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PERIODIC MESOPOROUS SILICA GELS

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ABSTRACT

We have synthesized monolithic particulate gels of periodic mesoporous silica by adding tetramethoxysilane to a homogeneous alkaline micellar precursor solution. The gels exhibit 5 characteristic length scales over 4 orders of magnitude: fractal domains larger than the particle size (>500 nm), particles that are ~150 to 500 nm in diameter, interparticle pores that are on the order of the particle size, a feature in the gas adsorption measurements that indicates pores ~10-50 nm, and periodic hexagonal arrays of ~3 nm channels within each particle. The wet gel monoliths exhibit calculated densities as low as ~0.02 g/cc; the dried and calcined gels have bulk densities that range from ~0.3-0.5 g/cc. The materials possess large interparticle (~1.0-2.3 cc/g) and intraparticle (~0.6 cc/g) porosities.

INTRODUCTION

Periodic mesoporous metal oxides can be formed by templating a molecular source of metal oxide around surfactant arrays [1-5]. Reported methods to synthesize periodic mesoporous silica yield precipitates of colloidal particles in a variety of sizes and shapes ranging from submicron spherical grains to ~1-2 mm hexagonal aggregates [1-5]. The grain size, morphology, and aggregation of primary particles is an important consideration for applications of a porous material. These geometric aspects control the access to porosity, the interparticle void volume, the flow rate of liquids through the packed material, the ability to use the material for industrial scale processes (such as pressure swing adsorption), as well as the ability to safely and conveniently handle the material.

We have developed a one-step binderless method to synthesize pellets and monoliths of periodic mesoporous silica (PMS) with a wide variety of sizes and shapes. The monoliths consist of aggregates of submicron ellipsoidal or spherical particles. Within each particle there is a periodic hexagonal array of 1-dimensional, unimodal 3 nm channels. Thus, the materials contain a tremendous inter- and intraparticle pore volume.

EXPERIMENTAL

A typical synthesis of a periodic mesoporous silica gel involves mixing deionized water, methanol, cetyltrimethylammonium bromide (C_{16}TMABr), NaOH, and tetramethoxysilane (TMOS). The water to methanol ratio is also fixed at 75:25 w/w and the micellar solutions, before the addition of TMOS, are 1, 2, 4, 8, 16, 32 wt% in C_{16}TMABr solutions. After addition of the TMOS, the silica concentrations are 0.2, 0.4, 0.76, 1.38, 2.33, 3.56 M, respectively. The H_2O:Si ratios vary from 195 to 4.2 across this range.

The porous materials were synthesized by injecting TMOS into a rapidly stirred, basic surfactant solution. The mixture turns translucent, then transparent, and then abruptly opaque as a white particulate gel forms. The gels were dried in air over several days and then calcined to remove the surfactant. The calcination process involved heating from 25 to 550 °C at 1 °C/min in flowing N_2 followed by a 1 h isotherm and a 1°C/min cool to room temperature; the process is repeated in flowing air except the isotherm lasted 5 h. This procedure avoids the pore collapse that can occur if the monoliths are calcined in air. The calcined products are white.

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X-ray diffraction data were collected on crushed monoliths using a Scintag PAD V instrument equipped with nickel-filtered Cu K_a radiation. Small angle X-ray scattering data were collected on a Bonse-Hart camera at Brookhaven National Light Source. High resolution magic angle spinning ^{29}Si NMR spectra were recorded on powder samples using a Chemagnetics instrument equipped with a 4.7 Tesla magnet. A JOEL 1200EX transmission electron microscope (TEM) with ASID (SEM) attachment was used to observe the microstructure and grain size of the powder samples on holey carbon film of a 3 mm copper grids. A PL Thermal Sciences STA 1500 combination TGA/DTA was used to monitor water evolution and template decomposition in the crushed samples. A heating rate 10°C/min was employed, and samples were analyzed under flowing air. A Micromeritics ASAP 2010 was used to collect isothermal N_2 adsorption data at 77 K on crushed and monolithic samples. Samples were degased overnight at 200 °C. 4-point BET analyses were performed to determine the apparent surface areas. Pore diameters were determined by application of the Kelvin Equation to the desorption branch of the data.

