Langmuir **2004,** *20,* 2523−2526

Ultrahigh Surface Area Nanoporous Silica Particles via an Aero-Sol−Gel Process

S. H. Kim, B. Y. H. Liu, and M. R. Zachariah*

Center for NanoEnergetics Research, Departments of Mechanical Engineering and Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0111

Received May 19, 2003. In Final Form: November 3, 2003

We describe a new salt-assisted aero-sol−gel approach to produce spherical nanosized mesoporous silica particles. As an alternative to expensive templating mediums in prior works, salt (NaCl) was employed as a templating medium because it is thermally stable, recyclable, and easily leached. Furthermore, we demonstrate the ability to carry out traditional sol−gel chemistry within an aerosol droplet. The role of salt in sol−gel chemistry and aerosol processing was investigated as a function of hydrolysis time. It was verified that salt accelerates the kinetics of silica gelation, and simultaneously becomes an excellent templating medium to support nano-sized pores inside silica structures in the aerosol processing route. The presence of salt results in a roughly ten-fold increasing in the pore specific surface area and pore volume, subsequent to leaching of the salt matrix. The surface area and pore volume of the as-produced nanoporous silica particles was found to increase with increasing sol−gel hydrolysis time.

Extending the range of available pore size and internal surface area is of great interest in catalytic supports, sorbents, and thermal insulation. Prior work to prepare macro- and mesoporous silica particles has usually employed templating procedures, usually in a batch reactor[1,2] or in some cases as aerosol processes.[3,4] However, these approaches require a secondary thermal process to remove the nanophase templates from the final product, which can result in collapse of the pore structure. Furthermore, most templating procedures require one-time-only use of templating materials and auxiliary solvent extraction, which makes such processes industrially uneconomical. In our new approach, we develop a rapid aerosol process to produce spherical nanosized nanoporous silica particles, in which salt (NaCl) is employed both as an agent to accelerate the kinetics of silica gelation and as a templating medium to support the formation and stability of pore structures. Salt inclusion also offers the advantage of being recyclable, inexpensive, thermally stable, and readily removed by aqueous wash. This approach can be extended to various material synthetic methods and other applications, including material properties enhanced by large internal surface area and pore volume.

To synthesize the nanostructured porous silica particles, we used either a colloidal or polymeric sol. In a colloidal sol, aqueous silica particles are electrostatically stabilized in an aqueous solvent. Aggregation begins when gelling agents such as NaCl or HCl, which destabilize the surface charges, are added. In contrast, the structure and properties of polymeric silica particles depend strongly on the processing parameters, such as the water to silicon molar ratio and the nature and amount of the catalyst used.[5−7] To form polymeric silica particles, tetraethoxysilane (TEOS, $Si[OCH_2CH_3]_4$) is generally used. The basic sol−gel chemistry[8] for silica formation is given below:

$$Si(OR)_4 + H_2O \Leftrightarrow Si{-}OH + ROH \quad \text{(hydrolysis)} \qquad (1)$$

$$Si{-}OH + OH{-}Si \Leftrightarrow Si{-}O{-}Si + ROH \quad \text{(alcohol condensation)} \qquad (2)$$

$$Si{-}OH + OH{-}Si \Leftrightarrow Si{-}O{-}Si + H_2O \quad \text{(water condensation)} \qquad (3)$$

where R is the alkyl group, ROH is the byproduct alcohol, Si−O−Si is the siloxane bond, and OH is the hydroxyl group.

Most previous synthetic methods have used sol−gel-based chemistries in batch reactor operations, which require long contact times, secondary thermal processes for template removal, and auxiliary solvent extraction. To overcome the disadvantages of batch reactor synthesis, aerosol-assisted sol−gel methods have recently been developed to produce mesoporous silica particles, with pore sizes ranging from 2 to 50 nm. By employing a vapor-phase synthetic method, aerosolized TEOS, H_2O, and HCl, mesoporous silica particles with a specific surface area of 400−600 $m^2\ g^{-1}$ and an average pore diameter of 5 nm were produced.[9] However, in the postdrying process significant pore collapse was observed.

