Preparation of Micrometer- to Sub-micrometer-Sized Nanostructured Silica Particles Using High-Energy Ball Milling

J. Eric Hampsey, Claudio L. De Castro, Byron McCaughey, Donghai Wang, Brian S. Mitchell,* and Yunfeng Lu

Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118

Nanostructured porous silica particles with sizes in the micrometer to sub-micrometer range are of great interest due to their potential applications as catalyst supports and nanocomposite materials. However, if these particles are to be used in industry, a process must be developed to affordably produce them on a large scale. This paper reports on a high-energy ball-milling process that has been used to create micrometer- to sub-micrometer-sized mesoporous silica starting from a silica xerogel prepared by a surfactant self-assembly sol–gel process. We have studied various milling conditions such as milling media (zirconia, stainless steel, or steel-centered nylon balls), milling time, and the presence of surfactants during milling and the resulting effect on particle size and pore structure. Results from transmission electron microscopy, scanning electron microscopy, X-ray diffraction, light scattering, and nitrogen adsorption demonstrate the feasibility of producing large quantities of nanostructured particles by this simple milling process.

I. Introduction

Since its discovery by Mobil researchers in 1992,1,2 MCM-41 and other ordered mesoporous materials have attracted great interest. These mesoporous materials are usually prepared by the cooperative self-assembly of surfactants and inorganic species such as silicates. Removal of the surfactant through either calcination or solvent extraction results in mesoporous materials with hexagonal, cubic, lamellar, disordered, or other pore channels. The size and structure of these pores can be controlled by careful choice of the surfactant system and reaction conditions. Among these materials, mesoporous silica synthesized in the form of thin films,3 aerogels,4 and particles are the most cited materials. Synthesis of mesoporous silica particles is of particular interest due to their possible use as catalysts, fillers, chromatographic materials and other applications. Mesoporous silica particles are typically synthesized in dilute solutions, and depending on the reaction conditions such as pH,5 stirring rate,6 choice of surfactant, or presence of cosolvents,7 various particle shapes and morphologies can be achieved. Mesoporous silica hollow rods,8 hard spheres,9,10 hollow spheres,11,12 and other curved shapes such as toroidal, dislikle, spiral, and gyroid morphologies13–15 have been reported in the literature. Mesostructured spherical particles have also been produced using an aerosol-assisted self-assembly process.16,17 However, these processes usually require large amounts of solvent and produce relatively small amounts of material.

High-energy ball milling has been a common physical technique used to produce sub-micrometer particles without the need for excessive solvent. During the high-energy milling process, the grinding media are accelerated to much larger velocities than those achieved in traditional ball milling. These large velocities provide a high transfer of kinetic energy from the balls to the sample resulting in the production of very fine powders. High-energy ball milling is usually used in three main applications: (1) mechanical alloying, (2) reactive milling, and (3) particle deformation, the latter of which will be the focus of this paper. Zoz and Ren used yttria-stabilized ZrO2 balls to mill SiC powder with a starting particle size of 850 µm.18 After 10 min of milling, the particle size was reduced to <0.15 µm, and after 60 min the particle size was further reduced to <10 µm with some particles in the 1–2-µm range. Quartz and Al2O3 powders were also milled and particle sizes of <1 and <5 µm, respectively, were achieved after 2 h of milling.

In this study, we use a high-energy ball-milling process and the coassembly of silica and surfactant to produce mesoporous silica particles. This simple process allows us to produce large quantities of mesoporous silica particles without using excessive solvent, making this process suitable for scale-up and industrial applications.

II. Experimental Procedure

(1) Chemicals

All commercial chemicals and surfactants were used as received. The surfactants chosen for this study were cetyltrimethylammonium bromide (CTAB; Aldrich), Brij-58 (C16H33(OCH2CH2)20OH; Aldrich), P123 (EO20PO70EO20; BASF), and F127 (EO106PO35EO106; BASF). EO and PO are used to designate ethylene oxide and propylene oxide, respectively. Tetraethyl orthosilicate (TEOS; Aldrich), ethanol (Aldrich), HCl (Aldrich), hexamethyldisilazane (HMDS; Aldrich), and deionized water were also used to prepare the xerogels.

