_2O_3 was obtained. Furthermore, hollow Al_2O_3 microspheres have been prepared via core/shell-structured PMMA/Al_2O_3 prepared by the mechanofusion method [18,19]. Mechanofusion is an effective dry-particle coating method in which relatively large particles (host particles) are coated with fine particles (guest particles) [20]. Using mechanofusion, the guest particles are attached to or embedded into the surface of the host particles by high shear and/or impaction forces, resulting in the core/shell structure of host particles/guest particles. Core/shell microspheres were prepared by mechanofusion of PMMA template microspheres coated with Al_2O_3 nanoparticles, and the core/shell microspheres were calcined to obtain the hollow Al_2O_3 microspheres. A uniform coating of the PMMA template with precursors, such as Al_2O_3 nanoparticles, using high mechanical strength is a novel feature of the hollow and porous structured products.

Supercritical fluids have attracted much attention as alternative solvents for the synthesis and processing of advanced materials [21–26]. In these applications, supercritical CO_2($scCO_2$) is the solvent of choice because it is readily available, inexpensive, and environmentally benign. Porous materials of metal oxides

* Corresponding author. Tel.: +81 92 871 6631; fax: +81 92 865 6031.
E-mail address: mtym@fukuoka-u.ac.jp (K. Matsuyama).

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doi:10.1016/j.supflu.2011.02.017

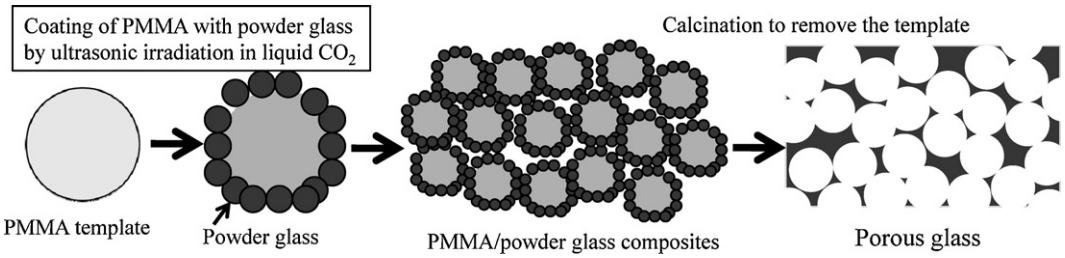

Fig. 1. Conceptual illustration of porous glass formation via core/shell-structured poly(methyl methacrylate)/powder glass prepared by ultrasonic irradiation in liquid CO_2.

have been prepared using $scCO_2$-assisted templates [15–17,27,28]. $scCO_2$ offers specific advantages for template structures because they have low viscosity and high diffusivity, and they never condense to the liquid phase above their critical temperature.

Therefore, we investigated the formation of porous glass via core/shell-structured PMMA/glass prepared by ultrasonic irradiation in high-pressure liquid CO_2. The high-pressure liquid CO_2 was applied to the formation of aligned porous materials [29] and porous hydrogel [30]. In previous work, we proposed $scCO_2$ technologies based on high shear mixing [31] and ultrasonic irradiation [32] to achieve coatings of polymer and inorganic materials using high shear and/or impact forces. Ultrasonic irradiation in liquid CO_2 is an effective method for dry-particle coating and mixing of particles [32–34]. The resultant coating is very closely related to the mixing parameters [20]. Sonication in liquid CO_2 can break agglomerates of particles by cavitation and cause mixing of particles. The acoustic pressure above Blake threshold pressure has to be applied in order to create cavitation phenomenon. The acoustic pressure P_A and Blake threshold pressure P_B are given as follows [35].

