Synthesis of Porous Nanostructured Silica Particles by an Aerosol Templating Method


*Korea Institute of Geoscience & Mineral Resources, Daejeon, Korea, hdjang@kigam.re.kr
**Sogang University, Seoul, Korea, smartian@sogang.ac.kr
***Kumoh National Institute of Technology, Gumi, Korea, tokim@kumoh.ac.kr
Hiroshima University, Higashi-Hiroshima, Japan, Okuyama@hiroshima-u.ac.jp

ABSTRACT

Nanostructured spherical silica (SiO$_2$) particles having both mesopores and macropores were prepared by using an aerosol templating method with colloidal mixtures of polystyrene latex (PSL) particles and silica nanoparticles. The as-prepared particles showed bimodal size distribution consisting of mesopores ranged 2 to 20 nm and macropores ranged 60 to 160 nm. As the PSL size decreased, mesopores size increased due to a reduction in packing rates of primary SiO$_2$ nanoparticles composing the walls of nanostructured porous particles. With an increment of the weight ratio of PSL/SiO$_2$, mesopores size increased but mesopores volume decreased due to the broken structure of particles and the reduction in the packing rates. Mesopores disappeared when the furnace temperature was 900 °C. The residuals of organic template were detected when furnace temperature and flow rate of carrier gas were below 600 °C and above 3 l/min, respectively.

Keywords: macro-mesoporous silica; nanostructures; aerosol templating; catalytic supporter

1 INTRODUCTION

Silica nano-materials with meso- and macroporosity are of great interest due to their variety of potential applications in catalysts, separations, coatings, chromatography, low dielectric constant fillers, pigments, microelectronics, and electro-optics. Especially, for the catalytic application of the nanostructured porous materials, controlled pore size as well as high surface area is required. Therefore, important progress has been made in the controlled synthesis of porous structures [1-4].

Sphere templating methods were able to fabricate macroporous (pore size > 50 nm) materials as well as mesoporous (2 nm < pore size < 50 nm) ones. The methods have several common steps; packing of sphere templates, filling of the interstitial space, and sphere remove [1]. The conventional templating method is time-consuming and somewhat complicate. Recently, Iskandar et al. reported in situ production of spherical silica particles containing self-organized mesopores [5] and the controllability of pore size and porosity [6]. However, their works were limited at the structural investigation of the mesoporous silica (SiO$_2$) particles. Although the optical properties of nanostructured porous SiO$_2$ particles having macroporous structure were reported by Chang and Okuyama [7], the characteristics of porous particles for the catalytic application have not been reported in detail, for example, specific surface area, pore size distribution and so on.

In this study, we report on the pore size-controlled synthesis of nanostructured porous SiO$_2$ particles having both mesopores and macropores via an aerosol templating method. Both of the pores are expected to play an important role in the application as a catalytic supporter, i.e., mesopores increase the activity of the catalysts and macropores permit reactant to approach to the inside of the porous materials. We investigated the effects of the size and mixing ratio of organic template spheres (polystyrene latex particles) in a colloidal mixture, precursor concentration, furnace temperature, and flow rate of carrier gas on the properties of as-prepared particles such as pore size distribution, particle size, particle morphology, and residual of the organic template.

2 EXPERIMENTS

The polystyrene latex (PSL) particles used as an organic template were prepared by following procedure [8]. The mixture of styrene monomer (6.0 g) and $n$-hexadecane (0.25 g) was added to the solution of sodium dodecyl sulfate (SDS) in 24 g of water. The mixture was stirred for 1 h, followed by ultra-sonication for 1 min to form miniemulsion. The miniemulsion was then heated to 70 °C, followed by the addition of 0.12 g of potassium persulfate for polymerization, under a nitrogen atmosphere, and the reaction proceeded for 2 h.

Colloidal suspension of silica nanoparticles (SS-SOL 30, Shin Heung Silicate Co., Korea) was used as a silica source for the preparation of nanostructured porous SiO$_2$ particles. The nominal average particle diameter of SiO$_2$ particles was 15 nm. Precursor suspension was prepared by mixing the colloidal suspensions of the PSL and the silica nanoparticles.