In a related work, porous silica particles have been produced by a "self-assembly" method, in which aerosolized droplets containing TEOS, ethanol (EtOH), H_2O, and polystyrene templating spheres were used to produce a multiphased nanostructured powder.[10] However, a secondary thermal calcination process was required to remove

---

* Corresponding author. Address: 111 Church St. S.E., Minneapolis, MN 55455. E-mail: mrz@me.umn.edu.

[1] Göltner, C. G.; Antonietti, M. *Adv. Mater.* **1997**, *9* (5), 431.

[2] Velev, O. D.; Jede, T. A.; Lobo, R. F.; Lenhoff, A. M. *Chem. Mater.* **1998**, *10*, 3597.

[3] Lu, Y.; Fan, H.; Stump, A.; Ward, T. L.; Rieker, T.; Brinker, C. J. *Nature* **1999**, *398*, 223.

[4] Fan, H.; et al. *J. Non-Cryst. Solids* **2001**, *285*, 71.

[5] Sharp, K. G. *J. Sol.-Gel Sci. Technol.* **1994**, *2*, 35.

[6] Bernards, T. N. M.; Janssen, M. J. C. H.; van Bommel, M. J. *J. Non-Cryst. Solids* **1994**, *168*, 201.

[7] Boonstra, A. H.; Baken, J. M. E. *J. Non-Cryst. Solids* **1990**, *122*, 171.

[8] Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.

[9] Hyeon-Lee, J.; Beaucage, G.; Pratsinis, S. E. *Mater. Res. Soc. Symp. Proc.* **1998**, *520*, 115.

[10] Fan, H.; et al. *J. Non-Cryst. Solids* **2001**, *13* (20), 1579.

10.1021/la034864k CCC: $27.50

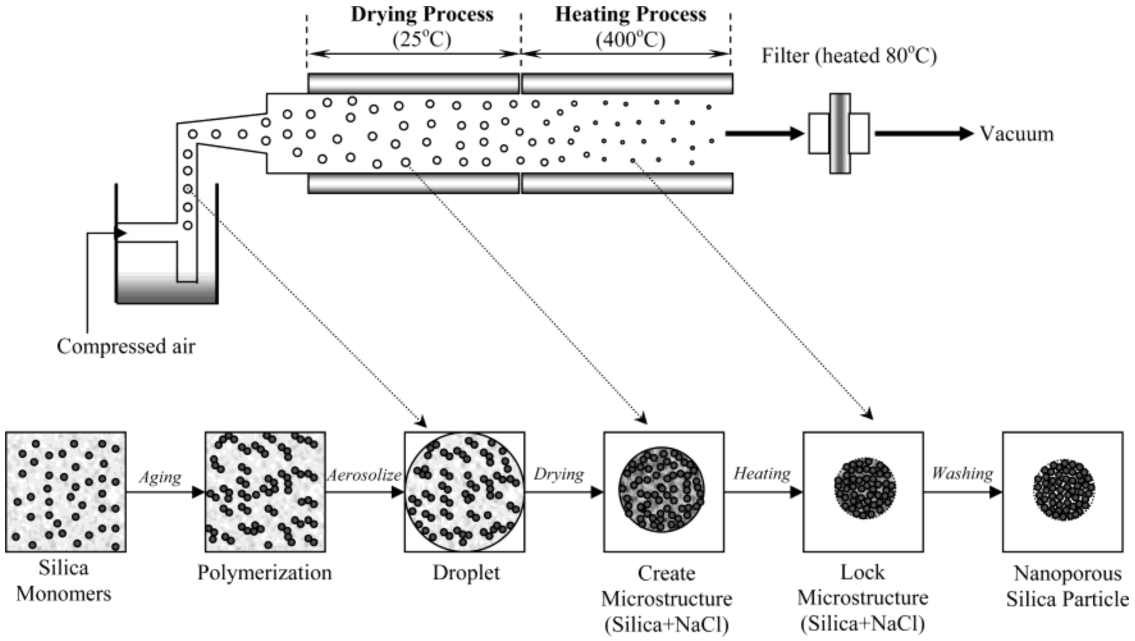

Figure 1. The schematic of the experimental setup and an illustration of the possible pathway of nanoporous silica particle formation.