(2) Preparation of Xerogels

Ordered mesoporous silica xerogels were prepared using a sol–gel technique. A typical sol was prepared using the molar ratios TEOS:EtOH:water:HCl:CTAB = 1:3.8:0:15:5:0.01. The mixtures were sonicated for 30 min and then placed in Petri dishes in thin layers to dry in an ambient condition for several days. The uncalcined xerogels were heated before the milling process under nitrogen at 110°C for 2 h. Mesoporous silica was prepared by removing the surfactant by either calcination in air at 450°C for 1 h or by a solvent extraction technique. The solvent extraction process was performed using a mixed solvent that contained 80% ethanol and 20% HMDS. The mixtures were sonicated for 1 h and then centrifuged to separate the solid. This procedure was repeated five times to ensure complete removal of the surfactant.

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*Member, American Ceramic Society.
(3) Milling of the Xerogels

All samples were milled with an 8000D SPEX CentriPrep Dual Mixer/Mill. The unit was operated in a Fisher Scientific Isotemp refrigeration unit maintained at 0°C. The grinding media used were 13-mm (½-in.) diameter stainless steel, zirconia, or nylon-coated stainless steel balls. The vials used for milling were made of either stainless steel or nylon, depending on the media. Milling times varied from 10 to 100 min, a ball to sample weight ratio of 10:1 was used, and the xerogels were milled without adding a dispersant such as ethanol.

(4) Analysis of the Milled Silica Particles

A JEOL JSM-5410 scanning electron microscope (SEM) was used to examine the size and morphology of the particles. Transmission electron microscope (TEM) images were taken using a JEOL JSM-2010 to show the ordered pore structures. A Philips Xpert X-ray diffractometer was used to obtain low-angle X-ray diffraction (XRD) patterns while the particle sizes were measured using a Brookhaven 90 Plus particle size analyzer. Nitrogen adsorption/desorption isotherms were obtained using a Micromeritics ASAP 2010, and the BET surface areas of the particles were calculated from the isotherms using the ASAP 2010 v.5 software.

III. Results and Discussion

(1) Preserving the Pore Structure during Milling

Calcined silica xerogels containing ordered pore structures were first milled using zirconia, stainless steel, and steel-centered nylon balls at different time intervals. While sub-micrometer-sized particles were achieved using this process, many of the features of the ordered xerogels were greatly reduced after milling. Figure 1 shows the nitrogen adsorption/desorption isotherms of CTAB-templated silica xerogels milled with nylon-coated stainless steel media at different milling times. At time zero, the isotherm is a type IV, consistent with mesoporous materials with high surface areas. After 10 min of milling, the isotherm still has the characteristics of type IV, but the volume adsorbed has decreased. As the milling time increases to 30 min and beyond, the isotherms no longer exhibit type IV behavior and the volume adsorbed decreases rapidly. The low-angle XRD patterns of the samples are also consistent with these findings. As shown in Fig. 2, at time zero the xerogel exhibits a sharp (100) peak at 2θ ~ 2.4° and a second broader (200) peak at 2θ ~ 4.5°. After 10 min of milling, the peaks are still visible but less intense. However, after 30 min of milling, the broader (200) peak has disappeared and the first (100) peak has become less intense. Finally, when the sample is milled for 60 min, both peaks virtually disappear.

To reinforce and preserve the pore structures of the xerogels during milling, samples were milled with the surfactant still inside the pore framework of the xerogel. The effect on the pore structure was quite remarkable. Figure 3 shows the nitrogen adsorption/desorption isotherms of calcined CTAB-templated silica xerogels milled with nylon-coated stainless steel balls with the surfactant.
inside the pores during milling. As before, at time zero the xerogel exhibits type IV behavior similar to that of mesoporous materials. However, unlike the precalcined xerogels (without surfactant in the pore framework during the milling process), the type IV nitrogen adsorption behavior is maintained throughout the milling process and the volume adsorbed decreases only slightly up to 100 min of milling time. Another important feature of the isotherms is the increase in the volume adsorbed near a relative pressure of 1. This corresponds to interparticle nitrogen condensation and indicates that smaller particles are being produced. The low-angle XRD data are also consistent with this result. As shown in Fig. 4, a sharp peak at 20 ~ 2.4° and a broader secondary peak at 20 ~ 4.5° are visible even after milling for 60 min. Only after a milling time of 100 min are these features absent.