RESULTS

Silica Source: The Key to Forming Monolithic PMSGs

Our discovery of periodic mesoporous silica gels (PMSG) resulted from an attempt to optimize solution homogeneity, kinetics, and product yield for bulk periodic mesoporous silica powders. We examined several silica sources and solvent systems (e.g. water plus alcohols, amides, glycols, acetates, or polyethers) and found that the use of solid silica sources, such as, fumed or precipitated silica, results in precipitated particles of PMS in less than optimal yield in several hours to several days [1,2,5]. The use of tetraethoxysilane (TEOS) in a purely aqueous solvent leads to precipitated colloidal particles in several minutes at 25 °C [3,4]. In both cases products are formed from inhomogeneous solutions, which can result in less than quantitative yield.

We reasoned that forming PMS from homogeneous solutions was the key to optimizing yield. In order to do this the reagents should be molecular (i.e. alkoxides) and must all be dissolved prior to product formation. The surfactant and base are dissolved in solution prior to the addition of the silica source, so the key then is to solubilize the alkoxide prior to the formation of PMS. Silicon alkoxides are not initially soluble in a pure water, but it is well known that alcohols act as homogenizing agents for alkoxides in aqueous solutions, so we added the cosolvent ethanol to the TEOS preparation. The ethanol reduced the long-range order of pores in the products and in some cases led to amorphous materials.

Because of the slow hydrolysis kinetics with TEOS we next examined tetramethoxysilane (TMOS) as the silica source; in this case we used methanol as the cosolvent. When the TMOS is added to the alkaline micellar water:methanol solution, an emulsion forms initially, but it quickly clears yielding a clear transparent solution. Within a matter of 5-7 seconds at room temperature white particulate gels of PMS are formed from these homogeneous solutions. The size and shape of the monoliths is obviously dictated solely by the geometry of the reaction vessel. Monolithic gels appear to form only when TMOS is the silica source; the use of TEOS, tetrapropoxysilane (TPOS), tetrabutoxysilane (TBOS), fumed silica, precipitated silica, silica sols, or water glass yields only precipitates of colloidal particles.

Aggregation and Gelation

As expected the kinetics of product formation are much faster when TMOS is used as the silica source as compared to TEOS, TPOS, or TBOS or non-molecular silica sources. The diminished steric bulk of the methoxy ligand as compared to alkoxides with larger alkyl groups results in more rapid hydrolysis and condensation of the precursors and product formation (~2

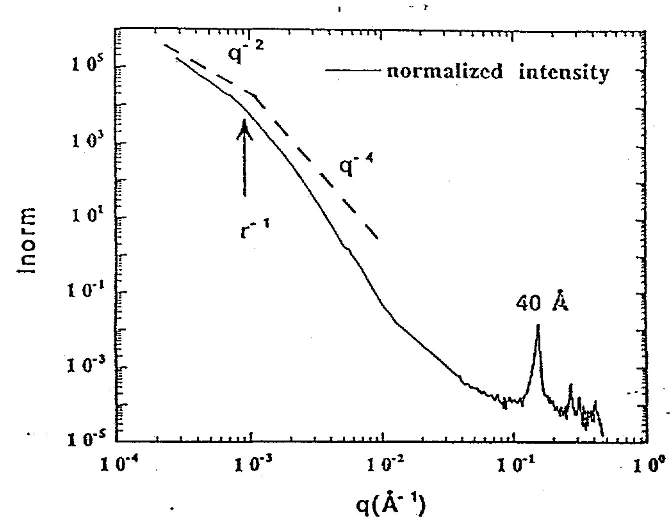

Figure 1. SAXS data show an extended regime of power-law scattering, indicative of aggregation of particles (mesophase domains) into fractal clusters of dimension 2. The slope of -4 in the Porod regime indicates the existence of smooth particles. The diffraction peaks at large q indicate the existence of a hexagonal array of unimodal ~4 nm pores.

orders of magnitude as compared to ethoxy), and the high solubility of TMOS as compared to non-molecular sources also augments the reaction rate (~3 to 4 orders of magnitude).