Our strategy for the controlled synthesis of nano structured porous SiO$_2$ particles having spherical shape is the same method with previous research [5-7]. Fig. 1 shows an experimental apparatus used in this work, which consists of an ultrasonic atomizer, an electric furnace, and a filter.
sampler. The ultrasonic atomizer was used to generate micron-sized droplets of the precursor suspension. The droplets were then carried by 1.0, 3.0 or 5.0 l/min of air into the low temperature zone of the electric furnace, in which submicron-sized and spherical SiO$_2$-PSL mixed particles were prepared by drying of solvent. And then, when the mixture particles were introduced into a high temperature zone, the evaporation of the PSL particles and the restructuring of SiO$_2$ nanoparticles resulted in nano structured porous SiO$_2$ particles. The length and diameter of heating zone were 54 cm and 25 mm, respectively. As-prepared nanostructured porous SiO$_2$ particles were finally collected by the filter sampler.

The morphology of PSL particles and nanostructured porous SiO$_2$ particles was observed by a transmission electron microscope (TEM; CM12, Philips), a field emission scanning electron microscopy (FE-SEM; Sirion, FEI) and a scanning electron microscope (SEM; JSM-6380LA, JEOL; S-4800, Hitachi), respectively. The size distribution of PSL particles was determined from TEM micrographs by measuring at least 100 particles. N$_2$ adsorption-desorption isotherms at 77 K were obtained using ASAP 2400 equipment from Micromeritics. The Brunauer, Emmett, and Teller (BET) equation was used for specific surface calculations. The pore size distributions were calculated using the Barrett, Joyner, and Halenda (BJH) method [9]. Fourier transform infrared (FT-IR) spectra were measured by a Nicolet 380 spectrometer (Thermo Electron Co.) from samples prepared as KBr pellets.

3 RESULTS AND DISCUSSION

TEM micrographs and size distributions of the as prepared PSL particles are shown in Fig. 2. The morphology of the PSL particles was spherical and particles size changed with the variation of amount of SDS at the fixed process conditions. The average particle diameter of PSL increased from 62 nm to 161 nm as the amount of SDS decreased from 40 mM to 50 mM. The particle size was very uniform. It was also found that the surface area of PSL was inversely proportional to the adding amount of SDS.

Fig. 2. TEM micrographs and particle size distributions of size-controlled PSL particles prepared with different concentrations of SDS by utilizing a miniemulsion method: (a) 40 mM, (b) 20 mM, (c) 5 mM.

Fig. 3 shows FE-SEM micrographs ((a)-(d)) and desorption pore size distribution (e) of nanostructured porous SiO$_2$ particles prepared with different sizes of PSL and furnace temperatures ((a) 161 nm, 600 °C; (b) 161 nm, 900 °C; (c) 83 nm, 600 °C; (d) 62 nm, 600 °C) while keeping the weight ratio of PSL/SiO$_2$, precursor concentration and flow rate of carrier air at 1.43, 0.1 M and 1 l/min, respectively. As-prepared nanostructured porous particles were nearly spherical and their porosity could be easily controlled by changing PSL sizes. The average diameter of macropores on the particle surfaces observed

Fig. 1. A schematic diagram of an experimental apparatus for the synthesis of nanostructured porous SiO$_2$ particles by an aerosol templating method.
by SEM was corresponded with PSL sizes. Desorption pore size distributions (Fig. 3(e)) and specific surface areas revealed the particles contained mesopores as well as macropores except the particles prepared at 900 °C. The desorption pore size distributions showed broad distributions of mesopores with diameter of 2-10 nm. With a decrement of PSL size, the mesopores size slightly increased. From this result, we could presume that the packing rate of primary SiO₂ nanoparticles composing the walls of nanostructured porous particle decreased when the smaller PSL was used as templates. Besides, we also found that the porous particles prepared at 900 °C could not contain mesopore due to sintering of intra-particles. It means that the sintering should be suppressed by keeping the furnace temperature below 900 °C for the application as a catalytic supporter.

![Fig. 3](image3.png)

Fig. 3. SEM micrographs ((a)-(d)) and desorption pore size distributions (e) of nanostructured porous SiO₂ particles prepared with different sizes of PSL and furnace temperatures ((a) 161 nm, 600 °C; (b) 161 nm, 900 °C; (c) 83 nm, 600 °C; (d) 62 nm, 600 °C) while keeping the weight ratio of PSL/SiO₂, precursor concentration and flow rate of carrier air at 1.43, 0.1 M and 1 l/min, respectively.

