Synthesis of Mesoporous Silica Nanoparticles from a Low-concentration C_nTMAX–Sodium Silicate Components

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The 30–100 nm primary particles of mesoporous silica have been conveniently synthesized from a highly dilute aqueous solution of C_nTAMX–sodium silicate.

The long-established uses of nano-sized fumed silica powders appear to be as a catalyst base, adsorbent, reinforcing filler of polymer, and additives for many industrial applications.[1] In principle, the mesoporous silicas with high porosity must possess the advantages (such as high porosity and surface area) over fumed silicas in applications only when the particle size can be reduced to nano-scale.[2,3] In this regard, various synthetic approaches using complicated compositions have been provided to prepare the nanoparticles of mesoporous silica.[4–6] Here, we judiciously designed a simple synthetic approach based on the concepts of kinetics to prepare the nano-size mesoporous silica from a highly-diluted aqueous solution of surfactant–sodium silicate, in which the mutual aggregation rate of the primary nanoparticle could be reduced.[7]

The detailed synthesis process is as followed; a proper amount of sodium silicate (Aldrich), sodium hydroxide and C_nTMAX (alkyltrimethylammonium halide, $n = 14$–18; X = Br or Cl) surfactant (Acrôs) were dissolved into a suitable amount of water to form a clear solution with pH value of 11–12 at 40 °C. The solution was stirred for 10–20 min, and then sulfate or acetate acid water solution was poured, and the pH value of the solution droped down to 9.0–5.5. The chemical composition of the gel solution in molar ratio is; 1.0 C_nTMAX:2.12 SiO_2:3.32 NaOH:5600 H_2O:(1.55–1.75) H_2SO_4 or (2.84–3.57) CH_3COOH. Because of the extremely low concentration of silicate–surfactants (ca. 1.0×10^{-2} M), a period of induction time about minutes was required to observe a gradual change of that clear solution to a translucent gel solution, rather than an immediate creation of white gel in a typically high-concentration silicate–surfactants solution (ca. 5.0–0.1 M).[8] The induction time increase with the decrease of pH value. The final gel solution is stable as a colloid suspension. Filtration, washing, and drying gave the as-made mesoporous silica product. For removing the organic templates, a 560-°C calcination in air for 6 h or a 1.0 HCl–ethanol solution-extraction process was performed.

Figure 1a shows the XRD patterns of the mesoporous silicas synthesized from different pH value of 9.0, 7.0, and 5.5, respectively. All products exhibit broad XRD peaks, and the mesoporous silica obtained at lower pH reaction media has larger *d*-spacing value. The TEM images reveal that the particle size of all these products is less than 100 nm (Figures 1a–1c). With careful observations, one can find that the content of the larger particles (ca. 80–100 nm) with well-ordered hexagonal mesostructures (indicated by an arrow in Figure 1b) is higher in the sample of pH = 9.0.[4] Besides, the averaged particle size decreases upon decreasing the pH value. When decreasing the pH value to 5.5, the particle size could be reduced to nearly 30 nm, and the particle size distribution become more uniform. The high-resolution TEM image shows that the small particles (<50 nm) are consisted of the wormhole-like mesostructures rather than the hexagonal structure of typical MCM-41silicas. Up to our knowledge, this is the first time to conveniently obtain the uniform nano-particles of mesoporous silicas using sodium silicate as the silica precursors under the neutral condition (i.e. pH value = 7.0–5.5).

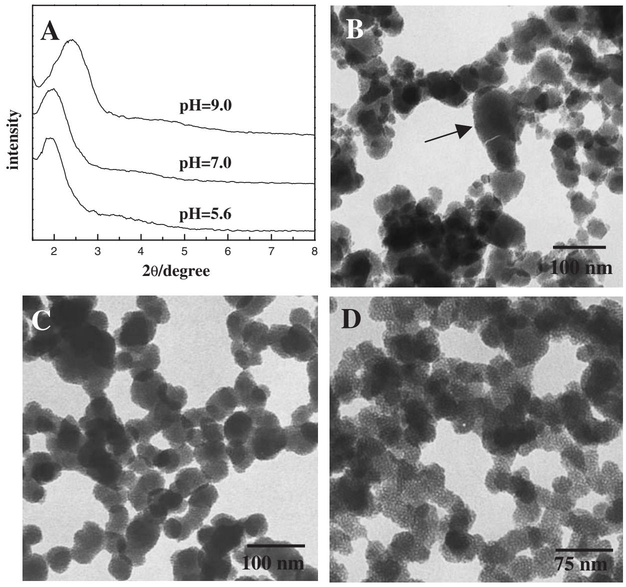

Figure 1. The XRD patterns (A) and TEM micrographs (B–D) of the mesoporous silicas synthesized from the C_{16}TMAB–sodium silicate-H_2O compositions at 40 °C in the reaction media of different pH values. Sample I. pH = 9.0; Sample II. pH = 7.0; Sample III. pH = 5.5; (B) TEM micrograph of Sample I, average particle size ca. 70 nm; (C) TEM micrograph of Sample II, average particle size ca. 50 nm; (D) TEM micrograph of Sample III, average particle size ca. 30 nm.

