

Highly Porous Silica Network Prepared from Sodium Metasilicate

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Abstract

Porous silica network was prepared from sodium metasilicate (Na_2SiO_3) at room temperature (27°C) using hydrochloric acid (HCl) as catalyst through the sol-gel method. The gel was dried at 120°C for 1 day and calcined at 800°C for 3 hours and the material obtained characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The results showed the formation of amorphous silica particles of average sizes 598 nm with ordered porous network of pore sizes ranging from 0.18-0.91 μm . This synthetic route uses sodium metasilicate as commercial precursor without pore forming templates which could be useful for large scale production.

Key words: Silica particles, Sodium metasilicate, Commercial precursor, Porous network

Introduction

Porous silica has received wide attention for application in the fields of selective separation⁽¹⁾, catalysis⁽²⁻⁴⁾, electric materials⁽⁵⁾ and prosthetic materials⁽⁶⁾ because of its high chemical and thermal stabilities, large surface areas and good compatibilities with other materials. Other areas of increasing interest in porous silica are as gas absorbents⁽⁷⁾, heavy metal ion absorbents⁽⁸⁾ and inorganic carriers for enzyme immobilization.⁽⁹⁾

Another very important area of application of porous silica is in chemical sensors. The sensing of a chemical environment is achieved mainly in the surface interactions of the sensor material with its chemical surroundings. To achieve this goal, a porous structure is therefore important in developing good chemical sensors. Porous silica is a unique matrix material for chemical sensors, combining many excellent physical and chemical properties, such as very high chemical stability, high thermal stability, very low thermal expansion, good thermal shock resistance, superior aging behaviour, very high chemical inertness, which makes it possible for a wide range of materials to be accommodated, and very high transparency from ultraviolet to infrared. The porous structure of porous silica also has many advantages for chemical-sensor applications,

such as the very large surface area, which can enhance the interfacial chemical reaction and thus improve the sensitivity, the various permeabilities of chemical species, which can improve the selectivity, the high thermal shock resistance, which can enhance the reliability, etc.

Porous silica have been prepared using different methods. Janet, *et al.*⁽¹⁰⁾ prepared porous silica with high surface area from tetraethyl orthosilicate and high molecular weight polyacrylic acid in acidic media by a sol-gel method. Santos, *et al.*⁽¹¹⁾ prepared porous silica glasses through sol-gel processing employing tetraethyl orthosilicate as precursor, with HNO_3 and HF as catalysts. Liu, *et al.*⁽¹²⁾ synthesized porous SiO_2 film with the thickness of $22\mu\text{m}$ on silicon substrate by spin coating the SiO_2 gel precursor solution. Ikeue, *et al.*⁽¹³⁾ described the synthesis of self-standing porous silica thin films with different pore structures by a solvent evaporation method. Caruso, *et al.*^(14,15) reported on the fabrication of hollow inorganic silica and inorganic-hybrid spheres through the colloid template electrostatic LBL self-assembly of silica nanoparticles to form SiO_2 -polymer multilayers, followed by removal of the templated core and, optionally, the polymer, opening the way to the production of novel core-shell materials of given size, topology and composition. However, the size

of the templates used is normally several hundred nanometers in diameter, and could hardly form nanosized hollow particles.

The sol-gel processing technique is inexpensive and offers the advantages of facility, versatility, purity, homogeneity and modifications of material properties by optimizing synthesis parameters.^(16,17) The mean pore size, the interconnectivity and the pore size distributions can be controlled by changing the molar ratio water/precursor, type of catalyst or precursor, temperatures of gelation, drying, and stabilization.

Several preparation methods of porous silica particles involve the use of expensive precursors⁽¹⁸⁻²⁰⁾ tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS), sometimes with templates to form pores. The aim of this work is to synthesize porous silica network at room temperature without a template from sodium metasilicate, an inexpensive starting material.

Materials and Experimental Procedures

Materials

The reagent chemicals used for synthesizing the porous silica network were: sodium metasilicate, Na₂SiO₃ with composition SiO₂ 24.9, Na₂O 20.9 and H₂O 54.2 wt % (Sigma-Aldrich, 98 %) and HCl (Riedel-DeHaen, 37 %).

Preparation of Porous Silica Network

Na₂SiO₃ (5 g) was dissolved in deionized water (10 ml) and 2 M HCl (26 ml) was added dropwise under stirring using a magnetic stirrer until a gel was formed at room temperature of 27°C.

Washing, Extraction and Drying Procedures

The gel prepared above was immediately poured into deionized water and washed successively, using suction to remove the NaCl formed during the hydrolysis stage of the reaction (eqn. 1). No precipitate was found when the liquid from the last filtration was tested using dilute AgNO₃ solution, indicating the complete removal of NaCl from the gel network.



Thermal Treatment

After washing, the gel was dried in an oven at 120°C for 1 day, calcined at 800°C for 3 hours in a furnace with a heating rate of 10°C/min and thereafter milled to form powders.

