Preparation of Hard Mesoporous Silica Spheres

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The use of emulsion biphase chemistry in materials synthesis has been recently demonstrated to offer the possibility of simultaneously controlling shape on the μm to cm length and the periodic mesostructure at the molecular mesoscale (15−100 Å).[1] The final product morphology can be structured using shear fluid flow, for example, the systematic tuning of shape from flat films to mesoporous silica fibers, then curved asymmetric shapes to hollow porous diatom spheres by the simple tuning of stirring speed in the synthesis mixture. This is, in fact, a small sampling since the macroscale morphology is limited only by the shapes that can be created using fluid flow and hydrodynamics and is not dependent on supporting substrates or preorganized shape molding surfaces.[2] Because the formation of microemulsions and emulsions involve long-range forces[3] with an energy of assembly, including shape fluctuations and interaggregate interactions, about the same as the thermal energy kT, structure modulation at μm or longer length scales are readily introduced by the application of small applied external fields. Furthermore this hydrodynamic route to hierarchical structures makes possible high-volume composite synthesis processes that utilize the reactions conditions of low-temperature, fluid-flow dynamics and kinetic control of inorganic polymerization that have been demonstrated to be applicable in the syntheses of these systems.

It is critical in composite materials design to be able to control strength and texture. Besides hardness, having optically transparent porous media makes it possible to rapidly quality check for interior fractures, pore degradation, and other bulk properties. In this paper we describe the successful synthesis of transparent, mesoporous marble-like spheres using surfactant-stabilized emulsion based chemistry.[4] The simple one-step synthesis of these materials provides a new dimension to emulsion hierarchical assembly, the definition of order, and/or shape on two or more different length scales. The high surface area spheres that can be prepared by this methodology are expected to be of interest to processes traditionally associated with chromatographic separation and supported phase synthesis or catalysis. The sizes of the silica spheres are uniform and can be controlled (from 0.1 to 2 mm). The mesoporous silica sphere exhibits a small pore size in the nanometer range (pore diameter 1−5 nm), a large surface area of greater than 1000 m^2/g, and a narrow pore size distribution.

At the macroscale level the performance of sorbents for chromatographic separation and solid-phase catalysts critically depends on the size, porosity, texture, and mechanical strength of the particles. Simultaneously, high surface areas and monodispersed pore sizes are needed to obtain the necessary space-flow velocity and molecular selectivity. This combination of properties at two different length scales is commonly obtained by packing and annealing together uniform-sized silica spheres at high temperatures.

Typically, silica can be gelled in spherical (diameter 0.1−5 mm) form by (1) forming small droplets of sol in the process of spray drying[5] or (2) spraying droplets into an immiscible liquid and gelling by chemical action or heating.[6−10] Spheres of different sizes can be obtained by varying the droplet size of the silica sol in an immiscible liquid before it gels. The silica source may be either a silicon ester, such as tetramethyl or tetraethyl orthosilicate (TMOS and TEOS) or a concentrated sodium silicate solution (water-glass).[11] The spherical hydrogel bodies of few mm are washed, dried at low temperature (e.g., 120 °C), and calcined at high temperature (e.g., 450 °C).

Solid spherical particles also can be made by the controlled hydrolysis of silicon esters.[12] For example, the partial hydrolysis of ethyl or methyl silicate such as poly(ethoxysiloxane), in alcohol with a little less than the theoretical amount of water and hydrochloric acid as a catalyst forms an emulsion in water−alcohol which solidifies to gel beads. Silica beads 0.2−0.5 mm in diameter with a pore diameter of 2 nm are obtained by this method.[13] The pore-size distribution, pore volume, pore shape, and surface texture of silica spheres require