Figure 2 demonstrates the N_2 adsorption–desorption isotherms of the samples in Figure 1. In addition to the typical mesoporous capillary adsorption at partial pressure (P/P_0) of 0.20–0.30, there exists the extra capillary condensation at $P/P_0 >$ 0.85. The appearance of this additional condensation is ascribed to the filling of the textural mesoporosity, which results from the inter-aggregation of the nanoparticles by a capillary force upon drying.[1,9] From an approximate calculation, about 60–70% total pore volume is from the textural mesoporosity, and the smaller primary particles intrinsically have the larger adsorption of textural mesoporosity. This characteristic observed in all the sam-

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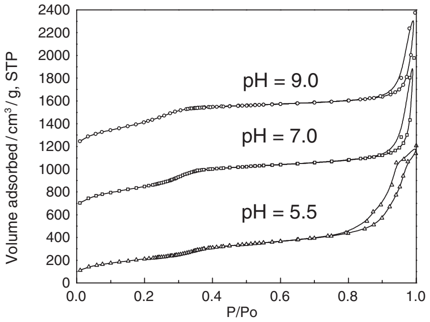

Figure 2. The N_2-adsorption–desorption isotherms of the calcined samples of Figure 1.

ples aforementioned indicates that the particles are in nano-dimension (<100 nm). In contrast, the micro-sized MCM-41 silica has little or no textural mesoporosity.[8]

Table 1 provides the basic physical properties of the mesoporous silica products. It is clear that all the nanoparticles of mesoporous silica samples possess the classic advantages of high surface area, porosity and uniform pore size as the typical MCM-41 mesoporous silicas. The mesopore size is not dependent on the pH value of the solution. Moreover, one can see that the $V_{\mathrm{text}}/V_{\mathrm{meso}}$ ratio increase with the decrease of the pH value. It should be also mentioned that the silica condensation degree is pH-dependent, and a higher condensation occurs at neutral pH.[1,7] Therefore, the mesoporous silicas prepared in a solution of near neutral pH value has the thicker silica-wall than that at high alkaline condition (Table 1). Thicker wall would make the mesostructures more stable, but reduces the surface area and porosity. With wall thickness of 2.82 nm, the mesoporous silica is hydrothermal stable for at least 2 days in 100 °C water.

From the SEM observations, the images displayed the particle size of all samples are homogeneously in nano-size, parallel to that observed in TEM micrographs. Moreover, the TGA plots show that the surfactant/silica ratio of the as-made products synthesized by this convenient procedure contains 40–50% surfactant as the typical MCM-41 materials.[4,8] This high surfactant content in the as-synthesized products reveal that the nearly absence of the surfactant-free amorphous silica as the by-products.

Basically, the main concept to manufacture the mono-dispersed nanoparticles is to avoid the mutual aggregation between nano-sized mesoporous silica particles. The mutual aggregation rate is dependent both on the concentration of primary particle and on the surfactant-silicate interaction strength. In a very dilute solution, serious mutual aggregations of nanoparticles could be intrinsically reduced. Besides, the strong electrostatic interactions of surfactant and silicate species progressively turn into weak hydrogen bonding with the change of pH value from 9.0 to 5.5.[8] The weaker aggregation strength of nanoparticles results in smaller nanoparticles.[7] This explains the effect of pH value on the particle size of the quaternary ammonium surfactant–silicate. Correspondingly, the weaker interactions lead to the wormhole-like mesostructure. In principle, there should be various determining factors (e.g., the surfactant/silicate ratio, the additives, solvent properties, etc.) for controlling the dimension and size-dispersity of mesoporous materials and further investigations are needed to set up a model.

Table 1. The physical properties of the mesoporous silicas synthesized from C_nTMAX–sodium silicate-H_2O composites in different pH value solution at 40 °C

Surfactant	pH Value of the Media	Pore Size /nm	Pore Volume /cm^3/g	BET S.A. /m^2/g	$V_{\mathrm{tetx}}/V_{\mathrm{meso}}$
$C_{16}TMAB$	9.0	2.23	2.01	1216	1.68
$C_{16}TMAB$	7.0	2.40	2.23	1122	1.97
$C_{16}TMAB$	5.6	2.52	1.76	774	2.34
$C_{14}TMAB$	5.6	2.08	1.35	760	2.68
$C_{18}TMACl$	5.6	2.71	1.23	782	1.29

[a] Pore volume obtained from N_2volume adsorbed at $P/P_0 = 0.99$.

[b] V_{meso}, framework pore volume obtained from the volume of N_2 adsorbed at $P/P_0 = 0.50$; V_{text} = Pore volume − V_{meso}.

This synthetic method also can be applied to other quaternary ammonium surfactant (C_nTMAX; $n = 14$–18). Changing the chain length of the surfactant, the pore size could be tuned, but the high textural porosity was still remained (Table 1). For the incorporation of aluminum into the silica framework of the mesoporous silica nanoparticles, the same procedure was performed except the addition of a proper amount of sodium aluminosilicates into the surfactant–silicate solution. For recovering the expensive quaternary surfactants, an extraction process in HCl–ethanol solution were employed instead of calcination.[8] In brief, using highly-diluted solution and well controlling on the surfactant–inorganic interactions can provide a new alternative to cheap produce the fine mesoporous materials.

In conclusion, we provided a convenient synthetic procedure to prepare the uniform mesoporous silica nanoparticles using the cheap silica source of sodium silicate. Because of the unique properties of high-connectivity, large porosity, and well-dispersion, the nano-sized mesoporous silica could be used for the synthesis of the high-performance nano-catalysts,[10] and mesoporous silica-polymer nanocomposites and for other applications in nanotechnology.

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