

Uniform Pore Structure of Mesoporous Silica Microspheres by Using Di(2-ethylhexyl)phosphoric Acid

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1. Introduction

Spherical morphology has been quite attractive in many special applications, such as display materials offering higher packing densities and lower light scattering for better performances in terms of both brightness and resolution, biosensors utilizing microspheres as an ideal dielectric cavities with high quality factors in optical domain, and standard reference particles for nuclear track analysis utilizing their simple well-defined geometry.[1-3] There are tremendously a wide variety of studies focused on colloidal spheres of 1 nm ~ 1,000 nm in diameter although the colloidal dimension can be extended further to 100 μm . [4] Some reports have described the sol-gel surfactant template synthesis of mesoporous silica spheres larger than 100 μm . [5] It is necessary for us to prepare the intermediate 10 ~ 100 μm -sized silica microspheres for the single particle manipulation by using optical microscope, rather than electron microscope, in a microanalytical technique such as thermal ionization mass spectrometry, secondary ionization mass spectrometry, and laser ionization mass spectrometry. Modified-Stöber processes in a homogeneous environment for preparing mesoporous silica spheres can hardly produce the silica particles larger than 10 μm . [6] Although the evaporation-induced self-assembly by using vibrating orifice aerosol generator can produce the mesoporous microspheres larger than 10 μm by adjusting the orifice dimension, its synthesis route has the disadvantages of requiring several steps and a high-temperature furnace during the synthesis. [7] There have been some reports on the mesoporous silica spheres smaller than 2 μm using n-alkylamine since the first introduction of n-alkylamine as a surfactant template by Pinnavaia and co-workers in 1995, and subsequently Kosuge and Singh directly synthesized the silica microspheres of 30 ~ 50 μm in diameter by using n-alkylamine as a surfactant template, and ethanol as a cosolvent in an acidic medium at room temperature. [8-10] But particle morphologies is highly dependent on the composition of the reactants and reactor design, and therefore a great care should be taken to get a reproducible and high-quality mesoporous silica microspheres.

2. Methods and Results

2.1 Synthesis of Mesoporous Silica Spheres

Based on the Kosuge's method [9], premixture of tetraethyl orthosilicate (TEOS, Acros, 98%), n-dodecylamine (Junsei, 98%), Di(2-ethylhexyl) phosphoric acid (HDEHP, TCI, 95+%), and absolute ethanol (EtOH, Daejung, 99.9 %) were quickly poured into the acidic aqueous solution, and stirred at a controlled rate of 400 rpm without special notice at ambient temperature for 1 h to prepare micrometer-sized mesoporous silica spheres. The molar composition of reaction mixture was depicted in Table 1. The effect of stirring rate was studied at 400 rpm, 500 rpm, and 600 rpm, respectively. 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. Experimental conditions of the mother liquor were depicted in Table 1.

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, and S_{BJH} is BJH adsorption cumulative surface area.

2.3 Pore Structures of Silica Microspheres

There were enormous changes in the N₂ adsorption and desorption isotherm curves for representative K-HCl series samples. Variation of hydrochloric acid concentration in a reaction mixture largely altered the pore structures, and showed complex and relatively broad pore size distribution due to the textural mesopores between the large mesoporous silica microspheres. Compared with the N₂ isotherms of silica microspheres synthesized in the absence of HDEHP, HDEHP played an crucial role in the formation of the

Table 1. Experimental conditions of the mother liquor.

sample	Molar ratio		
	X ^a	y ^a	z ^a
K-HCl-1	-	38	-
K-HCl-2	-	38	1.2×10 ⁻³
K-HCl-3	-	38	2.4×10 ⁻³
K-HCl-4	-	38	3.6×10 ⁻³
K-HCl-5	-	38	4.8×10 ⁻³
K-H ₂ O-3	-	262	19.0×10 ⁻³
K-HDEHP-1	0.06	38	4.8×10 ⁻³
K-HDEHP-2	0.12	38	4.8×10 ⁻³
K-HDEHP-3	0.18	38	4.8×10 ⁻³
K-HDEHP-4	0.24	38	4.8×10 ⁻³
m-H ₂ O-1	0.12	65	4.8×10 ⁻³
m-H ₂ O-2	0.12	131	9.5×10 ⁻³
m-H ₂ O-3	0.12	262	19.0×10 ⁻³
m-HCl-1	0.12	262	-
m-HCl-2	0.12	262	19.0×10 ⁻³
m-HCl-3	0.12	262	38.0×10 ⁻³

^a The molar composition of reaction mixture was 1 TEOS: 0.34 n-dodecylamine: x HDEHP: 0.9 EtOH: y H₂O: z HCl in a mother liquor.

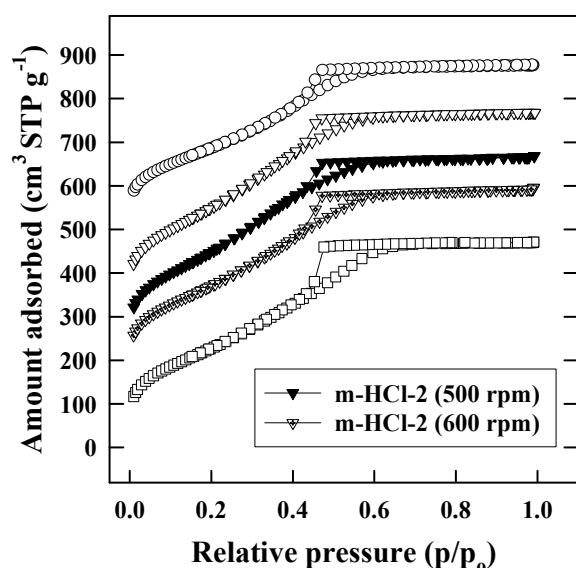


Figure 1. N₂ adsorption/desorption isotherms of (○) m-HCl-1, (▽) m-HCl-2, and (□) m-HCl-3. Inset legends designate m-HCl-2 samples prepared at a different stirring rate. The curves are shifted vertically against each other for a better visibility.

remarkably stable pore morphologies, in terms of surface area, pore volume, pore size, and pore size distribution, with the variation of hydrochloric acid concentration, as shown in Figure 1. A slight variation of stirring rate from 400 ~ 600 rpm inducing a big changes in the morphologies of the silica microspheres in the absence of HDEHP had little effect on the pore structures of the m-HCl series samples thanks to the contribution of HDEHP as a wetting agent to the formation of the uniform pores.

3. Conclusion

HDEHP or any structurally related surfactant molecules such as sodium di(2-ethylhexyl)sulfosuccinate (AOT) has never been used as a cosurfactant in the surfactant template synthesis for the preparation of mesoporous silica microspheres. The dual role of HDEHP as a suspension stabilizer and cosurfactant with a surfactant template agent in the mesoporous silica microsphere synthesis was found through this study. Besides our special interests in a well-divided silica microsphere as a standard reference particle with uniform pore structures in a microanalytical technique, application of 10 ~ 100 μm mesoporous silica microspheres via the robust synthesis method will be promising for the biotechnologies, e.g., cell-mimicking microspheres, versatile platforms for high-throughput protein assays, and microfluidic immunoassays.

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