The Synthesis of Mesoporous Silica Spheres by Octylamine Templating

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Mesoporous silica hollow spheres have been synthesized by a simple route of hydrolysis of acidic tetraethylorthosilicate solution with octylamine surfactant at ambient temperature.The resultant silica spheres have high BET surface areas of 850 to 950 m^2/g and mesopore diameters of *ca.* 2 nm after the samples were calcined in air at 500 °C. The shell thickness of the spheres can be varied by changing the synthesis composition of the reaction system.

Due to its regular pore structure and appreciable high surface areas, M41s type mesoporous silica offers unique properties in separation science and technology. M41s type had been used as a packing material in size exclusion chromatography,[1a] normal phase chromatography[1b] and capillary gas chromatography.[1c] To develop M41s type as an efficient packing material in chromatography, the control of definite particle size and morphology of M41s might be a neccessity. The reported synthesis of mesoporous silica spheres of M41s type[2] by modifying Stöber's procedure of monodisperse silica spheres[3] open up the possibilities of efficient uses of M41s type in chromatography.

In Stöber's procedure of monodisperse silica spheres and in modified Stöber's procedure for mesoporous M41s type silica spheres, aqueous ammonia or a strong base (NaOH, KOH, LiOH, RbOH or, TMAOH) was used as a catalyst to initiate the hydrolytic polycondensation of the drops of tetraalkylorthosilicate. Recently, without any base catalyst, Schacht *et. al* [4] have produced silica hollow spheres of M41s type by controlled hydrolysis of tetraalkylorthosilicate in a stabilized emulsion of a biphasic system. The synthesis by this route involves the use of long alkyl chain (C_{19}) quaternary ammonium surfactant, an organic auxillary and an acidic aqueous solution.

We synthesized mesoporous silica hollow spheres of different shell thickness by a simplified method, closely related to that of Schacht *et. al*, the difference being use of low cost, short alkyl chain (C_8) octylamine as a surfactant and no auxiliary organic. The additional sovent which is commonly used in M41s type synthesis, such as, alcohol was also not employed. The resultant mesoporous silica spheres have high BET surface areas of 850 to 950 m^2/g and mesopore diameters of *ca.* 2 nm after the sample were calcined in air at 500 °C. The shell thickness of the spheres can be varied by changing the synthesis mixture composition .

A typical procedure for the synthesis is as follows: tetraethylorthosilicate (TEOS) was mixed with HCl aq. in a molar ratio of 1:0.4, followed by addition of octylamine (the molar ratio of octylamine to tetraethylorthosilicate was 1:1.7). The mixture was then vigorously stirred for 24 h and the solid products were separated by centrifugation, dried at 50 °C and finally calcined at 500 °C for 2 h to yield mesoporous material. The morphological change was not observed before or after calcination at 500 °C. No special precautions (heating steps during ramping, atmosphere) are needed during the calcination.

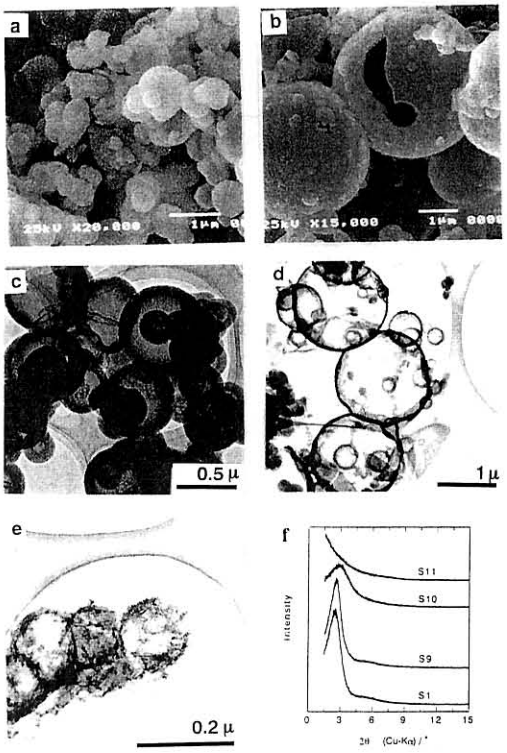


Figure 1. Scanning electron micrographs for (a) S5, (b) S9 samples. Transmission electron micrographs for (c) S5, (d) S9 and (e) S10 samples. X-ray diffraction patterns (f) of samples (Sample S1, S9, S10, S11) after the samples were calcined at 500 °C.

Figure 1a-d shows scanning and transmission electron microscopy images of two samples (Sample S5 and S9) at different magnifications. As shown by the electron micrographs, the sample S9 shows a thin wall hollow spheres, in contrast to a thick wall hollow spheres of sample S5. For the sample (Sample S10), obtained at very low acid concentration of the synthesis mixture, only few imperfect spheres are seen (Figure 1e) and the XRD intensity of d_{100} reflection is considerably weak and broad (Figure 1f). Further, at high acid concentration (>0.020 moles of dissolved HCl in the acidic aqueous solution), the tetraethylorthosilicate is not completely hydrolyzed and, thus mesostucture quality considerably decreases (datas are not shown).