Methods of Characterization

The silica particles were characterized by X-ray diffraction (XRD, X'pert PRO PANalytical) using CuK α radiation (0.154060) source operated at 40 kV and 40 mA. The diffraction patterns were obtained in the 2 θ range from 10-80°. The morphology of the material and particle sizes were investigated using scanning electron microscopy (SEM, EVO/MAIO). The sample was carbon-coated and observed at an accelerating voltage of 10kV. Fourier transform infrared (FTIR, Buck Scientific 500), in the wavenumber range of 4000-600 cm⁻¹ employing KBr pellets was used to monitor the types of bonds present in the particles.

The bulk densities of the silica particles were measured from their weight to volume ratio using the formula

$$\text{Bulk density, } \gamma_b = \frac{M}{V} \quad (2)$$

where, M is the mass of the sample measured with microbalance (10⁻⁵ g accuracy), and V is the volume measured by filling the silica particles in a column of known volume.⁽²¹⁾

The specific surface area of the particles in m²g⁻¹ was calculated using the equation^(22,23)

$$\text{Specific surface area, } S_p = \frac{6}{\gamma_p D_p} \quad (3)$$

in which γ_p is specific density assumed to be 2.0 x 10⁶ gm⁻³ for amorphous silica particles based on the spherical model (a typical average density of silica prepared via wet-synthesis conditions⁽¹⁷⁾ and D_p is the average particle diameter.

The porosity was estimated using the relationship⁽²⁵⁾

$$\text{Porosity} = \left[1 - \frac{\gamma_b}{\gamma_p} \right] \times 100 \quad (4)$$

Results and Discussions

XRD

Figure 1 presents the XRD pattern of the silica particles. The spectrum appears as a broad band with a peak at $2\theta = 22^\circ$, which indicates that the material is amorphous and contains pure SiO_2 .^(26,27) The smoothness of the band also indicates that multiple washings with deionized water was efficient in removing the NaCl impurities trapped in the pores of the gel network. NaCl is formed during the hydrolysis stage of the reaction (eqn. 1), which must be eliminated because it destroys the gel network.

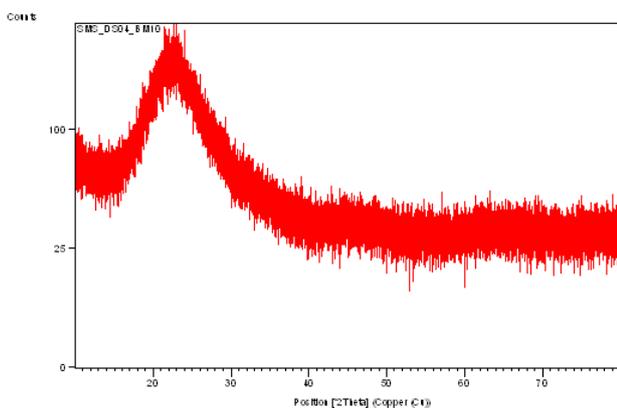


Figure 1. XRD pattern of the silica powders.

FTIR

The FTIR spectrum of the silica particles is shown in Figure 2. The FTIR spectra obtained for the silica particles is characterized by a broad band centred around 3400cm^{-1} and a smaller signal around 1630cm^{-1} that corresponds to O-H absorption band.⁽²⁷⁾ Furthermore, a diagnostic Si-O-Si asymmetric stretching vibration is centred on 1132cm^{-1} ⁽²⁸⁻²⁹⁾, the absorption signal at 920cm^{-1} is assigned to the stretching vibration of silanol groups on the surface of the amorphous solid.⁽³⁰⁾

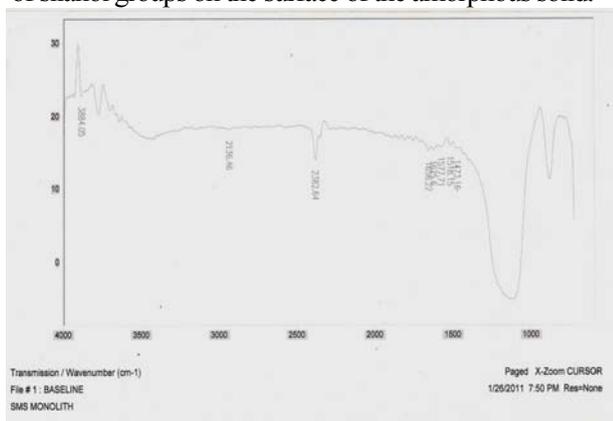


Figure 2. FTIR Spectrum of the sample calcined at 800°C for 3 hours.

