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Synthesis and Characterization of Amorphous Silica Nanoparitcles from Aqueous Silicates Uisng Cationic Surfactants

Maurice. ABOU RIDA[1*] and Faouzi. HARB[2]

[1] Laboratory of Molecular Chemistry, Lebanese University, Faculty of Sciences II, Fanar, Lebanon
[2] Laboratory of Solid State Reactivity, Lebanese University, Faculty of Sciences II, Fanar, Lebanon

Abstract

In this work amorphous silica was synthesized using sodium silicate and hydrochloric acid by precipitation according to Stőber method. A system of chemical reactions has been developed which permits the controlled growth of silica particles using two different cationic surfactants as the dispersing agents. These surfactants were cetyltrimethylammonium bromide [CTAB] and dodecyltrimethylammonium bromide [DTAB]. The synthesized silicas were characterized by using X-ray diffraction (XRD), Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDX) and Dynamic light scattering (DLS). Addition of a dispersing agent in the reaction reduced the particle size of the silica produced. The average size of silica nanoparticles can be finely tuned in the range 148–212 nm by changing the chain length of cationic surfactant. XRD results showed that the synthesized silica was predominantly amorphous.

Key words: Silica, Sodium silicate, Cationic surfactant, Cost-effective, sol-gel, Microwave drying
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Introduction

Nanotechnology has contributed to the creation of smart functional materials, devices and systems through manipulation of matter in the nanometer scale and exploitation of novel phenomena and properties which arise because of the nanometer size. Recently, silicon oxides, commonly named silicas, in their corpuscular form, have become useful materials in various fields because they have new physicochemical properties which do not appear in the corresponding bulk materials.

Moreover, amorphous precipitated silicas are used as dielectric materials, elastomeric materials (such as rubber), in flat panel displays, sensors, filters for exhaust gases, adsorbents, separations, biomedicine, sensors, drug delivery systems, oil-spill clean-up, heterogeneous catalysts in various chemical reactions and food materials.(1-7) Usually, alkyl orthosilicates are used for the preparation of silica nanoparticles. However, they are not the best commercial sources of silica due to their high cost, flammability, and difficulties in handling and storage. Therefore, their replacement with a comparatively less expensive and robust inorganic silica source is desired.(8-13) Sodium silicate (water-glass) is a cost-effective source of silica compared to the more commonly used tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS). Moreover, by using a purely aqueous medium, the expensive and very often toxic solvent could be avoided. Sodium silicate could be a good source of silica for industrial, large-scale production of precipitated silica powders.

The properties of precipitated silica depend strongly on the conditions of its synthesis, such as the synthesis temperature, time of precipitation, pH, addition of surfactants, and modes of washing and drying. These factors influence the size of the SiO_2 particles, their morphology, aggregation and specific surface area.

In the present work, water glass was used as a precursor for the precipitation of amorphous SiO_2. The effect of cationic surfactants CTAB and DTAB (figure 1) on the physical properties of synthesized silica was investigated. The precipitated silica produced as described in the present work can be used for further academic investigations, and also as a valuable commercial product.

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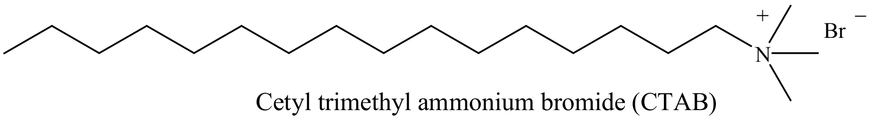
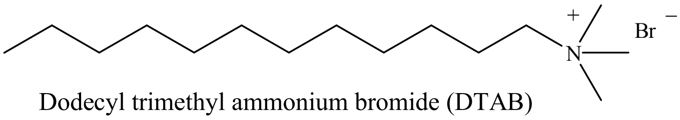
*Corresponding author E-mail : mauriceabourida@hotmail.com



Cetyl trimethyl ammonium bromide (CTAB)



Dodecyl trimethyl ammonium bromide (DTAB)

Figure 1. Surfactant used in the synthesis process of silica nanoparticles

Materials and Experimantal Procedures

Materials: Sodium silicate solution (SIGMA-ALDRICH contains ~14%NaOH ~27% SiO_2), hydrocholric acid (Aldrich), cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB) were purchased from Aldrich. All reagents were used without any further purification.