In fact, periodic mesoporous silica particles aggregate and gel within 1 s at room temperature as determined by the transparent to opaque transformation. A reasonable scenario is as follows: After hydrolysis of the TMOS to form multidentate, multiply charged silicate oligomers and displacement of monodentate, monovalent surfactant counter- ions from the electrical double around the surfactant arrays, microdomains of liquid crystalline silica/ surfactant begin to form. The microdomains assemble into small, size-stable particles, the exterior of which are coated with uncondensed, highly reactive Si-OH and Si-OMe groups. (This view is supported by ^{29}Si NMR, in which we measure $Q^3/Q^4 = \sim 2.1$ five minutes after gelation.)

Through collisions, these particles aggregate and become chemically bonded by the formation of Si-O-Si bonds across two particles. This process continues until the hydrodynamic volume of the clusters fills the solution. At this point the fractal aggregates percolate to form a wet gel. The particulate gels consist of aggregates of submicron ellipsoidal or spherical mesophase particles, typically 150-500 nm in diameter. Within each particle there is a periodic hexagonal array of 1-d channels.

We have examined the gels on several length scales with X-ray scattering measurements: First, for dimensions large compared to the particle size, we have found the fractal dimension is $D \cong 2$, Figure 1. From the fractal dimension one can usually determine the type of aggregation [6]: $D \sim 1.75$ indicates Diffusion Limited Cluster-Cluster Aggregation DLCA), in which clusters stick upon first contact, and $D \sim 2.1$ indicates Reaction Limited Cluster-Cluster Aggregation (RLCA), in which the sticking probability for clusters is less than unity. As the value falls between these limits, assignment of a growth mechanism is ambiguous for PMSGs. Generally, growth kinetics studies can be employed to resolve ambiguities, but, unfortunately, the aggregation is too rapid in PMSGs for growth studies. The mechanism is most likely DLCA, however, as indicated by the rapid formation kinetics and the high concentration of reactive hydroxyl and alkoxy species, which favor particle-particle bonding. Second, in the Porod region, we see a slope of –4 in Figure 1, which is indicative of smooth colloidal particles, as seen in SEM. Third in the Bragg region of Figure 1 and from X-ray diffraction we see 4 peaks that can be indexed as the *100*, *110*, *200*, and *210* reflections of a hexagonal cell ($a \approx 46$ Å). This is definitive evidence for a periodic mesoporous silica 1-d channel structure. TEM of the particles also confirms that they contain periodic hexagonal arrays of 3-4 nm pores.

Controlling the Interparticle Porosity

The interparticle porosity is primarily determined by the volume fraction of particles (ϕ_p), which is determined by the initial concentration of silica in the precursor solution. As the density of particles, excluding the weight of the solvent, is quite low in the wet gel (~0.02-0.2 g/cc), the interparticle volume is quite large, Figure 2. The total monolith volume shrinks ~60 to 90%

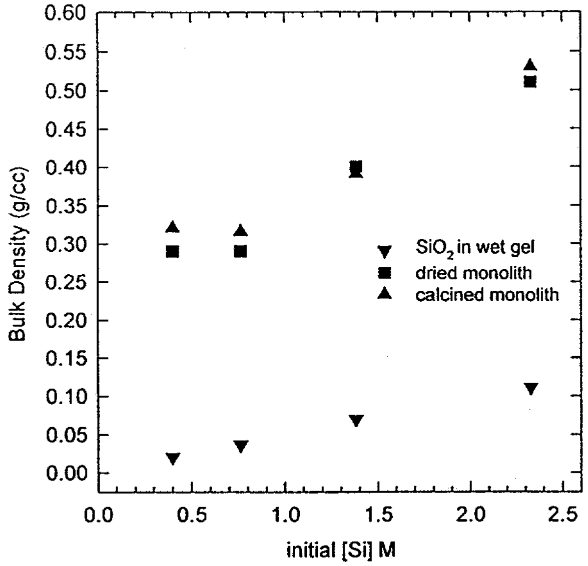

Figure 2. Bulk density varies approximately linearly with initial silica concentration for PMSG monoliths. Samples were dried in air from 75:25 water:methanol pore fluid and calcined in N_2 followed by O_2.