the nanophase polystyrene templating powders. Unlike the studies which have employed either organic-based surfactants or polystyrene spheres, both of which require the irreversible destruction of the templating medium, we have developed an aerosol method to produce nanoporous metal oxide particles, in which a recyclable salt matrix is employed to support pore structures.[11]

In our new approach, salt is employed as a templating medium to support the developing pore structure, along with a gelling agent to accelerate the sol−gel chemistry. Allowing for a sufficient hydrolysis time (<50 h), the aqueous silica particles are allowed to grow and form three-dimensional gel networks in solution. After the precursor solution is aged, the solution is aerosolized. And the aerosolized droplets containing silica, H_2O, EtOH, and salt are solidified in a drying process at room temperature as shown in Figure 1. Subsequent heating (400 °C), in which both the silica and salt (melting temperature 800 °C) remain stable, completes the aerosol−gel chemistry. The importance of the salt remaining solidlike is a necessary condition to prevent the salt from phase separating.

The first and most difficult problem was that addition of EtOH into TEOS and NaCl causes immediate salt crystallization. Furthermore, the addition of the HCl catalysts increases the concentration of chlorine, which also enhances salt precipitation. To overcome this difficulty, a series of batch experiments were conducted to avoid immiscibility of TEOS and H_2O during solution preparation. This required a controlled water addition to obtain a mixed solution of TEOS/EtOH/H_2O/HCl with salt. The batch experiments also showed, as expected, that the use of salt significantly reduced the gelation time, which was considered at the point when there was no observed fluidity of the solution. Silicate species are not highly ionized at low acidities (pH = 0−2), so the agglomeration of primary silica particles is relatively slow. The addition of salt increases the van der Waals attraction forces between silica polymers by reducing the thickness of double layer. However, as the silicate source gets used up the rate of hydrolysis and condensation of silica particles gets slower with increasing aging time. As such, the function of salt as a gelling agent is completed and its primary function becomes one of templating.

With an optimum solution condition determined from the batch experiments, we perturbed the growth of the aqueous silica particles by varying the hydrolysis time (t_H). Here t_H is defined as the time elapsed from addition of the acid and salt fraction into the TEOS/EtOH/H_2O solution. It is known that the extent of silica monomer size and agglomeration is strongly dependent on hydrolysis time. Under acidic catalyzed conditions, silica monomers are grown by condensation of small primary alkoxide molecules, randomly branched silica polymers form slowly, and drying results in collapse of the porous network due to capillary forces.[12]

At a selected t_H condition, the solution was aerosolized by a Collison nebulizer with a droplet flow rate of 3 L min^{-1} and an initial droplet size of around 900 nm measured by a high-sensitivity laser aerosol spectrometer. In the drying and subsequent heating process, the three-dimensional network of aqueous silica and salt matrix would shrink into a nanocomposite. The as-produced particle size distribution as shown in Figure 2 was measured in real time using a differential mobility particle sizer,[13] for various t_H's. With increasing hydrolysis time, the geometric mean diameter (GMD) and geometric standard deviation (GSD) increased from 141 nm and 1.48 for very short hydrolysis times ($t_H = 1$ h) to 177 nm and 1.61 at the near-gel point ($t_H = 50$ h). This is consistent with the conceptual model that as the cross-linked polymer system is more highly reacted, it can better resist the compressive forces of surface tension during solvent evaporation.

Once this polymeric sol at a given aging time is aerosolized, the function of salt from a gelling agent to a templating/filler for supporting the silica porous network occurs. In an evaporating droplet, the solute concentration

---

[11] Kim, S. H.; Liu, B. Y. H.; Zachariah, M. R. *Chem. Mater.* **2002**, *14*, 2889.

