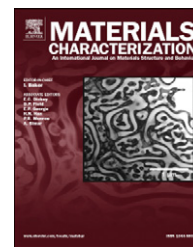


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Synthesis and characterization of high-surface-area millimeter-sized silica beads with hierarchical multi-modal pore structure by the addition of agar



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ABSTRACT

Millimeter-sized spherical silica foams (SSFs) with hierarchical multi-modal pore structure featuring high specific surface area and ordered mesoporous frameworks were successfully prepared using aqueous agar addition, foaming and drop-in-oil processes. The pore-related properties of the prepared spherical silica (SSs) and SSFs were systematically characterized by field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), small-angle X-ray diffraction (SAXRD), Hg intrusion porosimetry, and N₂ adsorption–desorption isotherm measurements. Improvements in the BET surface area and total pore volume were observed at 504 m² g⁻¹ and 5.45 cm³ g⁻¹, respectively, after an agar addition and foaming process. Despite the increase in the BET surface area, the mesopore wall thickness and the pore size of the mesopores generated from the block copolymer with agar addition were unchanged based on the SAXRD, TEM, and BJH methods. The SSFs prepared in the present study were confirmed to have improved BET surface area and micropore volume through the agar loading, and to exhibit interconnected 3-dimensional network macropore structure leading to the enhancement of total porosity and BET surface area via the foaming process.

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1. Introduction

Mesoporous materials with tunable properties are of interest in many applications for separation processes such as catalysts, catalytic supports, and adsorbents. For the industrial application of mesoporous materials as catalysts, the fabrication of porous monoliths with a hierarchical pore structure is required [1,2]. There are two reasons for this. First, it is reported that confined nanochannels in mesoporous materials usually reduce the diffusion of reactants and thereby decrease the catalytic activity [3,4]. In an attempt to overcome this problem, several studies have recently investigated the role

of larger pores in bimodal mesoporous materials. The results indicate that the activity of the catalyst was enhanced because of the enhanced diffusion of reactants [5–8], clearly suggesting that the presence of macropores helps open active sites of micropores and mesopores and thus improves the mass transfer of reactants. Accordingly, a hierarchical mesoporous–macroporous structure needs to be developed to enhance the catalytic activity of mesoporous materials. Second, due to the difficulty in handling and installing fine mesoporous materials in practical applications, the materials need to be fabricated as a monolith rather than as a powder.

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Foam monoliths are known to have high porosity, excellent fluid permeability, and high mass transfer of the reactants because of their unique structure with interconnected three-dimensional spherical pores [9–13]. According to a recent study which evaluated the characteristics of mass transfer and differential pressure using three types of porous systems with identical geometric surface area (a foam, a honeycomb, and a reactor packed with bead-type catalysts), the foam was superior to the beads-packed reactor from the viewpoint of combined high mass transfer and low pressure drop [12,13]. The beads-packed reactor showed the highest mass transfer efficiency, but the differential pressure was relatively high. Thus, the fabrication of silica beads with a hierarchical mesoporous-macroporous structure promises to offer a material that could be used as a new catalyst or a novel support with excellent activity and ability to reduce differential pressure [14,15].

Recently, we reported a simple and environmentally friendly method for the preparation of sizable and uniformly sized silica beads by combining a drop-in-oil method with the agar gelation process [16,17]. Our very recent study revealed that the cell size and window size could be controlled by agar addition [18], but we only focused on the structure of macropores, not micropores, which are known to have a significant impact on the specific surface area. The specific surface area of the ceramic foams prepared in that study ranged from 9.6 to 14.2 m² g⁻¹ [18], which was much lower than that of commonly known foams with hierarchical pore structure. Therefore, in the present study, we attempted to fabricate hierarchically multi-modal porous silica beads with high specific surface area (i.e. enhanced formation of micropore volume), high pore volume, and ordered mesoporous frameworks by combining the addition of agar, mesopore synthesis, foaming, and drop-in-oil processes. Furthermore, we investigated the effect of agar addition and foaming process on the pore-related properties of the silica beads, particularly the BET surface area, pore size distribution, and pore volume. Several complementary techniques, including FE-SEM, TEM, SAXRD, nitrogen sorption isotherm, mercury intrusion porosimetry, and image analysis, were used to systemically evaluate the textural properties of the calcined silica bead composites.