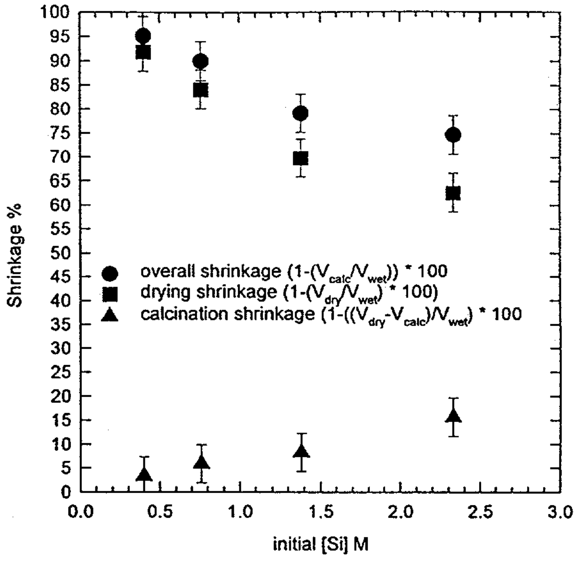

Figure 3. Drying and overall shrinkage of monoliths decrease approximately linearly with initial silica concentration. Calcination shrinkage, relative to the *dried* volume remains constant at about 40% (not shown).

when the wet gels are dried in air at ambient pressure and temperature, Figure 3, and results in a substantial reduction in the interparticle volume. The shrinkage is caused by capillary tension developed when the pore fluid evaporates acting on the compliant gel network. The drying shrinkage can be significantly reduced by exchanging the pore fluid with one that has a lower surface tension. For example, the drying shrinkage for an acetone exchanged [Si] = 0.4 M gel is only ~30% compared to ~85% for 75:25 water:methanol. The large difference in drying shrinkage for the samples dried from 75:25 water:methanol sample is consistent with the difference in ϕ_p in the samples.

The difference in ϕ_p between samples is also reflected in the bulk densities of the dried gels, which increase from ~0.29 g/cc for the [Si] = 0.4 M sample to ~0.51 g/cc for the [Si] = 2.33 M sample. The greater density of the dried samples made with higher [Si] indicates a closer packing of the primary particles. A closer packing indicates a higher coordination number for each particle (assuming particle size does not change with reactant concentration) and presumably a greater modulus. All of the dried monoliths are friable, but those made with from [Si] = 0.4 M or greater can be handled and manipulated with little risk of breaking.

The very low theoretical densities (~0.02 to 0.20 g/cc) for the wet gels (as calculated from the weight of the material dried in air divided by the volume of the wet solid) suggest that if the pore fluid were supercritically extracted (it would be desirable to exchange the water:methanol mixture for a fluid with a lower critical pressure) low density, aerogel type materials could result. Supercritical drying studies are in progress.

Accessing Intraparticle Porosity

The intraparticle porosity is accessed by carefully calcining the monolith to remove the surfactant template. When the template is removed, a further shrinkage occurs (Figure 2), but the bulk density remains nearly constant (Figure 3). The constant density is a fortuitous balance of the weight loss owing to pyrolysis, which tends to decrease the density, and the volume shrinkage owing to particle shrinkage, which tends to increase the density. The experimental weight