[12] Brinker, C. J.; Scherer, G. W. *J. Non-Cryst. Solids* **1985**, *70*, 301.

[13] Fissan, H.; Helsper, C.; Thielen, H. J. *J. Aerosol Sci.* **1983**, *14*, 354.

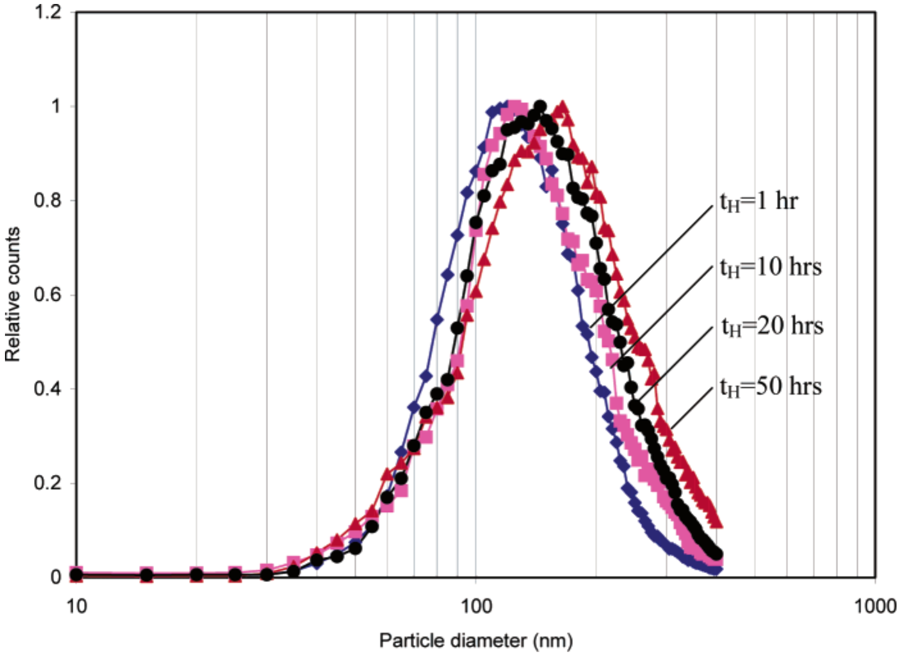

Figure 2. Particle size distribution for various aging times of the precursor solution (TEOS/EtOH/H_2O/HCl/NaCl = 1:22:60:30:2).

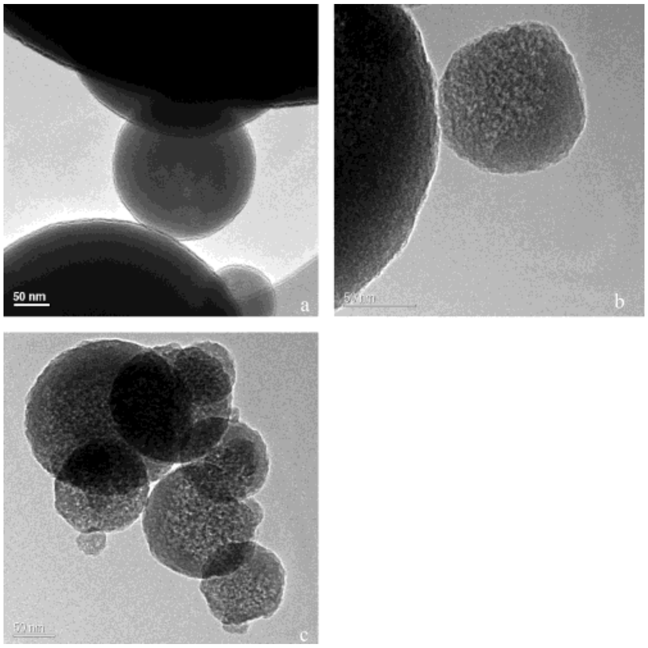

Figure 3. TEM images of silica particles: (a) TEOS/EtOH/H_2O/HCl/NaCl = 1:22:60:30:0 (t_H = 20 h), (b) TEOS/EtOH/H_2O/HCl/NaCl = 1:22:60:30:2 (t_H = 20 h), and (c) TEOS/EtOH/H_2O/HCl/NaCl = 1:22:60:30:2 (t_H = 50 h).