Preparation of wet-gel silica slurry through the drop-wise addition of hydrochloric acid into an aqueous sodium silicate solution

Silica wet-gel slurry was prepared from an aqueous sodium silicate solution through the addition of hydrochloric acid using the precipitation method under constant stirring. The sodium silicate solution was diluted in distilled water in the ratio of 1:5 by volume to obtain a 15% solution. A concentrated HCl solution was diluted in distilled water to obtain a 2.5% solution. This HCl solution was used to neutralize 200 ml of the previous silicate solution to which 1 gr of the cationic surfactant (A or B) was added and stirred until complete dissolution.

The temperature was adjusted to 55°C under constant stirring at a speed of 300 rpm. The 2.5% HCl was added to the alkaline silicate solution in two steps. In the first step, 2.5% HCl was added drop wise to the mixture; the semi-gelatic point was achieved at pH 9-9.5. In order to prevent the formation of a strong silica gel, the solution was stirred for an additional 10 minutes with no further addition of HCl. The second step involved the addition of more 2.5% HCl until the pH of the silica slurry reached 3-3.5.

At this pH, 10 mL of a 10% NaCl aqueous solution were added to the reaction mixture and stirred for additional 20 minutes. After this final addition, the precipitated wet-gel silica slurry was aged for 24 hour at 50°C without any further stirring. The prepared wet-gel silica slurry was thoroughly washed with distilled water until there was a negative reaction for chloride ions, as controlled with 0.1M AgNO3 solution. Furthermore, the washed cake was dried using microwave heating technique.

Microwave Drying and Calcination

In order to obtain a well structured silica powder with enhanced textural properties, particularly a narrow grain size distribution with reduced agglomerates size, we decided to combine the microwave drying to the oven drying technique.(14) In the microwave drying, the water present in the wet-cake absorbs the microwaves throughout the entire mass, causing molecular vibrations with respect to the oscillating electric field of the microwaves and thus uniformly heating the wet-cake.(15) This preliminary drying was followed by oven drying where the heat energy is transferred to the interior of the cake via conduction. The heat conduction rate depends on the thermal conductivity of the silica cake and decreases significantly as the moisture content in the cake decreases, thereby prolonging the drying process.(16,17)

Therefore, the wet-cake was dried at an ambient pressure in a microwave oven (operating on 240 volts, a. c., at a frequency of 2450 MHz, 800 Watts). The total drying time was 70 mn for each sample applied seven times in an intermittent interval of 10 mn. The time interval between successive microwave exposures was also 10 minutes. The dried cake was calcined at 650°C for 3 hours in a muffle furnace with a heating rate of 10°C/min and thereafter milled to form powders.

Instrumentation

Types of bonds present in the particles were determined using the Fourier transform IR spectra recorded using a *Perkin-Elmer* spectrometer (Model 2000) and covered the range from 400–4000 cm^{-1}. The specimen was pressed using a spectroscopically pure KBr matrix.

X-ray diffraction (XRD) of the synthesized silica was obtained by using an (XRD Bruker AXS D8 Focus) diffractometer. The diffraction patterns were obtained in the 2θ range from 3-50°.

The particle size and the frequency distribution of the particles were determined by a dynamic light scattering (DLS) laser granulometer (Horiba laser scattering particle size distribution analyzer LA-950V2).

The morphology of silica particles was observed by scanning electron microscopy (SEM) using a HITACHI S4800 microscope (Chiyoda-ku, Japan) linked to an EDX/INCA 350 (energy dispersive X-ray analyzer) manufactured by *Oxford Instruments Ltd.* (UK). Samples were copper coated.

Results and Discussion

XRD

Figure 2 shows an X-ray powder diffraction pattern of precipitated SiO_2. The spectrum appears as a broad band with the equivalent Bragg angle at 2θ = 22°, which indicates that the material is amorphous. The smoothness of the band also indicates that multiple washings with deionized water were efficient in removing the NaCl impurities trapped in the pores of the gel network. Absence of sharp peaks confirms the absence of ordered crystalline structure in the prepared silica nanoparticles.(18)

