Synthesis of Mesoporous Silica Microspheres by Using Di(2-ethylhexyl)phosphoric Acid as a Potential Sorbent for Radioactive Material

Suk Bon Yoon, Jong-Yun Kim, Myung Ho Lee, Yong Joon Park, Kwang Yong Jee, and Won-Ho Kim
Korea Atomic Energy Research Institute, 150, Yuseong-gu, Daejeon, 305-353
ysb@kaeri.re.kr

Much efforts for the mesoporous inorganic synthesis by using organic or inorganic templates have been devoted to the synthesis of the mesoporous materials with various structures and shapes, thanks to the discovery of M41S silica families by Mobil scientists in 1992 [1]. Since the advantage of spherical morphology is clearly manifested in a variety of academic and industrial applications [2], synthesis and morphology control of spherical mesoporous silica nanoparticles less than 1 ㎛ have been extensively investigated to discover any unexpected physical and chemical properties, generally owing to their large surface-to-volume ratios or quantum-size effect. Prior investigations thus far show that the size of mesoporous silica spheres larger than *ca.* 10 ㎛ can hardly be obtained by the method based on Stöber process in the presence of structure-directing agent. A few studies, on the other hand, are available on the mesoporous silica spheres larger than 100 ㎛ [3]. In addition, it requires at least 1 day to complete the reaction or hydrothermal condition. Novel rapid synthesis of 10 - 100 ㎛ mesoporous silica spheres via $S^+X^-I^+$ assembly process was first reported by Kosuge and Singh [4].

In this study, based on Kosuge's method, tetraethyl orthosilicate (TEOS), n-dodecylamine as a structure-directing agent, and/or di-2-ethylhexyl phosphoric acid (HDEHP) as a cosurfactant, hydrochloric acid as a acid catalyst were used to prepare micrometer-sized mesoporous silica spheres. In a typical synthesis, TEOS (Acros, 98%), n-dodecylamine (Junsei, 98%), HDEHP (TCI, 95+%) and EtOH (Daejung, 99.9%) were premixed for 30 min. The premixture was quickly poured into the acidic aqueous solution, and mechanically stirred at a controlled rate with a Teflon-coated half moon impeller using a RW20 DZM.n (Janke&Kunkel Gmbh&Co, IKA-Labortechnik, Germany) at room temperature for 6 hours. The resultant as-synthesized silica suspensions were filtered and washed with EtOH. Samples were then dried at 80 °C for overnight, and calcined at 550 °C for 7 h in air. The molar composition of reaction mixture was 1 TEOS: 0.34 n-dodecylamine: 0-0.30 HDEHP: 0.85 EtOH: 32.7-261.5 H_2O: 0-0.038 HCl depending on the amount of HCl. As shown in Fig. 1 ~ Fig. 3, polydisperse mesoporous silica spheres were successfully prepared.

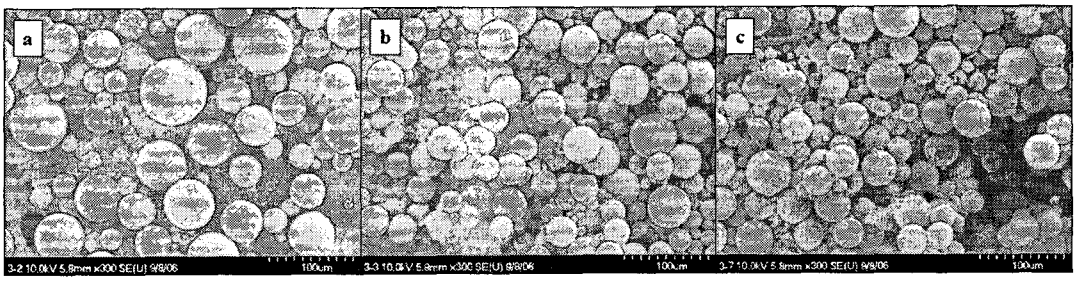

Fig. 1. Effect of stirring rate on the morphology of mesoporous silica microspheres. (a) 400 rpm, (b) 500 rpm, and (c) 600 rpm