N_2 adsorption-desorption isotherm of two samples (S6, S9) and corresponding HK plot[5] are shown in Figure 2. The materials have high BET surface areas of *ca.* 850-950 m^2/g, framework pore volumes of 0.5-0.7 cm^3/g (framework pore volume is determined by *t*-plot analysis[6]) and uniform mesopore diameters of *ca.* 2 nm. In Table 1, examples of porous properties of the samples obtained by different synthesis mixture

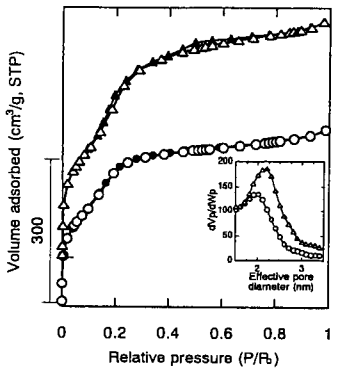


Figure 2. N2 adsorption-desorption isotherms and the corresponding HK plots for two samples (Δ S6; O S9) after the samples were calcined in air at 500 °C; open symbols indicate adsorption branch; closed symbols indicate desorption branch.

Table 1 Porous properties of mesoporous silica spheres obtained by using octylamine as a surfactant

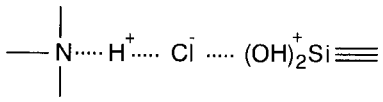
S[a]	V[b] (ml)	HCl[c]/ moles	BET[d] $m^2.g^{-1}$	PV[e] $cm^3.g^{-1}$	d[f] nm
S1	20	0.0100	864	0.68	2.4
S2	20	0.0126	954	0.66	2.1
S3	20	0.0150	919	0.58	2.0
S4	20	0.0176	913	0.60	2.0
S5	20	0.0200	844	0.45	2.0
S6	25	0.0125	981	0.66	2.2
S7	30	0.0150	974	0.65	2.1
S8	35	0.0175	951	0.57	2.0
S9	40	0.0200	874	0.49	2.0
S10	5	0.0020	1269	0.72	1.1
S11	50	0.0020	701	0.48	1.2

[a]Sample numbers; [b]The volume of acidic aqueous solution and it is the corresponding volume for a given 10 ml of tetraethylorthosilicate in the synthesis composition system; [c]moles of dissolved HCl in the given acidic aqueous solution; [d]BET surface area; [e]Framework pore volume and is determined by *t*-plot; [f]pore diameter and is determined by HK plots, except for the 'sample S10 and S11' which is determined by MP plots.

compositions are listed. The samples obtained from the synthesis mixture having an acidic aqueous volume of 20-40 ml containing 0.01-0.02 moles of HCl (S1, S2...S9) have mesopore diameters of *ca.* 2 nm whereas the samples (S10, S11) with low acid concentration (0.002 moles of HCl) of acidic aqueous solution have the micropore diameter of *ca.* 1 nm (as revealed by HK and MP plot analysis[7]). As indicated above, the surface morphologies and their porous properties are strongly influenced by concentration and volume of acidic aqueous solution of the synthesis mixture.

The above results of electron microscopy, X-ray diffraction and N_2 adsorption-desorption isotherm are the clear indications of mesoporous silica spheres with uniform framework-confined pores. These silica hollow spheres might be nucleated on the functionalized surface, formed by preorganized supramolecular organic-inorganic assembly in acidic aqueous medium. The possible mechanism for the formation of these hollow spheres are discussed as below.

The tetraethylorthosilicate hydrolyze in acidic medium to silicic acid or positively charged oligomeric intermediates, such as $\equiv Si(OH_2)^+$.[8] The positively charged silica species are attracted electrostatically to the protonated amine template through coordinating anions forming an electrical triple layer as below.



The ions, (which coordinate the silicic acid and amine template through Coulombic interaction), might act as structural buffer that can stretch and pack to accomodate the density of the ordered inorganic and organic supramolecular assemblies. This stabilized inorganic-organic emulsion formed by coordinationg ions might be responsible for the formation of mesoporous silica spheres since silica spherical particles are usually made from controlled hydrolysis of silicon esters in a stabilized emulsion of a biphasic system.[2,3]

The occurance of the following events seems to be indicated by the experiments. The tetraethylorthosilicate hydrolyze in acidic aqueous medium to positively charged oligomeric intermediates. The positively charged silica oligomers are attracted electrostatically to protonated amine template through the coordinating anions of acidic aqueous solution. Precipitation and polymerization of silica occurs on the surface of templating primary amine aggregate. The curvature of the templating aggregate-acidic aqueous-silica oligomers is controlled by Coulombic interaction between them. Depending on the degree of curvature, different surface pattern of mesoporous silica are resulted.

In conclusion, mesoporous silica hollow spheres have been synthesized by a simple route of hydrolysis of acidic tetraethylorthosilicate solution with octylamine surfactant. This material may play an important role in the developement of packing materials for chromatography and in the mineralization of biomimetic materials.

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