![Fig. 4](image4.png)

Fig. 4. SEM micrographs ((a)-(d)) and desorption pore size distributions (e) of nanostructured porous SiO₂ particles prepared from various precursors having different weight ratios. With an increment of the weight ratio of PSL/SiO₂, the number of macropores increased. However, further increase in the PSL ratio led to the brittle and broken structure. For three contacting spheres (PSL particles) of diameter D (here, D = 161 nm) with a hexagonal packing arrangement, the maximum diameter, d, of a smaller sphere (SiO₂ nanoparticle) that can fit within the void space between sphere is $d = 0.155D \approx 25$ nm [6]. The increase in PSL/SiO₂ ratio led to a hexagonal packing arrangement of PSL in a PSL/SiO₂ mixed particle (Fig. 4(c) and 4(d)) and reduced the void space for SiO₂ nanoparticles to be packed. Considering the nominal diameter (15 nm) of SiO₂ nanoparticles, the maximum diameter (d ≈ 25 nm) is too small for SiO₂ nanoparticles to be packed and composed of the internal structure. Therefore, when the PSL packed hexagonally was removed, the brittle and broken structure was obtained. The weight ratio for the stable formation of macroporous particles was below 2.39 in our experiment. The pore size distribution showed broad distributions of mesopores with diameter of 3-6 nm (Fig. 4(e)). With an increment of the weight ratio of PSL/SiO₂, the mesopores size increased but the mesopores volume decreased gradually because the increment of PSL/SiO₂ ratio led to the brittle and broken structure and a reduction in the packing rates of primary SiO₂ nanoparticles.
ratios of PSL/SiO$_2$ ((a) 0.48, (b) 1.43, (c) 2.39, (d) 4.77; PSL size: 161 nm).

In order to investigate the effect of precursor concentration on the particle size, nanostructured porous SiO$_2$ particles were prepared from different concentrations of SiO$_2$ nanoparticles. The furnace temperature, PSL diameter, weight ratio of PSL/SiO$_2$, and flow rate of carrier air were kept at 600 °C, 161 nm, 2.39 and 1 l/min, respectively. The geometric mean diameters of the as-prepared particles according to the increment of precursor concentration were 0.56 μm (0.05 M), 0.68 μm (0.1 M), 0.91 μm (0.5 M) and 1.07 μm (1.0 M).

The furnace temperature and the flow rate of carrier gas were manipulated to find process conditions for the removal of residual of the organic template. Fig. 5 shows the FT-IR spectra of nanostructured porous SiO$_2$ particles prepared at different furnace temperatures and flow rates of carrier air: (a) 400 °C, 1 l/min; (b) 500 °C, 1 l/min; (c) 600 °C, 1 l/min; (d) 600 °C, 3 l/min; (e) 600 °C, 5 l/min. The FT-IR spectra revealed the C-H stretching vibrations at 3000-2850 cm$^{-1}$, the C=O stretching at 1715 cm$^{-1}$, C-H bending at 1375 cm$^{-1}$, C-O stretching at 1230 cm$^{-1}$, and Si-O-Si stretching at 1100 cm$^{-1}$. The vibrations by carbon content such as methyl and carbonyl groups continuously disappeared with an increment of furnace temperature and a decrement of flow rate of carrier gas. It was required to remove the residual of the PSL in our experiments at the furnace temperature above 500 °C and flow rate of carrier gas below 5 l/min.

4 CONCLUSIONS

Pore size-controlled synthesis of nanostructured porous silica particles containing both mesopores and macropores by the aerosol templating method was successfully conducted for the catalytic application. The smaller PSL template led to the decrement of the packing rate of primary SiO$_2$ nanoparticles composing the walls of nanostructured porous particles, resulting in the larger volume of mesopores. High furnace temperature reduced mesopores volume due to the sintering of intraparticles. Therefore, for the application as a catalytic supporter, the sintering should be suppressed by keeping the furnace temperature below 900 °C. The increment of PSL/SiO$_2$ ratio resulted in a brittle and broken structure of particles and a reduction in the packing rates of primary SiO$_2$ nanoparticles. It was required to remove the residual of the PSL in our experiments at the furnace temperature above 500 °C and flow rate of carrier gas below 5 l/min.