2. Materials and Methods

2.1. Synthesis of the silica beads

The flow chart in Fig. 1 shows the synthesis process of the modified mesoporous silica and the silica beads (spherical silica (SSs) and spherical silica foams (SSFs)). To prepare the modified mesoporous silica, 4 g of triblock copolymer P123 (PEO₂₀PPO₇₀ PEO₂₀, Sigma-Aldrich) was dissolved in 120 g of 2 N aqueous HCl solution (BP153-1, Fisher Scientific) and 30 g of distilled water, and the mixture was stirred at 60 °C. Forty milliliters of 0.5 wt% aqueous agar solution (Myung Shin Agar Co., Korea) at 60 °C was added to the mixture solution and vigorously stirred for 1 h at 60 °C. Then, 8.5 g of tetraethylorthosilicate (TEOS, Sigma-Aldrich) was added, and the solution was then vigorously stirred for 20 h at 90 °C and aged for 24 h at 90 °C. The precipitated products were filtered, and the filtered samples were washed thoroughly with distilled water. Then, the as-prepared samples

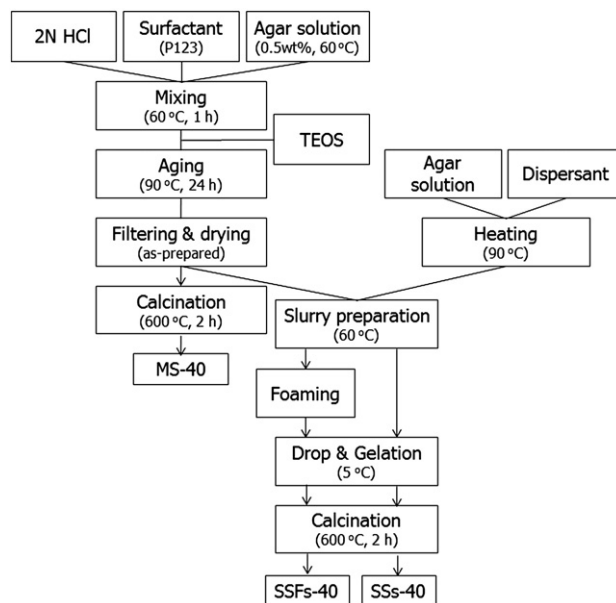


Fig. 1 – Flow chart for preparing the modified mesoporous silica (MS-40) by the addition of aqueous agar solution and the silica beads (SSs-40 and SSFs-40) using a foaming process.

were calcined at 600 °C for 2 h, and the temperature was increased at a rate of 3 °C min⁻¹. The modified mesoporous silica particles were named MS-x (where x is the volume of the added agar solution).

To prepare the SSs and SSFs, after immersing the precipitated mesoporous silica without calcination (the as-prepared samples) in a 100-ml aqueous agar solution (9.5 wt% agar and 0.8 wt% sodium hexametaphosphate (SHP; Sigma-Aldrich) with respect to the precipitated product), the solution was vigorously stirred for 24 h at 90 °C. After mixing the product with aqueous agar solution, the final concentration of the slurry product was determined to be 12.5 wt%. The slurry was then mechanically foamed for 3 min and then pelletized via drop-in-oil method and an agar gelation process. More detailed procedures can be found elsewhere [16,17]. The gelled beads were collected from the bottom of the liquid paraffin column, dried at room temperature for 24 h, and then calcined in air at 600 °C for 2 h at a heating rate of 1 °C min⁻¹. The spheres fabricated using the foaming method are referred to as SSFs and the spheres prepared without the foaming process are called SSs. For example, SSFs-40 represents spheres prepared using the foaming method from precipitated product with 40 ml of agar solution (as-prepared MS-40).

2.2. Characterization

The morphology and microstructure of the samples were investigated using FE-SEM (JSM-6701F, JEOL). The FE-SEM images of the Au-sputtered samples (of the whole part and inner surface of the samples) were taken at acceleration voltages of 5 and 15 kV. TEM observations were conducted with a JEOL-2100F microscope operated at 200 kV. The samples for TEM measurements were suspended in ethanol and dropped onto holey carbon films that were supported on Cu grids for imaging. The SAXRD (Bruker D8 HRXRD) patterns were

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