Aero-Sol−Gel Synthesis of Nanostructured Silica Powders

Jingyu Hyeon-Lee,† Gregory Beaucage,*,† and Sotiris E. Pratsinis‡

Department of Materials Science and Engineering, ML 0012, and Department of Chemical Engineering, ML 0171, University of Cincinnati, Cincinnati, Ohio 45221

Received May 9, 1997. Revised Manuscript Received September 12, 1997⊗

Nanostructured silica powders are synthesized by a nonpyrolytic, room-temperature aero-sol−gel process. Hydrolysis and condensation of tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) precursors produce nanosized silica powders that have specific surface areas greater than 400 m^2/g. This paper reports on a novel synthetic approach and characterization of the morphology, particle growth process, surface area, and chemical composition using small-angle X-ray scattering (SAXS), N_2 adsorption, and elemental analysis. Structural models for the morphology and growth process of the silica particles are suggested. The effects of reactant temperature and powder sintering on the specific surface area of silica are discussed.

Introduction

The synthesis and characterization of nanoparticles have received considerable attention in recent years as these particles can be used for a variety of commercial applications including colorants, fillers, pigments, sensors, and adsorbents as well as catalytic supports.[1−3] Silica nanoparticles, in particular, are considered important materials that have many potential applications such as catalytic supports.[4] The properties of these nanoparticles such as high surface areas are highly desirable for catalytic support because high surface area provides more active sites for gas/solid interactions. Moreover, the morphology of nanosized amorphous silica powders is of great interest since many of the mechanical, electrical, and other properties of existing materials can be improved or modified. The characterization of these properties or morphologies can ultimately lead to new potential uses. For example, highly porous silica powders with high surface area can also be used as insulating materials for microelectronic packaging since silica has a relatively low dielectric constant among inorganic oxides.

A wide range of scientifically interesting and technologically important nanoparticles have been produced by various methods such as sol−gel synthesis,[5−7] flame synthesis,[8−12] and other aerosol processes using different energy sources such as laser[13,14] or thermal plasma.[15] The main industrial route to these powders involves a pyrolytic reaction of oxygen and an inorganic precursor such as silicon tetrachloride ($SiCl_4$) at high temperature (T >1000 °C) and pressures (up to 10 atm). The pyrolysis temperature usually limits the surface area to below 400 m^2/g due to sintering of the particles.

This paper presents, for the first time, an aero-sol−gel technique for production of powders with extremely high specific surface areas at room temperature by a nonpyrolytic aerosol process. This novel approach offers reduced cost of production as well as making available new morphologies with higher specific surface areas than are possible with conventional pyrolytic routes.

Experimental Section

Preparation of Silica Powders. A schematic of the synthetic approach is shown in Figure 1. A laminar-flow chamber (controlled flow chamber in Figure 1) is used to make silica particles. The laminar flow chamber is comprised a series of concentric PVC tubes similar to the configuration of flame aerosol reactors.[8] The central tube is 5 mm in diameter and the spacing between successive tubes is 1 mm. The length of the tubes is 20 cm. In the flameless process reported here silica powder formation occurs via an aerosol-based hydrolysis/condensation reaction. TEOS ($Si[OCH_2CH_3]_4$) has increasingly been used as a silicon source because of relative ease of handling and chemical stability. TMOS ($Si[OCH_3]_4$) is more volatile and more toxic than TEOS. Both TEOS and TMOS were obtained from Aldrich Chemical Co. The flow rates of all reactants were measured by rotameters. Moreover, pressurized air is bubbled into each reactant bottle with a flow rate of 130 cm^3/s and passed through each tube of the reactor.

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* To whom correspondence should be addressed.

† Department of Materials Science and Engineering.

‡ Department of Chemical Engineering.

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.