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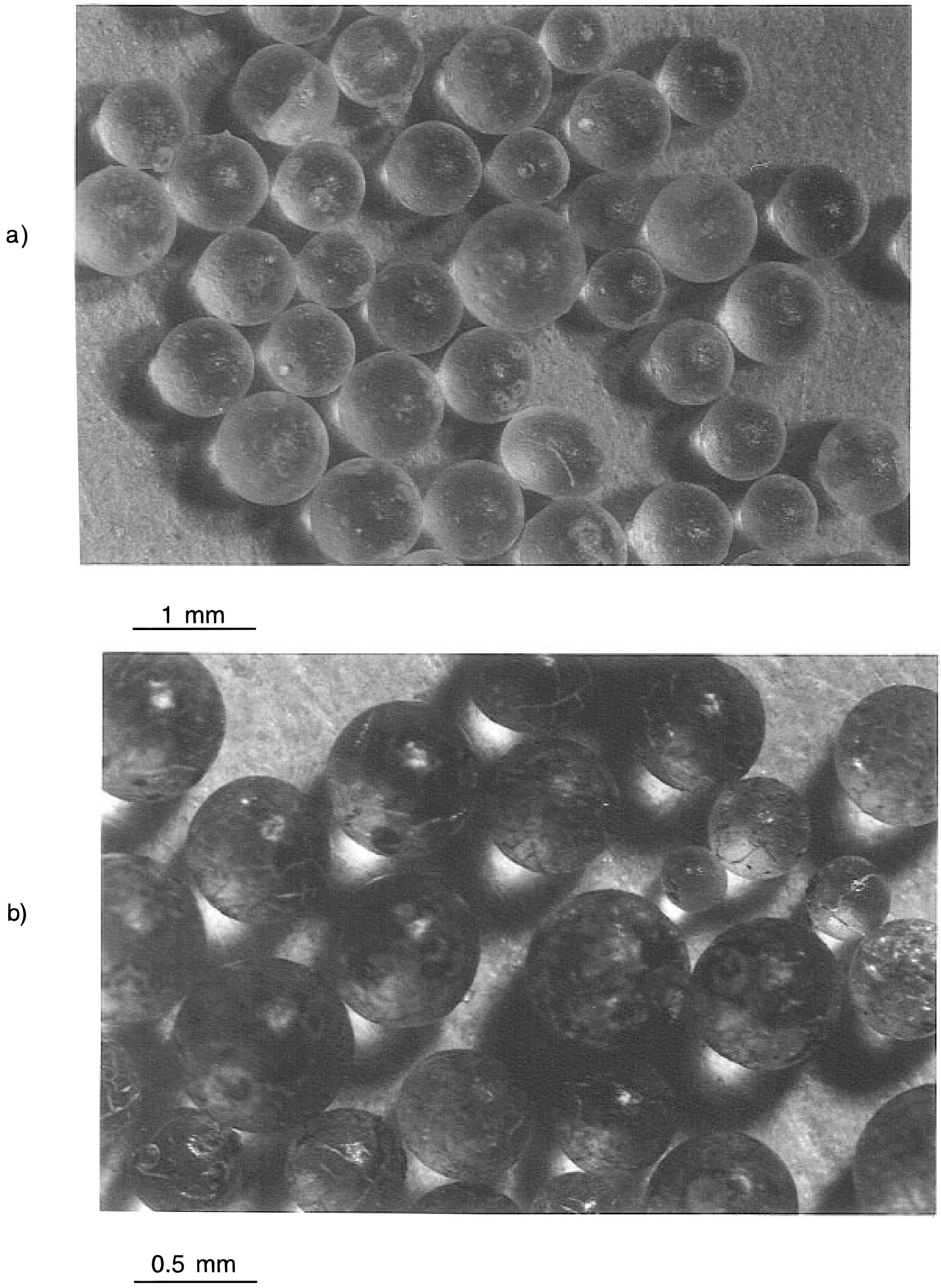

Figure 1. Size and shape of spheres using CTAB as surfactant: (a) as-made sample; (b) calcined at 500 °C sample.

careful fine-tuning of the preparation and modification conditions.[14,15] In general, the silica spheres prepared by the above methods have irregular shapes, a broad pore-size dispersion, and relative low specific surface areas (30−690 m^2/g).[9]

The present mesoporous silica spheres can be prepared in one step in a procedure closely related to that initially reported for the synthesis of MCM-41,[16,17] the primary difference being that the phase separation and

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emulsion chemistry which results from the hydrophobic nature of TBOS and BuOH are utilized to create the desired morphology. The details are as follows. Combine the organic surfactant as the pore structure directing agent, an optional source of base catalyst (e.g., NaOH, KOH, or tetramethylammonium hydroxide) and water. Add one or a combination of organic compounds of silicon. Stir the mixture at a constant speed (about 300 rpm using a magnet stirrer) for 15−30 h, at room temperature. The sphere product is separated from the liquid and recovered. A practice example is as following: 0.6 g of cetyltrimethylammonium bromide (CTAB) was dissolved in 35 g of water, and then 3.5 g of NaOH (2 M) was added. A clear solution was obtained. To this solution, 4.5 g of tetrabutyl orthosilicate (TBOS) was added with stirring. More concentrated solutions of TBOS did not result in the formation of a spherical particles. The stirring was continued for overnight. The resultant product, a collection of hard spheres, was filtered, air-dried at room temperature. The yield of spheres produced is very close to 100% and under these reaction conditions, only spherical shapes are observed.The sizes of the silica spheres can be controlled by varying the stirring conditions and reaction volume.