SEM

The surface morphology of the silica particles obtained after calcinations at 800°C for 3 hours is shown in figure 3, which indicates that the average particle size is 598nm. Figure 4 is the SEM micrographs of the same silica powder at different magnifications. In Figure 4(a) the silica particles are seen to be dry after the thermal treatment. The high surface area resulting from the distribution of the particles is better appreciated in figure 4(b), while the degree of arrangement of the particles to give a highly interconnected porous network is evident in figure (4c). The result shows that pore spaces were of the range $0.18 - 0.91\mu\text{m}$ and were well distributed in the material. Initially, large pores are formed in the gel after washing, which can be attributed to the confinement of large amounts of ionic liquid within the silica matrix during the synthesis, which on subsequent extraction of the ionic liquid led to porous silica of large sized pores depending on the ionic liquid content.⁽³¹⁾ Calcination of the dry gel at high temperature led to the formation of microporous silica network with attendant high surface area⁽³²⁾, which was calculated to be $5.02\text{m}^2\text{g}^{-1}$ (Table 1). The porosity of this material, estimated to be 76.3 % and consequently, its low bulk density of 0.474Mgm^{-3} (Table 1) is due to presence of an open structure⁽²²⁾ as can be seen in figure 4(c).

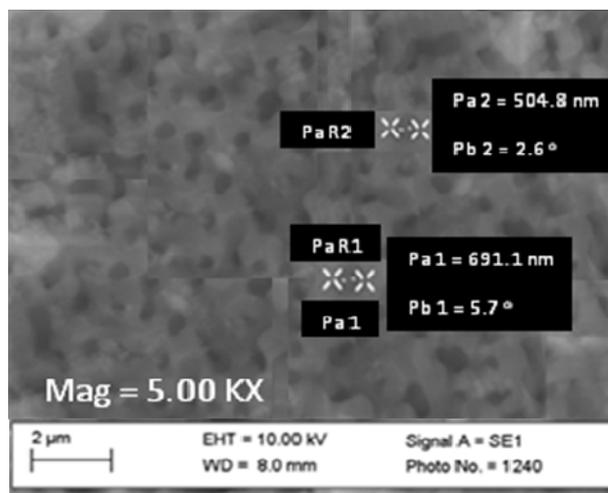
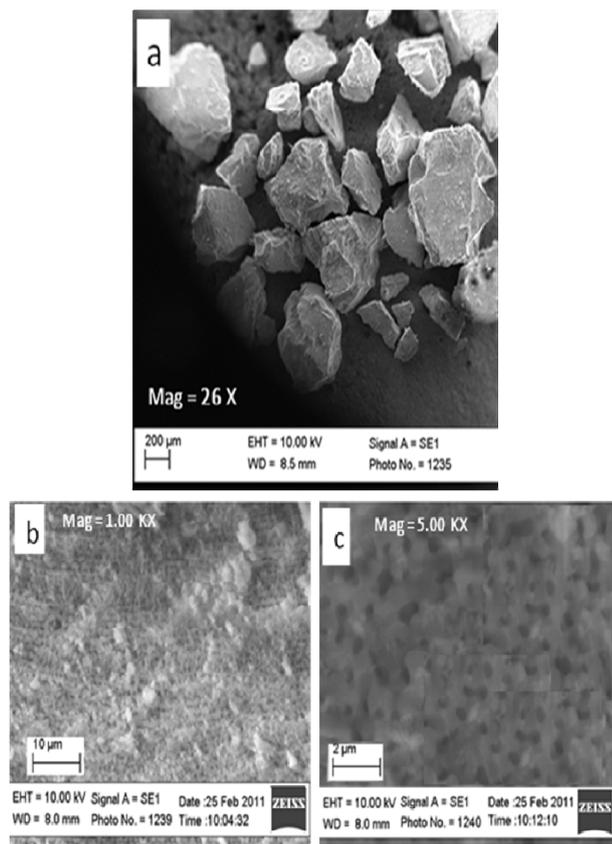


Figure 3. SEM micrograph of the silica powders showing particle distribution and sizes measured at two locations Pa R1 and Pa R2 at positional angles of Pb 1 and Pb 2 respectively.

Table 1. Physicochemical characteristics of the silica obtained.

Average particle size (nm)	598
Bulk density (Mgm ⁻³)	0.474
Porosity (%)	76.3
Specific surface area (m ² g ⁻¹)	5.02

**Figure 4.** SEM micrographs of the same sample of the silica particles at different magnifications showing the arrangement of particles and interconnected pores.

Conclusions

Highly interconnected porous silica network with pore sizes in the sub-micron range of 0.18-0.91 μ m has been successfully formed by using sodium metasilicate as a cheap source of silica and HCl as a catalyst without applying a template. The successful extraction of sodium from the gel network through washing with deionized water and subsequent drying at 120°C for 1 day and calcination at 800°C for 3 hours provided optimal conditions for the generation of

microporous silica network via the sol-gel route. Sodium metasilicate may be utilized as a commercial starting material instead of expensive high quality precursors for preparing porous silica.

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