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S0897-4756(97)00348-7 CCC: $14.00

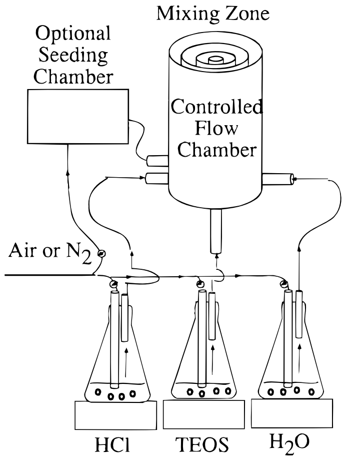

Figure 1. Schematic of the synthetic process.

To provide appropriate vapor pressure, TEOS and H_2O were heated at various temperatures, as reported below. The vapor pressure of the HCl, which is a catalyst for this sol−gel reaction,[16] at room temperature is sufficient for its controlled delivery to the reactor. The precursor silicon alkoxide (TEOS or TMOS) vapor was carried into the central tube of the reactor, while HCl and H_2O were introduced through the second and third tubes of the reactor, respectively.

Powder samples were collected in a plastic funnel above the reactor and dried at room temperature. A seeding chamber is sometimes used in this process (Figure 1) although it was not used in the work reported here.

Characterization. The specific surface area of the powder was measured by nitrogen adsorption (Gemini 2360, Micrometrics) at 77 K using the BET equation.[16] Samples were degassed in the oven at 403 K for more than 18 h and a six-point BET analysis was conducted to obtain the specific surface areas [$0.01 < p/p_0 < 0.3$, N_2 molecular cross section area = 0.162 nm^2]. Small-angle X-ray scattering (SAXS) data were collected using a Rigaku 12 KW rotating anode X-ray generator (Cu Kα, $\lambda = 0.1542$ nm) with a 10 m pinhole camera at Oak Ridge National Laboratories. The radius of gyration and the fractal-dimension were determined by analysis of the Guinier and mass-fractal (power-law) regions, respectively.[17,18] The q range covered in SAXS were from 2×10^{-3} to 0.6 Å^{-1}. Furthermore, elemental analysis was performed by combustion analysis of the powders (For C, H, and N).

Results and Discussion

Growth Process and Morphology of Silica Powders by SAXS. Many studies have shown that the growth process of nanometer-scale silica powders exhibit characteristics of fractal growth.[19−21] Fractal growth lies between the two extremes of linear growth and uniform 3-d colloidal particle formation.

The fractal morphology of silica powders was characterized with small-angle X-ray scattering. Silica powders were synthesized using TEOS as a precursor which was preheated at different temperatures, while the temperature of water was kept at 75 °C. Figure 2 shows SAXS data of silica powders produced by this novel approach, which is plotted as a log−log plot of intensity I vs scattering vector q. Lines correspond to power-laws such as mass-fractal scaling laws.[18] The slope of log I vs log q was measured as −2.5 for the silica powders synthesized with TEOS at a temperature of 80 °C and −1.33 for those synthesized at 70 °C. In none of the TEOS samples has a primary particle been observed despite the fairly high q obtained in the SAXS measurement. This indicates an extremely small primary structure to the mass-fractal aggregates on the order of molecules. A fractal dimension of 1 theoretically represents linearly connected primary particles. For the case of silica with fractal dimension of 1.33, this corresponds to the growth of rather linearly connected fractals. Compared to this, silica powders with fractal dimension of 2.5 indicate formation of more highly branched structures.

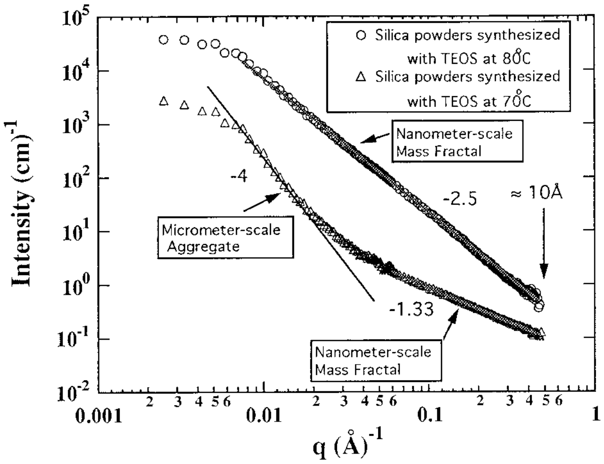

Figure 2. SAXS data for silica powders synthesized with TEOS under different temperatures.