To further illustrate this marked difference between the two types of milled xerogels, a comparison of the BET surface area as a function of milling time is displayed in Fig. 5. As shown in the figure, the surface areas of the xerogels milled after the surfactant was removed decreases rapidly as the milling time increases. However, the xerogels milled with the surfactant still inside the pore framework show a much smaller decrease in surface area. This result suggests that the surfactant reinforces the pore walls of the xerogel and prevents the collapsing of the pores during the milling process. Another possible factor is that the silica framework of the precalcined milled samples is more brittle than the unc calcined milled samples due to further silica condensation and cross-linking during the calcination process. Whatever the case may be, it was determined that all samples should be milled with the surfactant still incorporated in the pore network to preserve the mesopore structure.

(2) Characterization of the Milled Silica Particles

TEM micrographs were taken of the milled samples to confirm that the ordered pore structures were maintained throughout the milling process. Figure 6 shows representative TEM images of CTAB-templated silica xerogels (a) before milling and after (b) 10, (c) 30, and (d) 60 min of milling with nylon-coated stainless steel balls. As shown in the figure, the ordered pore structures are maintained in the silica even after milling for 30 min. However, after 60 min of milling, the ordered pore structures become less apparent.

After analyzing the milled particles under a SEM microscope, very few differences in particle size and agglomeration could be determined between different milling media. Figure 7 shows representative SEM images of CTAB-templated silica xerogels after milling with nylon-coated stainless steel balls for (a) 0, (b) 10, (c) 30, (d) 60, and (e) 100 min. After 10 min of milling, the particle sizes are greatly reduced from >100 to <5 μm. As the milling time increases to 30 min and above, it appears that greater amounts of sub-micrometer particles are being produced. However, it is difficult to quantify the particle sizes due to the large amount of agglomeration of the particles during the milling process.

To determine more accurately the particle sizes of the milled xerogels, light scattering measurements were performed. Figure 8 displays the effective diameter and polydispersity of the CTAB-templated silica xerogels after milling with nylon-coated stainless steel for 10, 30, 60, and 100 min. As shown in the figure, the effective diameter decreases from ~900 nm after 10 min of milling to less than 650 nm after 100 min of milling. It is important to note that the particle size distribution was quite large with particle sizes ranging from 100 nm to over 5 μm. Also, the polydispersity of the particles is observed to increase over milling times of 10, 30, and 60 min but decrease after milling for 100 min.

(3) Effect of Different Milling Media

Employing different types of milling media is known to affect the outcome of a milled material. While stainless steel and zirconia balls are commonly used in the milling of ceramic materials, the use of polymeric media has also been studied. Stainless steel balls coated with nylon have recently been demonstrated to be an effective milling medium for contamination reduction in a high-energy ball-milling process.\(^{19}\) To eliminate contamination from the nylon media, the nylon wear particles in the sample can simply be removed by thermal treatment or solvation after milling, resulting in a high-purity product.

While examining the effect of different milling media on the mesoporous silica particles, significant differences in the BET surface area were observed for samples milled with different types of balls. Figure 9 shows the BET surface area of CTAB-templated silica xerogels milled at different times with zirconia, stainless steel, and nylon-coated stainless steel balls. At a milling time of 10 min, all three samples display similar surface areas. After 30 min, there is a sharp decrease in the stainless-steel-milled samples, and
after 60 min both the zirconia- and stainless-steel-milled samples show significant decreases in surface area. The nylon-coated stainless steel balls, however, show the smallest decrease in surface area while producing the same micrometer-sized agglomerated particles.

(4) Effect of Different Surfactant Systems

The effect of using different surfactant systems such as CTAB, Brij-58, F127, and P123 was also investigated. Different surfactants are used to synthesize different pore structures, but the properties of each surfactant system also have large influences in the high-energy ball-milling process. Table I lists the BET surface area and the total volume adsorbed for silica xerogels with different surfactants milled for 100 min. After milling, the CTAB system exhibits the largest decrease in surface area (33%) followed by F127 (26%) and Brij-58 (8%). However, unlike the F127 and Brij-58 systems, the CTAB system has a substantial increase in the pore volume. Since the total volume of nitrogen adsorbed may be comprised of the pore volume and the interparticle volume, this indicates a significant contribution from the interparticle volume. The P123 system is not shown in the data due to the poor condition of the xerogel after milling. Instead of having the consistency of a fine powder like the other systems, the P123 xerogel formed a dense coating on the interior of the milling vial. Sub-micrometer- or micrometer-sized silica particles were also not evident during SEM investigation. Instead, large continuous silica agglomerates were observed (data not shown).