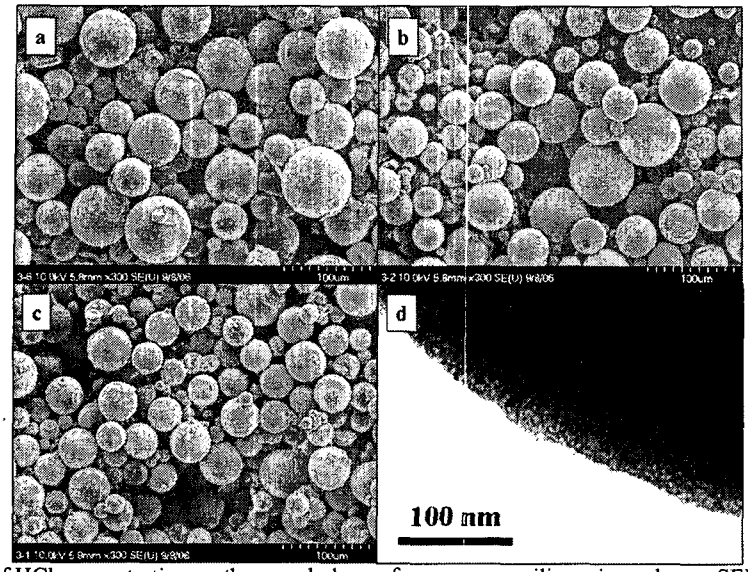

Fig. 2. Effect of HCl concentration on the morphology of mesoporous silica microspheres. SEM images of silica microspheres using (a) no HCl, (b) 0.42 mL HCl, (c) 0.83 mL HCl, respectively, and (d) TEM image of mesoporous silica synthesized using 0.83 mL HCl.

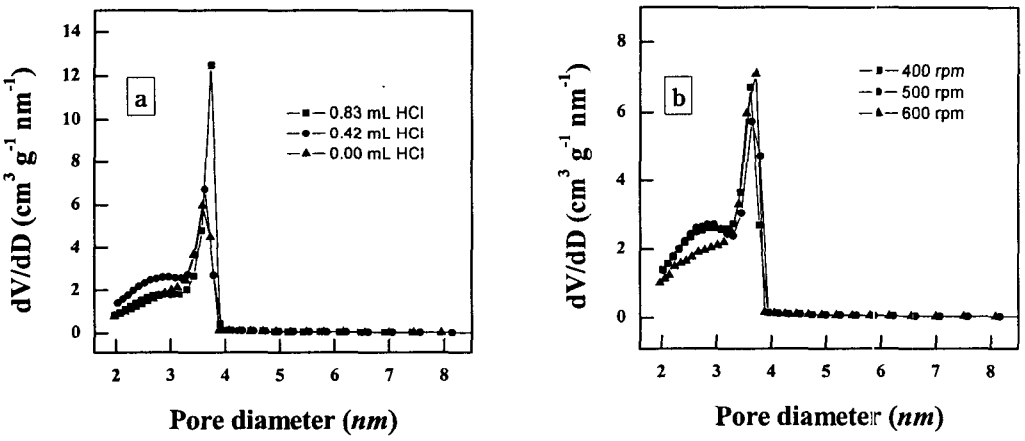

Fig. 3. Pore size distribution of mesoporous silica spheres. Effect of (a) HCl concentration, and (b) stirring rate.

References

1. Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli J.C., and Beck, J.S., " Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism", Nature, 359, 710 (1992).
2. Xia, Y., Gates, B., Yin, Y., and Lu, Y., "Monodispersed colloidal spheres: Old materials with New Applications", Adv. Mater. 12(10), 693 (2000).
3. Huo, Q., Feng, J., Schuth, F., and Stucky, G.D., "Preparation of Hard Mesoporous Silica Spheres", Chem. Mater. 9(1), 14(1997).
4. Kosuge, K., and Singh, P.S., "Rapid Synthesis of Al-Containing Mesoporous Silica Hard Spheres of 30-50 ㎛ Diameter", Chem. Mater. 13, 2476 (2001).