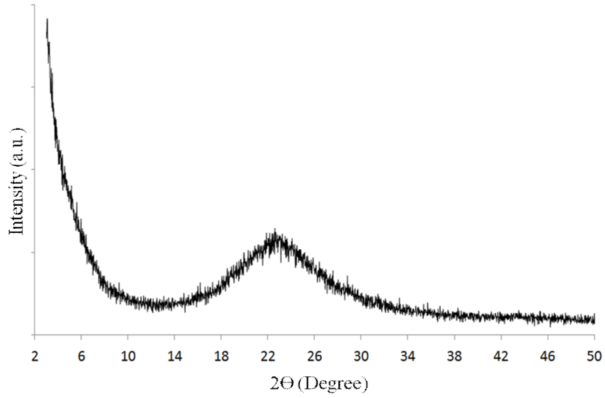


Figure 2. XRD pattern of the silica powders

FTIR

The FTIR spectrum of the silica particles is shown in Figure 3. The band around 3440 cm^{-1} is due to –OH stretching vibration of the silanol or adsorbed water molecules on the silica surface. The bending vibration of the trapped water molecules in the silica matrix was detected as an intense peak at 1635 cm^{-1}. This band could not be completely removed by heating, but its intensity however, decreased.(19) The strong band at 1092 cm^{-1} corresponds to the asymmetric vibration of the siloxane bond, Si–O–Si. This bond forms the backbone of the silica matrix. The presence of an absorption band at 800 cm^{-1} is assigned to the stretching vibration of Si–O–Si bond.(20) The band observed at 472 cm^{-1} is due to the bending vibration of the Si–O–Si bond.(21) The presence of a band 972 cm^{-1} indicates the Si–O stretching vibration of the silanol group.(22)

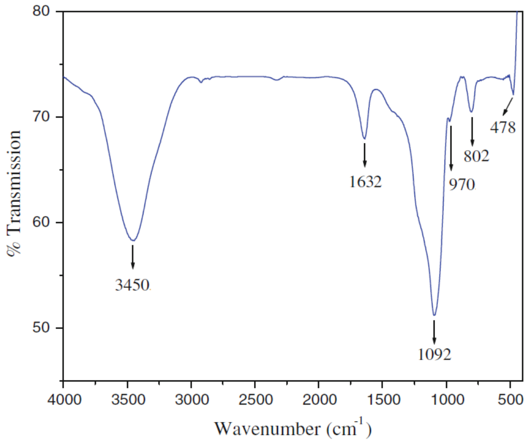


Figure 3. FTIR Spectrum of the sample calcined at 600°C for 3 hours.

SEM

The surface morphology of the silica particles obtained after calcinations at 650°C for 3 hours is shown in figure 4. Analysis of the Scanning electron microscopy (SEM) micrographs illustrates that amorphous silica particles were obtained. The majority of primary SiO_2 particles had a uniform size varying from ~50 to ~ 70 nm in size. These primary particles showed a big tendency to aggregate and form larger particle clusters. Particle size could be controlled by varying the chain length of cationic surfactant. Particles produced using the aqueous silicate precursor solution with cetyltrimethylammonium bromide surfactant (figure 4. A) displayed better dispercivity and smaller size than those made with dodecyltrimethylammonium bromide (figure 4. B) cationic surfactant.

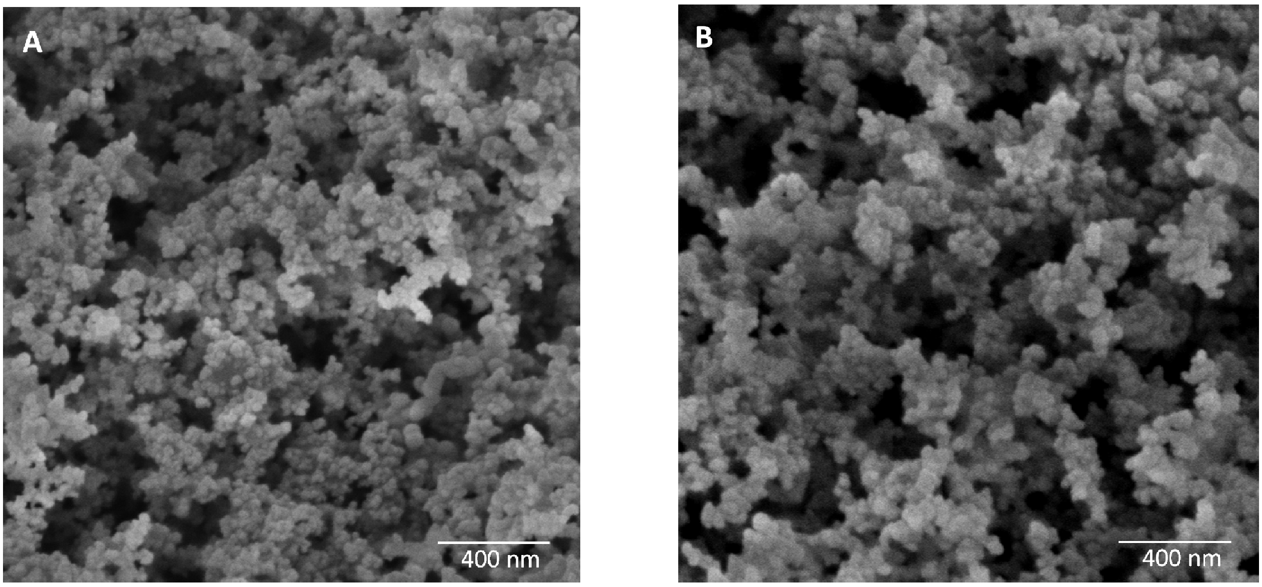
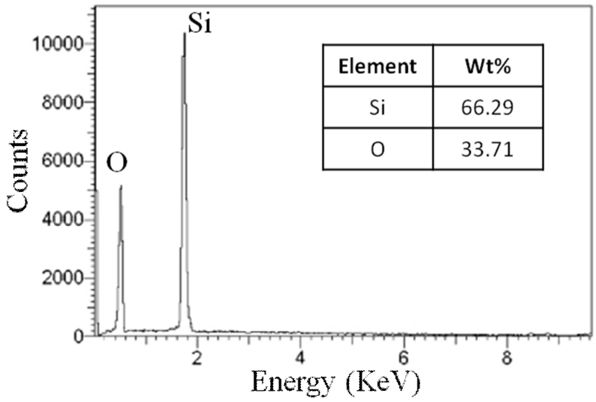