There are several key elements that control particle growth, such as the reactants (either monomer or cluster), their trajectories, the relative rates of reactions, and transport.[16] According to the key elements, several kinetic growth models are suggested. Formation of silica powders with fractal dimension of 2.5 can be modeled by the diffusion-controlled monomer-cluster aggregation mechanism described by Witten and Sanders.[22] As TEOS monomers are provided continuously through a laminar diffusion flow chamber in the novel reactor, it is highly plausible that the released monomers contact with growing clusters. Here, the term monomer refers to molecular TEOS species. Therefore, growth may occur preferentially at exterior sites of clusters, which leads to the fractal dimension of 2.5. This is contrasted with silica powders synthesized with TEOS at 70 °C where the measured fractal dimension is 1.33, which suggests more linear growth of fractals. The vapor pressure of TEOS at 70 °C (20 mmHg) is lower than that at 80 °C (34 mmHg), which means the concentration of TEOS monomers will be lower at 70 °C. Therefore, there might be fewer opportunities to form highly branched clusters, resulting in more linearly connected fractal structures. Similarly, SAXS analysis has been performed on silica powders synthesized with TMOS as a precursor at 35 °C. Figure 3 shows SAXS

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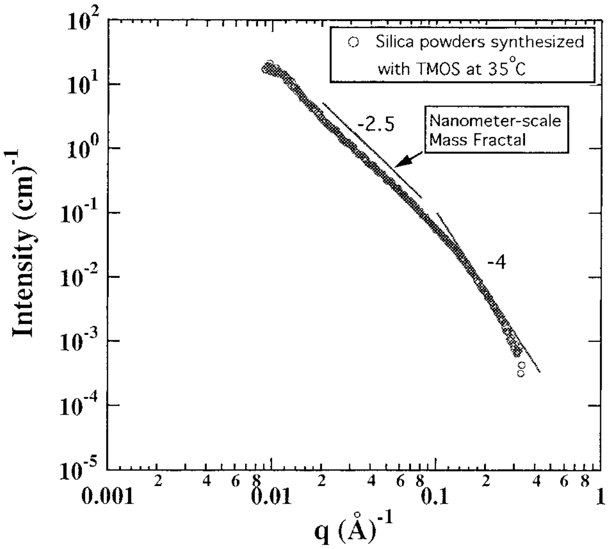

Figure 3. SAXS data for silica powders synthesized with TMOS at 35 °C.

Table 1. Specific Surface Area of Silica Powders under Various Kinds of Reaction Conditions

precursor	temp (alkoxide/H_2O, °C)	specific surface area (m^2/g)
TEOS	70/75	444
TEOS	80/75	398
TMOS	25/75	122
TMOS	35/75	422
TMOS	50/75	107

data of silica powders synthesized with TMOS, which are plotted as a log–log plot. The measured fractal dimension is 2.5, which follows the diffusion-limited monomer-cluster aggregation mechanism as observed in TEOS system (Figure 1, top curve). In TMOS the primary particles of this small fractal aggregate are on the order of 25 Å in diameter (Guinier fit[17] $D \approx 2.6R_g$ for spheres) as reflected by the knee in Figure 3 at high *q*.