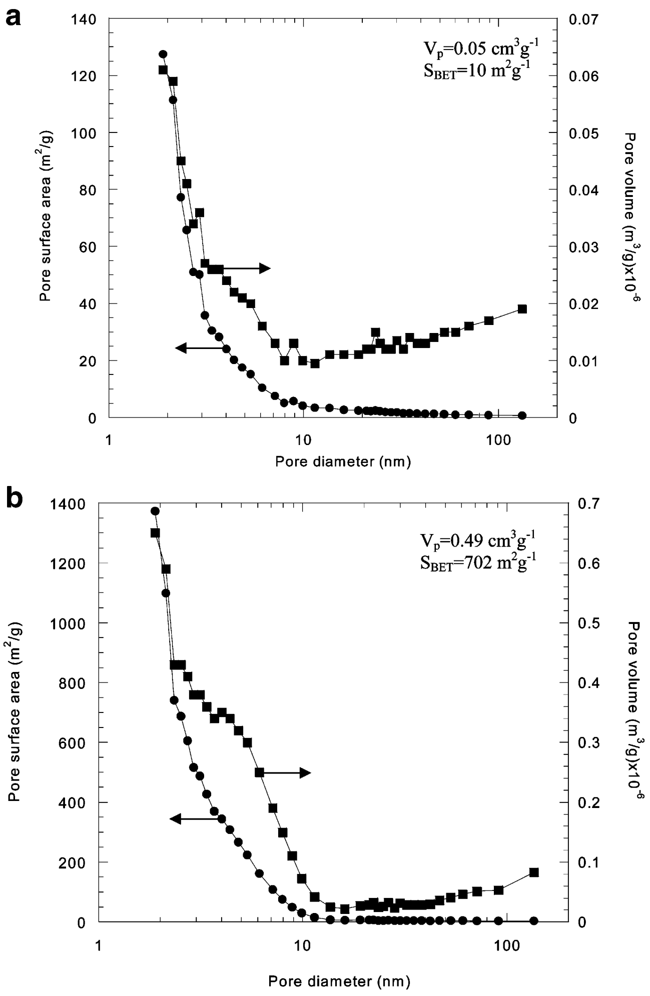

Figure 4. Pore surface area and volume distribution (a) before and (b) after salt removal (t_H = 50 h, BJH adsorption curve).

will eventually reach a supersaturated state and begin to nucleate. Since the loss of solvent occurs at the drop surface, it is here that the salt will be in highest concentration. In our process, the nature of the salt precipitation and its location are intimately connected to the generation of the porous network. Once salt precipitation is complete, the formation of the porous network is effectively also complete, since the salt matrix is no longer able to move. Once the salt precipitation is completed, the nanostructured silica is immobilized in the salt matrix. The only opportunity to perturb this network is presumably during heating, which could cause chain mobility and pore collapse resulting from the melt of the salt matrix.

Transmission electron microscopy (TEM) images of particles shown in Figure 3 illustrate that the use of the salt matrix can be a very simple and ultimately highly economical templating medium to produce nanoporous aerosol particles upon aqueous rinse of salt. In the absence of the salt matrix, an evaporating aqueous silica aggregate would experience pore collapse and the formation of a near dense silica particle as shown in Figure 3a. However, use of a salt matrix results in significant preservation of the pore structure and the ability to tune the surface-to-volume ratio. The TEM images, shown in Figure 3b,c, clearly show the formation of a porous structure which seems to increase with increasing hydrolysis time. We note that the images in Figure 3b,c are after the aqueous wash process and imply that the removal of the matrix does not result in collapse of the porous network.