The SEM micrographs of the CTAB, F127, and Brij-58 systems are shown in Fig. 10. In these images, the F127 (Fig. 10(a)) and CTAB (Fig. 10(c)) systems appear to be comprised of small agglomerations of sub-micrometer-sized silica particles. However, in the Brij-58 system (Fig. 10(b)), the individual particles are not apparent due to very high agglomeration. In fact, the Brij-58 system agglomerated into particles as large as 100 μm (data not shown). It is believed that the texture of the

Fig. 6. Representative TEM images of CTAB silica xerogels (a) before milling and after milling with nylon-coated stainless steel balls for (b) 10, (c) 30, and (d) 60 min.
surfactant plays a large part in the agglomeration of the particles. At room temperature, P123 has a sticky and resinlike texture, while Brij-58 has a waxy texture. Both of these systems exhibited large amounts of agglomeration. However, the CTAB and F127 systems both have a texture more like a dry powder, and both of these systems resulted in the production of sub-micrometer-sized particles.

(5) Prevention of Agglomeration

Finally, in an attempt to reduce the agglomeration of the particles, the surfactant was removed from the xerogels after milling by a solvent-extraction technique that involves ultrasonication instead of calcination. The results did show some improvement in the agglomeration of the particles. Figure 11 shows a representative SEM image of CTAB-templated silica.
xerogels milled with nylon-coated stainless steel balls and the surfactant removed by solvent extraction. As seen in the figure, individual particles in the micrometer to sub-micrometer range with almost no agglomeration were observed. It is believed that the ultrasonication of the particles in solution helps break up the agglomerates. However, when examining the nitrogen adsorption/desorption isotherms of the solvent-extracted samples (Fig. 12), marked differences from that of the calcined particles are observed. The volume adsorbed decreases more rapidly with increased milling time and has less interparticle adsorption in the solvent-extracted samples than in the calcined samples. It is believed that the solvent-extraction and centrifugation cycles

Table I. Surface Area and Pore Volume of Silica Xerogels before and after Milling

<table>
<thead>
<tr>
<th>Surfactant system</th>
<th>Milling time (min)</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>0</td>
<td>937.3</td>
<td>0.570</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>630.5</td>
<td>0.716</td>
</tr>
<tr>
<td>F127</td>
<td>0</td>
<td>384.9</td>
<td>0.342</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>285.3</td>
<td>0.237</td>
</tr>
<tr>
<td>Brij-58</td>
<td>0</td>
<td>708.0</td>
<td>0.365</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>651.6</td>
<td>0.372</td>
</tr>
</tbody>
</table>

† Milled with zirconia balls.
milling process. In addition, nylon-coated stainless steel balls were found to preserve the surface area of the silica better than the zirconia and stainless steel balls. Milling times of 10–30 min were sufficient for producing sub-micrometer particles, and milling times greater than 30 min just produced more excessive agglomeration. When examining different surfactant systems, CTAB and F127 were found to be suitable surfactants in this process, while Brij-58 and P123 surfactants promoted excessive agglomeration. A solvent-extraction technique was found to reduce the agglomeration of the particles but also removes many of the sub-micrometer particles. Future directions of this project include surface modification of the silica and incorporation of metal nanoparticles into the pore framework for use at catalysts.

IV. Conclusions

From these findings, it is concluded that mesoporous silica particles in the sub-micrometer to micrometer range can be produced from silica xerogels using a high-energy ball-milling process. It was discovered that the pore structure of the silica is reasonably maintained throughout the milling process if the surfactant is not removed from the xerogel before milling. The surfactants help to stabilize and reinforce the pore walls during the milling process. In addition, nylon-coated stainless steel balls were found to preserve the surface area of the silica better than the zirconia and stainless steel balls. Milling times of 10–30 min were sufficient for producing sub-micrometer particles, and milling times greater than 30 min just produced more excessive agglomeration. When examining different surfactant systems, CTAB and F127 were found to be suitable surfactants in this process, while Brij-58 and P123 surfactants promoted excessive agglomeration. A solvent-extraction technique was found to reduce the agglomeration of the particles but also removes many of the sub-micrometer particles. Future directions of this project include surface modification of the silica and incorporation of metal nanoparticles into the pore framework for use at catalysts.

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References