

Effect of Synthesis Conditions on the Morphology of Mesoporous Silica Microspheres

Sun Kyung Ji, Yong Suk Choi, Yong Joon Park, Jong–Yun Kim*

Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daedukdaero 1045,
Yuseong-gu, Daejeon, 305-353, Korea

*Corresponding author: kjy@kaeri.re.kr

1. Introduction

Since the study by Stöber *et al.* in 1968 on the synthesis of monodisperse non-porous silica spheres by using tetraethoxysilane (TEOS) as a silica precursor in an alcoholic medium under a highly basic condition, plenty of papers have been published in regard to the sol-gel surfactant template synthesis of mesoporous silica spheres smaller than 10 μm through the modified Stöber process [1]. However, mesoporous silica materials are generally non-spherical micrometer-sized powders, and only a few studies on silica microspheres larger than 10 μm via surfactant-template method have been reported, where the emulsion technique in the surfactant template synthesis methods was used to prepare macrospheres larger than 100 μm (Stucky *et al.*, Mizukami *et al.*, and Mou *et al.*), while Kosuge and Singh have directly synthesized the silica microspheres of 30~50 μm in diameter [2-8]. But the spherical morphologies of the particles produced by using the emulsion technique are highly dependent on the synthesis conditions such as the shape of the impeller, the composition of the reactants, the size of the reactor, stirring rate, etc. Therefore, it is extremely difficult to prepare a high-quality mesoporous silica microsphere in a reproducible way.

Recently, we reported on a new direct synthesis for the silica microspheres of 10~100 μm in diameter by using HDEHP as a cosurfactant. Our new synthesis resulted in well-segregated silica microspheres with uniform pore structures compared to the microspheres synthesized by Kosuge and Singh. In this preliminary study, the effect of the synthetic conditions such as the type of the stirrer, stirring rate, etc. on the morphology of the silica microspheres is investigated for the development of mass production process.

2. Experimental Details and Results

2.1 Materials

Tetraethyl orthosilicate (TEOS, 98%) purchased from Sigma-Aldrich Co. was used as the silica precursor. N-dodecylamine (98%) as a templating agent was obtained from Junsei Co. Di(2-ethylhexyl)phosphoric acid (HDEHP) as a cosurfactant obtained from Merck Co.

2.2 Preparation of mesoporous silica microspheres

Based on our previous synthesis [9], premixture of TEOS, n-dodecylamine, HDEHP and absolute ethanol

(EtOH) were directly poured into on aqueous solution with or without an acid catalyst, and stirred at a controlled rate at room temperature for 1h. The resultant as-synthesized silica suspension were filtered and washed with distilled water. Samples were the dried at 80 $^{\circ}\text{C}$ for 9h, and calcinated at 550 $^{\circ}\text{C}$ for 8h in air.

The molar composition of a premixture in a mother was 1 TEOS: 0.34 n-dodecylamine: 262 H₂O: 0.12 HDEHP: 0.9 EtOH: 0.019 HCl. To examine the effect of the type of mixing on the particle morphology, two-blade folding impeller and magnetic stirrer were used in the present study as shown in Fig. 1.

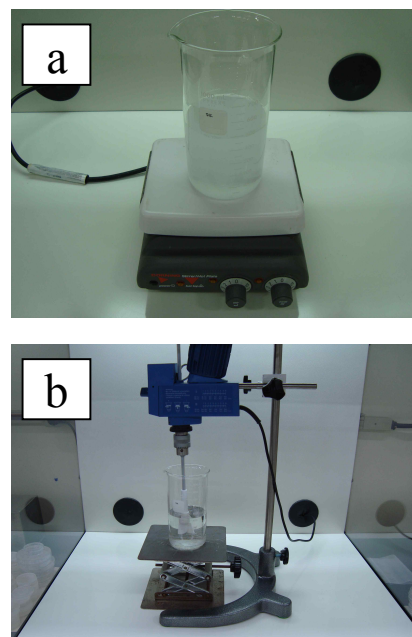


Fig. 1. Experimental apparatus for the preparation of silica microspheres. (a) magnetic stirrer, and (b) mixer equipped with two-blade folding impeller.

2.3 Characterization

The nitrogen adsorption and desorption isotherm measurements were made with a Micromeritics ASAP 2010 at 77 K. The samples were pretreated by a vacuum degassing overnight at 573K before the isotherm measurements. Pore size distribution was calculated from the adsorption branch of the nitrogen isotherm by using the BJH (Barrett-Joyner-Halenda) method. The BJH adsorption average pore diameter was obtained

from the Gurvitch method, by assuming a cylindrical pore geometry.

