

Synthesis of Mesoporous Silica Microspheres by Using Polymeric Surfactant

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1. Introduction

Since mesoporous M41S families were discovered by Mobil Corporation researchers [1,2], synthesis of the mesoporous materials with novel morphologies and pore structures because of their potential applications as versatile catalysts, catalyst supports, separation media, and hosts for clusters and have been reported through various synthetic strategies by using surfactant-templated process. Spherical morphology has become quite attractive in many applications such as a packing material in chromatography or as an easy-to-handle form for catalytic purposes [3]. Based on modified Stöber process [4], the synthesis of the spherical mesoporous silica particles with sub-micrometer size has been reported [5-7]. However, Modified-Stöber process in a homogeneous environment for preparing mesoporous silica spheres rarely produce silica particles larger than 10 μm . Recently, Kosuge and Singh have directly synthesized the silica microspheres of 30 ~ 50 μm in diameter by using n-alkylamine ($\text{C}_{12}\text{-NH}_2$) and ethanol in an acidic medium at room temperature [8]. Also, Stucky et al. reported the slow sol-gel surfactant template synthesis of mesoporous silica spheres larger than 100 μm [9]. In our previous study [10], we reported a new robust surfactant-template synthesis strategy for the stable suspension of large silica microspheres by introducing an additional cosurfactant. Bis(2-ethylhexyl)phosphate (BEHP) as a cosurfactant played a key role in suspension stabilization without distorting the spherical morphology as well as in the formation of uniform pore structures. Although most mesoporous silica particles above mentioned possess the narrow pore size distribution, high surface area, and large pore volume, their pore structure consists to the single pore system. Recently, mesoporous materials with bimodal pore systems are of considerable interest for applications in catalysis and separations, since they combine the benefits of each pore size regime [11-13].

2. Methods and Results

2.1 Synthesis of Mesoporous Silica Spheres

Premixture of tetraethyl orthosilicate (TEOS, Acros, 98 %), n-dodecylamine ($\text{C}_{12}\text{-NH}_2$, Junsei, 98 %), and absolute ethanol (EtOH, Daejung, 99.9 %) were quickly poured into the round bottom flask containing acidic aqueous solution and polymeric surfactant. IKA RW20 DZM.n motorized stirrer with PTFE collapsible impeller was used for mixing at a controlled rate of 400 rpm at

ambient temperature for 1 h. The initial reactant mixtures were comprised of TEOS/ $\text{C}_{12}\text{-NH}_2$ /polymeric surfactant/EtOH/HCl/ H_2O . The resultant as-synthesized silica suspensions were filtered and washed with EtOH. Samples were then dried at 70 $^\circ\text{C}$ for overnight, and calcined at 550 $^\circ\text{C}$ for 7 h in air.

2.2 Characterization

Scanning electron microscope (SEM) images were collected with Hitachi S-4700 microscope operated at an acceleration voltage of 10 kV. Transmission electron microscope (TEM) images were obtained using EM 912 Omega microscope operated at 120 kV. The nitrogen adsorption and desorption isotherm measurements were made on a Micromeritics ASAP 2000 at 77 K. The samples were treated by vacuum degassing overnight on the ASAP 2000 at 623 K before isotherm measurements. Pore size distribution was calculated from the adsorption branch of the nitrogen isotherm using the BJH (Barrett-Joyner-Halenda) method. The BJH adsorption average pore diameter was obtained from Gurvitch ($4V_{\text{BJH}}/S_{\text{BJH}}$) method, assuming a cylindrical pore geometry, where V_{BJH} is BJH adsorption cumulative pore volume for pores between 1 and 350 nm in diameter.

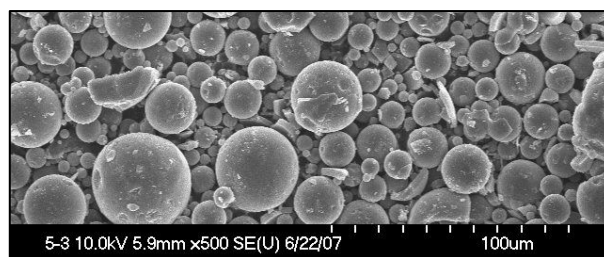


Figure 1. Representative SEM images for the mesoporous silica microspheres synthesized by using a polymeric surfactant.

2.3 Pore Structures of Silica Microspheres

Scanning electron microscope (SEM) images for the mesoporous silica microsphere in this study showed that the silica particles with spherical morphologies were successfully obtained by using $\text{C}_{12}\text{-NH}_2$ and polymeric surfactant as templates (Fig. 1). Spherical morphology of the mesoporous silica microspheres prepared in this work was retained, as expected from the previous study [10], although some broken particles were shown in

SEM image. Also, mesopore structures for the silica microspheres synthesized by using a polymeric surfactant were clearly seen in transmission electron microscope (TEM) images (Fig. 2). It is interesting to observe that polymeric surfactants plays an important role for the formation of the large mesopores and the suspension stability of the silica particles, compared with the silica microspheres prepared by using only C_{12} - NH_2 as a template in our previous report [10].

The N_2 adsorption and desorption isotherms and pore size distribution curves for the samples prepared by using a polymeric surfactant were also investigated. These materials exhibited type IV adsorption isotherms with a hysteresis loop according to the IUPAC classification [15]. BET surface area and total pore volume for the samples synthesized were $\sim 1,000 \text{ m}^2/\text{g}$ and $\sim 1.5 \text{ cm}^3/\text{g}$, respectively. Mesopores were within the wide range from 1 \sim 30 nm in diameter.

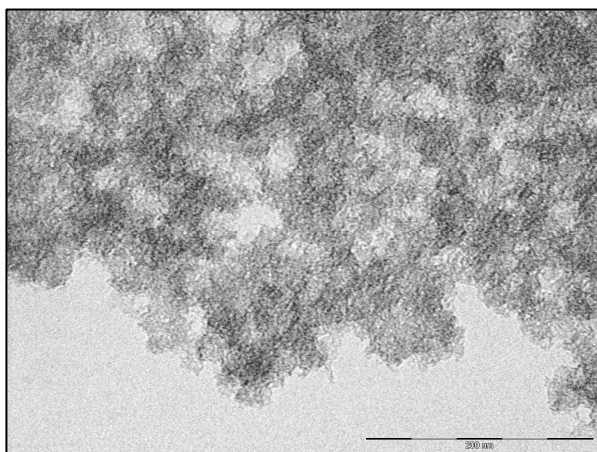


Figure 2. Representative TEM images for the mesoporous silica microspheres synthesized by using a polymeric surfactant.

3. Conclusion

Synthesis of mesoporous silica microspheres was investigated by using C_{12} - NH_2 and a polymeric surfactant as a soft template. In our study, it was found that a polymeric surfactant as a cosurfactant played an important role for the formation of the large mesopores and the suspension stability of the mesoporous silica microspheres, compared with those prepared by using C_{12} - NH_2 in the absence of a cosurfactant. In addition, the role of polymeric surfactant as a suspension stabilizer was found to be similar with that of BEHP as mentioned in our previous report. The mesoporous silica microspheres prepared using a polymeric surfactant in this study will be useful in many applications for the catalysis, separation and purification process, biotechnologies, single particle microanalyses, and column packing materials.

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