$$P_A = \sqrt{2\rho c I_{US}} \tag{1}$$

$$P_B = P_0 - P_V + \frac{4}{3}\sigma\sqrt{\frac{2}{3}\frac{\sigma}{(P_0 + 2\sigma/R_0 - P_V)R_0^3}} \tag{2}$$

where ρ is density of fluid, c is the speed of sound, I_{US} is intensity of ultrasound, P_0 is external pressure, P_V is vapor pressure, σ is surface tension, and R_0 is equilibrium radius of cavitation bubble. According to Eq. (2), P_B are strongly depended on the values of P_V and σ. It is well known that the pressure and temperature strongly influence the thermophysical properties of high-pressure fluid such as P_V and σ. In previous work, we demonstrated the experimental condition to create the cavitation by ultrasonic irradiation in high-pressure liquid CO_2 [32]. Fig. 1 shows a conceptual illustration of the process proposed in the present study. After ultrasonic irradiation in liquid CO_2, the shock waves generated by collapsing cavitation bubbles accelerated the mixing of particles and the deagglomeration of the guest glass particles. The deagglomerated glass particles tended to adhere to the host PMMA template particles. The PMMA template microspheres were coated with glass particles. The host PMMA microspheres and guest glass particles were then easily separated from CO_2 by depressurization. As a result, core/shell-structured PMMA/glass was obtained. After removing the PMMA template by calcination in air, porous glass was obtained. We investigated the effects of several experimental conditions on the morphology of the products.

2. Materials and methods

2.1. Materials

Carbon dioxide (CO_2) (99.9% minimum purity) was purchased from Fukuoka Sanso Co., Ltd. The crosslinked (MX-1000, Souken Kagaku Co., Ltd.) and non-crosslinked (MB-8C, Sekisui Plastic Co., Ltd.) PMMA microspheres, with mean particle sizes of 9.8 μm and 8.5 μm, respectively, were used as templates.

Powder glass was used as a precursor for porous materials. The powder glass (ASF1094), purchased from Asahi Glass Co., Ltd., had a primary particle diameter of 0.9 μm and consisted of SiO_2, B_2O_3, and Bi_2O_3.

2.2. Methods

Details of the experimental apparatus for particle coating using ultrasonic irradiation in liquid CO_2 are described in our previous paper [32]. The experimental apparatus consisted of a 150 cm^3 high-pressure vessel (34 mm in diameter, 165 mm in height) equipped with a titanium ultrasound horn and a quartz glass window. The cavitation phenomena that occurred on the tip of the ultrasound horn and during the coating process were observed through a quartz glass window; images were captured using an optical unit (CCD camera) and were displayed on a monitor.

The high-pressure vessel was immersed in a water bath at the desired temperature. The temperature of the sample in the cell was measured with a platinum resistance thermometer. Prior to the coating experiments, known amounts of PMMA template microspheres and coating particles (powder glass) were loaded directly into the high-pressure vessel in a weight ratio of 1:1 (1.0 g:1.0 g). The vessel was then charged with CO_2 until the desired pressure was achieved.

After the high-pressure vessel reached the desired pressure and temperature, ultrasonic irradiation was performed using an ultrasonic processor (VC-750, Sonic and Materials Inc.) that produced ultrasonic waves at a frequency of 20 kHz with a maximum power capability of 750 W. During ultrasonic irradiation, the ultrasonic processor delivered waves of constant amplitude by automatically adjusting the power supply. The maximum amplitude was 61 μm with the amplitude control set at 100%. The power delivered by the ultrasonic processor depended on the experimental conditions such as the volume of the experimental vessel, horn size, viscosity of the mixture, pressure, etc. All coating experiments were carried out at constant amplitude. The amplitude was set at 31 μm (the amplitude control was set at 50%). Ultrasonic irradiation was performed for 5 min at 293 K and 6.5 MPa. To prevent a rapid temperature increase, the ultrasonic irradiation was carried out intermittently (on time: 5 s; off time: 5 s), and the ultrasonic horn was cooled by a cooling jacket. After each experiment, the vessel slowly depressurized to atmospheric pressure for approximately 30 min, and samples were removed. The system pressure was controlled by the back pressure regulator. Prior to depressurization, the system temperature was set to 313 K (above the critical temperature of CO_2: 304.2 K) to prevent the appearance of the liquid–vapor interface because the capillary pressure at the liquid–vapor interface would accelerate the aggregation of particles.

The PMMA/powder glass composites were calcined at 823 K in air flow to remove the PMMA template.