2.4 Morphology of mesoporous silica microspheres

Transparent mesoporous silica microspheres were obtained by using the simple surfactant template synthesis method as shown in Fig. 2. Mesoporous silica microspheres prepared without HDEHP seemed to be translucent and smaller than silica prepared from the reactant mixtures containing HDEHP, which is a double-tail anionic surfactant forming reverse micelles in apolar media. As reported in our previous study, surface of the as-synthesized silica microspheres prepared with HDEHP were hydrophilic whereas those of the particles prepared without HDEHP were hydrophobic. Both magnetic stirrer and mixer equipped with two-blade folding impeller made no significant impact on the spherical morphology of the silica particles. The effect of the size of the reactor was also examined by using different size of the beaker. Size of the silica microspheres increased with the size of the beaker.

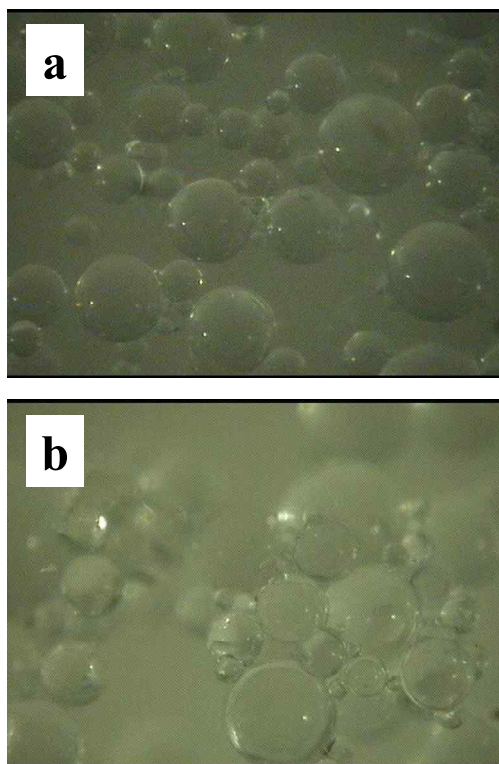


Fig. 2. Representative optical microscopic images ($\times 300$) of mesoporous silica microspheres. (a) silica particles prepared by magnetic stirrer, and (b) silica particles prepared by using the mixer equipped with two-blade folding impeller.

3. Conclusions

Preliminary information on the effect of the synthesis conditions is of importance in the development of mass

production process, since the particle morphologies as well as the pore structures and their uniformity depend on the synthesis conditions of the mesoporous silica via a surfactant template synthesis route. In our previous report, mixer equipped with a two-blade folding impeller was used to prepare the silica microspheres. Magnetic stirrer was found to be equally effective to obtain these mesoporous silica microspheres.

REFERENCES

- [1] W. Stober, J. Colloid Interface Sci., Vol.26, p. 62-69, 1968.
- [2] H. Izutsu, F. Mizukami, P. K. Nair, Y. Kiyozumi, and K. Maeda, J. Mater. Chem., Vol.7, p. 767-771, 1997.
- [3] Q. Huo, J. Feng, F. Schuth, and G. D. Stucky, J. Mater. Chem., Vol.9, p. 14-17, 1997.
- [4] C. -P. Kao, H. -P. Lin, C. -Y. Mou, J. Phys. Chem. Solids., Vol.62, p. 1555-1559, 2001.
- [5] H. -P. Lin and C. -Y. Mou, Acc. Chem. Res., Vol.35, p. 927-935, 2002.
- [6] K. Kosuge, P. S. Singh, Acc. Chem. Mater., Vol.13, P. 2476-2482, 2001.
- [7] K. Kosuge, T. Murakami, N. Kikukawa, M. Takemori, Acc. Chem. Mater., Vol.153, P. 3184-3189, 2003.
- [8] K. Kosuge, N. Kikukawa, M. Takemori, Acc. Chem. Mater., Vol.16, P. 4181-4186, 2004.
- [9] J. -Y. Kim, S. B. Yoon, M. H. Lee, Y. J. Park, W. H. Kim, and K. Y. Jee, Journal of Nanoscience and Nanotechnology, Vol.7, p. 3862-3866, 2007.