As expected for an emulsion synthesis, the stirring speed influences the formation of the spheres. When a Caframo motorized stirrer with a pitched blade propeller is used, low stirring speeds (<200 rpm) give soft gel particles, medium stirring speed (200−400 rpm) give spheres, and high stirring speeds (>450 rpm) give fine powders.

The size and shape of spheres synthesized with CTAB and TBOS are shown in Figure 1. The product remains in the form of spheres after calcination at 500 °C (from room temperature to 500 °C over 10 h in flowing nitrogen, then kept at 500 °C for 10 h in flowing air) with little evidence of fracture or breakage. The crush strengths of spheres depend on the dryness of spheres. For examples, as-made spheres (dried at room temperature) with average diameter 1.15 mm (~16 mesh) were crushed under 3.1 lb press force. Calcined spheres (at 500 °C) with average diameter 0.84 mm (20 mesh) were crushed under 7.1 lb press force. These values can be compared to crush strengths of 6 lb for 2.4 −1.7 mm (8−12 mesh) commercial 13 X zeolite-clay spheres and 11 lb for 2.4 to 4.8 mm (4−8 mesh) commercial 3A, 4A, and 5A zeolite-clay spheres.[18,19]

N_2 adsorption−desorption isotherms at 77 K were measured on a Micromeritics ASAP 2000. The BET surface area of the example sample (Figure 1b) is 1100 m^2/g, and the single-point total pore volume of pores less than 1318 Å diameter at relative pressure of 0.985 is 0.61 cm^3/g. Figure 2 is the adsorption−desorption isotherm of nitrogen at 77 K for this product. Figure 3 is the BJH (Barrett−Joyner−Halenda) pore size distribution plot from the adsorption branch.

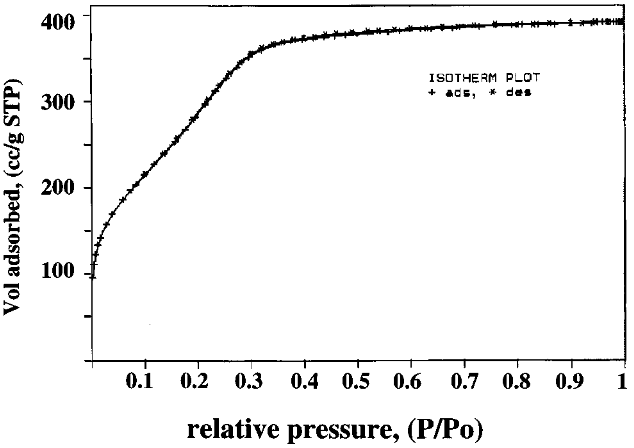

Figure 2. Adsorption−desorption isotherm of nitrogen at 77 K for the calcined (at 500 °C) spheres from CTAB surfactant synthesis system.

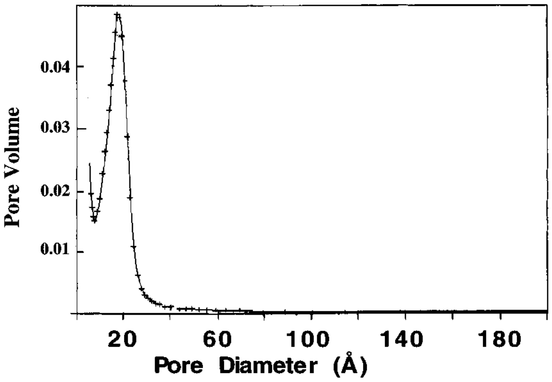

Figure 3. BJH pore-size distribution plot from adsorption branch. The same sample as in Figure 2.

The X-ray diffraction (XRD) pattern of this product shows a small broad peak at a *d* spacing value of ~40 Å. Two examples of the pore structure within the spheres as revealed by TEM images of thin transverse cross sections cut from spheres synthesized using C_{18}-TMABr are shown in Figure 4. Ordered arrays of pores similar to those found in MCM-41 are observed in some sections, while other areas show pores that appear to be monodispersed in size but with random orientation similar to the monosized pore distribution described by Pinnavia[20] for phases made with neutral surfactant and by Ryoo et al.[21] for disordered mesoporous silica material made with surfactant in the presence of organic salts.