Figure 4. SEM micrograph of the amorphous silica prepared with CTAB (A) and DTAB (B)

EDX

Chemical analysis was performed with energy dispersive X-ray spectroscopy EDX in scanning electron microscopy SEM mode. The observed EDX result (figure 5) shows that the precipitated silica contains 66.29wt % of silicon. It can be confirmed from EDX analysis that the sample contains more than 99% purity of silica with free silicon. In addition, the EDX measurement of the precipitated silica powder shows that the content of Si and O is, respectively, 99.9 (% in wt%) and 99.9 (% in at%) for both elements. The abovementioned results further confirm the absence of other elements such as C, Na and Cl or Br, which, in turn, confirms the formation of pure silica structures.



Element	Wt%
Si	66.29
O	33.71

Figure 5. EDX pattern of nano silica powder

DLS

Figure 6 shows the Dynamic light scattering (DLS) analysis of synthesized nano-silica. This graph indicates the relatively uniform size distribution of precipitated silica. As can be seen, most of the particle sizes are between 90nm and 250nm with an average of 148nm for the CTAB-prepared silica. For the DTAB-prepared silica most particle sizes are between 100nm and 350nm with an average of 212nm. These results are reasonable and consistent with those obtained by SEM.

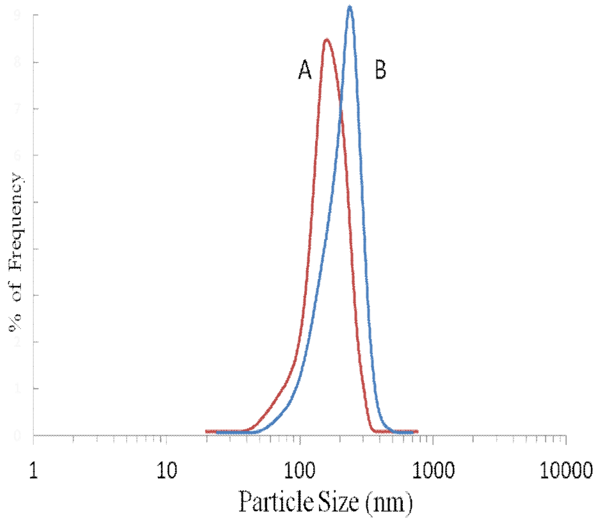


Figure 6. DLS graph of amorphous silica obtained with: CTAB (A) and DTAB (B)

Conclusions

Amorphous, silica nanoparticles can be prepared using aqueous sodium silicate as a cheap source of silica and HCl as a catalyst. The particle size of silica nanoparticles can be controlled using cetyltrimethylammonium bromide (148 nm), tetradecyltrimethylammoniumbromide (212 nm), as cationic surfactants. The particle size decreases as the chain length of the surfactants is increased. Both, sodium silicate and hydrochloric materials are available in the market at reasonable price as compared to the other raw materials used for silica synthesis. The investigations performed in this work have indicated that there is a great scope for their exploitation as raw materials for the production of amorphous silica nanopowder on industrial scale.

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