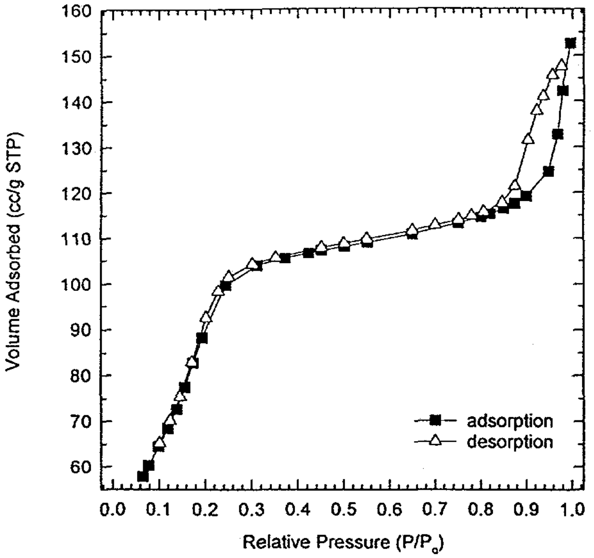

Figure 4. Sorption of N_2 at 77 K shows inflection at $P/P_o \approx 0.15$ indicative of uniform ~2.0 nm intraparticle mesopores and shows a hysteresis at high P/P_o indicative of large interparticle pores.

loss during calcination is ~40% regardless of initial silica concentration and the volume shrinkage at 550 °C is also ~40% (relative to the dried volume) regardless of initial silica concentration.

The shrinkage of the gel during calcination can be almost solely attributed to a shrinkage of the primary particles of the gel. X-ray diffraction data indicate the unit cell constant of the silica shrinks ~10% to 20% depending on exact experimental conditions. If we assume that the shrinkage of the particles is essentially isotropic (which certainly does not have to be the case in a 1-d system) and we calculate the particle volume shrinkage based on the cell shrinkage, we obtain a ~27 to ~49 % volume shrinkage for the particles (r^3 dependence). The observed ~40% shrinkage fits nicely in this range.

In the low temperature regime, the removal of adsorbed solvent and water vapor from the air tends to drive shrinkage through the capillary forces exerted on the pores. This effect is opposed by the coefficient of thermal expansion of the solid. The shrinkage (or expansion) in this region is typically small in amorphous silica. At slightly higher temperatures (e.g. > 150 °C) the template is pyrolyzed (~300 °C) and the framework continues to structurally relax and polymerize; the Q^3/Q^4 ratio decreases from ~2.1 in the wet gel to ~0.4 in the calcined gel. The condensation of silanol groups to form siloxane bonds and the structural relaxation, which is thermodynamically driven by the elimination of the excess free volume created by removal of the organic templates, probably account for the bulk of the shrinkage observed during calcination.

Measuring Inter- and Intraparticle Porosity

Calcined PMSGs exhibit sorption isotherms that indicate a bimodal pore size distribution, Figure 4. Similar to bulk materials, they show distinctive nitrogen isotherms that exhibit pronounced uptake of gas over a very narrow range of P/P_o corresponding to a narrow distribution of intraparticle mesopores (typically ~25 Å in diameter). In addition, they show a broad hysteretic uptake of nitrogen at high P/P_o, which corresponds to a broad distribution of interparticle mesopores (typically 10-50 nm in diameter). The total pore volume is ~1.6-2.9 cc/g ($V_p = 1/\rho_{bulk} - 1/\rho_{framework}$, where $\rho_{framework}$ is ~ 2.3 g/cc) of which about 0.6 cc/g is intraparticle and 1.0-2.3 cc/g is interparticle.

There is a report [7] of a silica material that contains two broad distributions of pore sizes; d_{ave} = ~30 Å (FWHM ~15 Å) and d_{ave} = ~110 Å (spread from 80 to 200 Å) that was synthesized by calcining an X-ray amorphous wet product derived from tetraethoxysilane (TEOS) and cetyltrimethylammonium chloride (C_{16}TMAC). Quite different from TMOS derived gels, the sorption isotherm for this material shows no discernible uptake of nitrogen in the P/P_o region that would correspond to 30 Å pores.

CONCLUSIONS

We have developed a one-step binderless method to form mesoporous periodic silica gel monoliths and pellets of arbitrary shape and size. The key to gel formation is the silica source, TMOS, the rapid kinetics associated with product formation, and the high degree of Q^3 species present at the gel point. PMSGs may be useful as high capacity storage materials for condensable gases, such as methane and other light hydrocarbons, as graded particle size/graded pore size separation media for liquid chromatography, as porous media in separation of gases via pressure swing adsorption, and as low density thermal insulation. As made from laboratory reagents, the cost for dried and calcined PMSG is ~$0.60/cc. By using reagents in bulk the cost could be lowered significantly.

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