The effect of the salt templating medium on the specific surface area and pore volume distribution of the resulting silica powders before and after salt matrix removal were determined by a gas sorptometer (nitrogen adsorption at 77 K using Brunauer–Emmett–Teller (BET) analysis). In Figure 4a, we see that the Barrett–Joyner–Halenda (BJH) specific surface area for the as-produced particles varies from about 10 to 120 $m^2\ g^{-1}$ with a BET specific surface area of 17 $m^2\ g^{-1}$. After removal of the salt, as shown in Figure 4b, the BJH specific surface area varies between 200 and 1200 $m^2\ g^{-1}$ in the pore size range of 2–10 nm. The BET specific surface area (S_{BET}) is about 700 $m^2\ g^{-1}$, or roughly a 10 fold increase over that of the unwashed particles. In addition, the pore volume (V_p) increased significantly in the mesopore size regime by also about a factor of 10 over the as-produced particles. For the washed particles, a large pore mode, likely corresponding to hollow particles in the 20–50 nm pore size range, was also observed; however, the overall surface area contribution from this mode is relatively small. These results are quite conclusive in demonstrating that salt can be used as an effective templating medium to produce ultrahigh nanoporous metal oxide particles using this aerosol–gel route.

The effect of hydrolysis time on the porous nature of as-produced particles is summarized in Table 1. The four samples presented are for hydrolysis times varying from 1 to 50 h. The overall particle diameter as measured by the DMPS system is only moderately affected by hydrolysis times, as the average particle size increases from 140 to 180 nm with increasing hydrolysis time and the specific surface area varies from 42 to 34 $m^2\ g^{-1}$. Upon removal of the salt, however, the specific surface area varies from 17 to 702 $m^2\ g^{-1}$ with increasing hydrolysis time. Most likely, at short hydrolysis times the extent of polymerization in the aerosolized droplets is insufficient to form a rigid and stable porous network. One might therefore conclude that the salt functions in this case to promote the polymerization as discussed previously but can only function as a pore former when sufficient polymerization has been allowed to take place so that the network is stable.

Table 1. Properties of Nanoporous Silica Particles Synthesized under Various Hydrolysis Times before and after Salt Removal (TEOS/EtOH/H_2O/HCl/NaCl = 1:22:60:10:2)

		before wash			after wash		
	t_H (h)	GMD (nm)	GSD	$S_{cal}{}^a$ ($m^2\ g^{-1}$)	$S_{BET}{}^b$ ($m^2\ g^{-1}$)	$V_p{}^c$ ($cm^3\ g^{-1}$)	APD^d (nm)
sample A	1	141	1.48	42	17	0.09	14.06
sample B	10	156	1.53	39	229	0.15	2.09
sample C	20	159	1.57	38	413	0.23	1.93
sample D	50	177	1.61	34	702	0.49	2.18

[a] S_{cal}: Specific surface area calculated under the assumption of nonporous silica particles with a density of 1 g cm^{-3}. [b] S_{BET}: BET specific surface area. [c] V_p: Primary mesopore volume. [d] APD: Average pore diameter = $4V_p/S_{BJH}$ where S_{BJH} is the BJH specific surface area.

Conclusions

We demonstrate in this paper the formation of ultrahigh surface area particles, based on a highly economical recyclable salt matrix. The process involves combining sol–gel chemistry and aerosol processing to produce spherical nanosized mesoporous silica particles. Salt (NaCl) is employed both as an agent to accelerate the kinetics of silica gelation and simultaneously as a templating medium to support the pore structure. Salt inclusion also offers the advantage of being recyclable, inexpensive, thermally stable, and readily removed by aqueous wash. This approach can be extended to various material synthetic methods.

Acknowledgment. Partial support for this work comes from the U.S. Army's DURINT Center for NanoEnergetics Research.

LA034864K