The base catalyst can be LiOH, NaOH, KOH, RbOH, or an organic base, such as TMAOH. Higher alkoxysilianes such as TBOS were used as the source of silicon in this study. Lower alkoxysilanes such as TMOS and TEOS give only fine powders, and no larger spheres were observed. The organic pore structure-directing agent can be quaternary ammonium surfactants which are good structure-directing agents for the formation of mesoporous silicates such as MCM-41 and MCM-48. The structure and sizes of the pores of the silica spheres are dependent on the molecular configuration of the organic pore structure directing agents and reaction conditions as described previously.[16,17,22,23] Thus the C_n-TMA (n = 12−18) series of surfactants gives good spheres under the same synthesis condition. Examples

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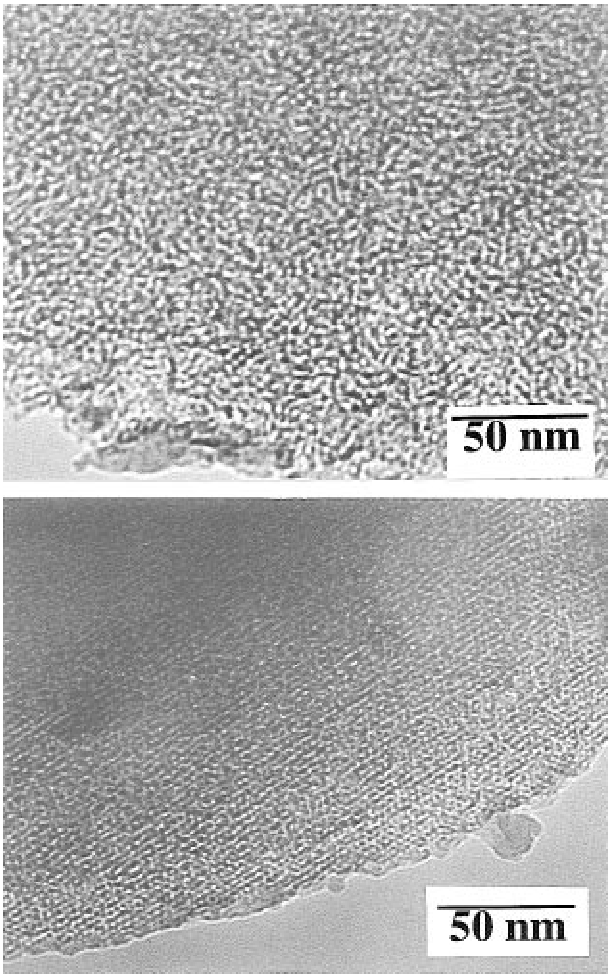

Figure 4. TEM of mesoporous silica sphere using C_{18}-TMABr: (a, top) disordered region; (b, bottom) ordered region.

of the pore properties of spheres using different surfactants are listed in Table 1. The small pore size of the spheres from a C_{12}TMA synthesis system results in specific surface area and pore volume comparable with those of zeolite phases.[24]

We suggest that the formation of porous spheres is another example of emulsion based synthesis of hollow mesoporous silica micro-sphere.[1] The oil component in this case is the hydrophobic, slow hydrolyzing silicon source TBOS. Under basic conditions TBOS undergoes hydrolysis to give butyl alcohol, which is immiscible with water. The oil-in-water emulsion formed during the early reaction stage thus contains BuOH and partially hydrolyzed TBOS as the oil phase. The quaternary ammonium surfactants play an important role for the stabilization of this emulsion, as is the case when an auxiliary hydrophobic "oil" (e.g., hexane) is used to form the emulsion as described previously.[1] However, in this case stablization of a surfactant−auxiliary oil interface[1] is not required so that strong base (S^+I^-) synthesis condition can be used. Hydrogen bonding between the BuOH and water molecules provides a diffusion pathway for the surfactant and water to penetrate the TBOS/BuOH oil droplets and promotes the hydrolysis of TBOS. The silicate formed from hydrolysis of TBOS polymerizes under the influence of the structure directing surfactant and transforms into solid spheres via a soft silicate gel.

Table 1. Properties of Spheres[a]

surfactant	pore diameter (Å)	specific surface area (m^2/g)	specific pore volume (cm^3/g)
C_{12}TMA	<14	484	0.24
C_{14}TMA	15.5	970	0.49
C_{16}TMA	18	1100	0.61
C_{18}TMA	20	903	0.54

[a] Pore diameter: BJH pore diameter from nitrogen adsorption branch. Specific surface area: BET surface area. Specific pore volume: single point volume at relative pressure 0.99.

Additional experiments have been carried out to prepare spheres containing Cu^{2+}. Copper nitrate as a Cu^{2+} source was added at the beginning of preparation, so that the calcined spheres can be directly used as catalyst beads, for example in a "floating gas−solid fluidized bed" reactor.[25] Other transition metals, e.g., Co, Ti, Zr, or V, can be introduced into the silica sphere during synthesis or postsynthesis treatment.

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