Effect of Reactant and Sintering Temperature on Specific Surface Area. Hydrolysis and condensation reactions in silicon alkoxides depend on reactant concentrations as well as process conditions such as reactant temperature. The specific surface area of silica powders made at different temperatures of silica precursors are given in Table 1. All of the surface area measurements are determined from nitrogen adsorption. However, this definition of surface excludes microporosity that nitrogen molecule cannot access. Therefore, for example, if we use *n*-heptane as gas adsorbate, the surface area will be lower than that by N_2 measurements (see, for example, Table 1 by Ross et al.[23]). When TEOS is used as a precursor, the surface area shows the highest value at 70 °C. Below 70 °C, powders are formed, but the process yield is small. The surface area at 80 °C is lower than that at 70 °C. As the vapor pressure increases by increasing temperature of TEOS, the initial particle number concentration may increase, resulting in higher collision rates and formation of larger and denser aggregates of primary particles with more contact points between them. This results in lower specific surface area of powders in agreement with the effect of precursor concentration in flame synthesis of titania as was observed by Pratsinis (Figure 10).[8] For the case of silica powders made by TMOS, the surface area initially increases sharply as the temperature increases. The surface area shows a maximum at 35 °C. As the temperature increases beyond 35 °C, the specific surface area drops sharply. As TMOS has higher vapor pressure compared to TEOS, this leads to the formation of powders at lower temperature. Furthermore, water molecules can more easily attack the silicon backbone for TMOS compared to TEOS because the methoxy group in TMOS is relatively small compared to the ethoxy group in TEOS, which provides sterically less hindered environments in TMOS. It seems that condensation between hydrolyzed alkoxy groups leads to easy formation of silica powders when TMOS is used as a precursor.

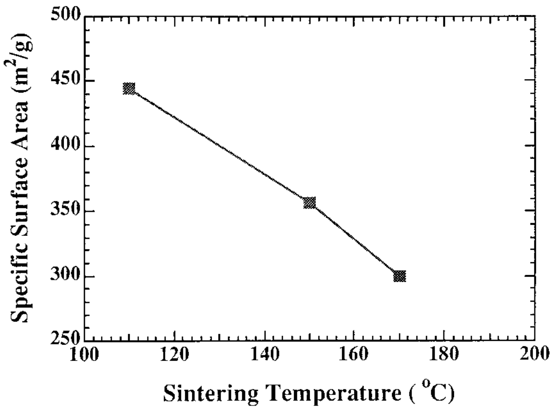

Figure 4. Surface area of silica powders as a function of sintering temperature.

Powders produced by this novel approach display a sensitivity to postsynthesis thermal treatments that may be related to the extremely small primary particles. Powders were heated for 20 h at several temperatures before measurement of specific surface areas. Figure 4 shows the effect of sintering temperature on the specific surface area of silica powders made from TEOS at 70 °C. The specific surface areas decrease as the sintering temperature increases. This lowering of the surface area with increasing temperature may be related to sintering of extremely small primary particles of the mass-fractal aggregates.

Finally, combustion elemental analysis of as synthesized powders showed low organic contents, C = 0.35%, H = 2.42%, and N = 0%, respectively. The amount of carbon is less than 0.35%, indicating that almost all of the alkoxy functional group is hydrolyzed into hydroxyl groups in the synthesis process.

Conclusions

Nanosized silica powders have been synthesized using a novel aero-sol–gel process. This inexpensive, room temperature process can produce nanoscale fractal-like silica powders with extremely high specific surface area (>400 m^2/g) comparable to those made by high-temperature or laser vaporization processes. The measured specific surface area depends on the reactant temperature and powder sintering temperature. The fractal dimension displays a wide and tunable range from 1.33, for silica powders synthesized with TEOS at 70 °C, to 2.5, for silica powders synthesized with TEOS at 80 °C.

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Silica powders synthesized with TMOS at 35 °C also show a fractal dimension of 2.5, which is consistent with diffusion-limited aggregation. The measured surface areas of powders synthesized using TEOS can exceed 400 m^2/g and decrease as the TEOS temperature increases. The surface area shows a maximum value at 35 °C (larger than 400 m^2/g) when TMOS is used as a precursor. Further, the surface area of powders monotonically decreases as sintering temperature increases. This indicates that some structural change occurs with sintering, which may be related to extremely small primary particles.

Acknowledgment. This work was partially supported by the National Science Foundation, Grants CTS-9612107 and CTS-9731458. We are grateful for the assistance of J. S. Lin at Oak Ridge National Laboratories in the collection of SAXS data.

CM9703482