Preparation and properties of silica nanoparticles from oil shale ash

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ABSTRACT

The method of preparing spherical silica nanoparticles from the oil shale ash (OSA) via the ultrasonic technique in the hydrolysis-condensation stage followed by azeotropic distillation, was reported. The effects of ultrasonic and azeotropic distillation on the particle size and distribution have been investigated. Further, the morphology and properties of the silica particles were examined. The X-ray fluorescence spectroscopy (XRF) and Brunauer Emmett Teller (BET) analysis confirmed that the powders consist of silica nanoparticles with high purity, 99.90% and specific surface area of 697 m^2/g. X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) analysis indicate that the silica nanoparticles are amorphous and that the surface of silica nanoparticles is modified by the organics. The transmission electron microscopy (TEM) images of the sample show that good dispersion and uniform silica particles with an average diameter of about 10 nm are prepared. The results obtained in the mentioned method prove that the oil shale ash (OSA) can be used for production of silica nanoparticles.

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1. Introduction

A by-product of oil shale processing is ash, which is considered a serious environmental problem. Therefore, there is a need for a proper strategy for ash handling, disposal and utilization. Recent studies have demonstrated that the OSA can be used for production of cement and concrete [1–3], sorbents [4–8], tobermorites [9–11], soil treatment for agricultural purpose [12], while the large portion is dumped in landfills.

It is found that the OSA is mixture of inorganic and organic components, whose major chemical compositions are silicon dioxide (SiO_2) and alumina (Al_2O_3) etc., and whose major mineral compositions are quartz (SiO_2), illite [$K(Al,Fe)_2AlSi_3O_{10}(OH)_2 \cdot H_2O$], kaolinite [$Al_4(SiO_{10})(OH)_6$], chlorite [$(Mg,Fe)_5(Al,Si)_5O_{10}(OH)_8$] and calcite [$CaCO_3$] [5]. So, an alternative manner is the conversion of this ash into a high-grade silica product, which is considered an environmental friendly product. However, there is little available information about extraction of silica from OSA.

Ultrafine silica (SiO_2) powder has considerable potential for a wide range application including catalysts, adsorbents, light-weight structural materials, humidity sensors, colloidal damper in the field of mechanical engineering, and other fine precision equipment [13–15]. However, the large scale commercial production of silica nanoparticles has been limited for mainly two reasons: (i) the use of high-cost alkoxides [tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS)] in the sol–gel or W/O emulsion synthesis, and (ii) nanoparticles

aggregating into large particles during dryness. An important topic in silica nanoparticles research area is to explore cheap raw material for silica nanoparticles production and to find a conformable drying method.

Sonochemistry arises from acoustic cavitation phenomenon, that is the formation, growth and implosive collapse of bubbles in a liquid medium [16]. The extremely high temperatures (>5000 K) and pressure (>20 Mpa) and very high cooling rates (>107 K s^{-1}) attained during acoustic cavitation lead to many unique properties in the irradiated solution. This method is a simple and effective route for preparing ultrafine powders on a nanometer scale and with homogeneous particle size distribution [17,18]. In the recent years many kinds of nanomaterials have been prepared by this method, such as ZnO, MnO, SBA-15 [19–21]. Incidentally, so far, no attempt has been made to prepare silica nanoparticles through sonochemical route.

In the present work, the spherical silica nanoparticles were synthesized using OSA as silica source via the ultrasonic technique in the hydrolysis-condensation stage followed by azeotropic distillation. The effects of ultrasonic and azeotropic distillation on the particle size and distribution were investigated.

2. Experiment

2.1. Materials and reagents

The OSA was used as silica source for synthesis of silica nanoparticles. It was taken from oil retorting factory of Jilin province. The chemical compositions of the OSA are shown in Table 1, and it indicates that the OSA consists of a wide variety of acidic, basic,

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Table 1
Chemical compositions of the OSA before and after the pretreatment and the silica powders

Component	Raw oil shale ash (wt.%)	Calcined and leached oil shale ash (wt.%)	Silica powders (wt.%)
SiO_2	64.7232	86.8561	99.9034
Al_2O_3	15.8514	8.1541	0.0128
TFe_2O_3	8.6109	1.8061	0.0084
P_2O_5	0.5117	0.3163	0.0155
CaO	0.9907	0.0781	0.0049
MgO	1.8221	0.3032	0.0083
TiO_2	1.0411	0.7010	0.0107
Na_2O	0.7046	0.4501	0.0111
K_2O	1.1733	0.6511	0.0054
MnO_2	0.1701	0.0381	0.0010
LOI	3.4237	0.6458	0.0035

amphoteric oxides and incorporated hydrocarbons. All chemical reagents were analytical grade supplied by Beijing Chemical Reagent Research Institute.

2.2. Experimental procedure

2.2.1. Pretreatment of the OSA

The pretreatment of the OSA consisted of the mechanical, thermal, acid treatments. The OSA was crushed to about 0.1 mm, and burned in a muffle furnace at 550 °C for 2 h to remove all incorporated hydrocarbons.

An acid washing step was used to remove the small quantities of minerals prior to silica extraction from OSA in the following manner. The calcined OSA (10 g) was acid-leached with 30 wt.% sulfuric acid solution (50 ml) at 100 °C for 2 h in a pyrex three-neck round-bottom flask equipped with a reflux condenser in a hemispherical heating mantle. Then the slurry was filtered and washed with distilled water for several times until the pH value equaled 7.

2.2.2. Preparation of sodium silicate solution

30 wt.% sodium hydroxide solution (50 ml) was added to the pretreated OSA and boiled for 5 h in a pyrex three-neck round-bottom flask equipped with a reflux condenser in a hemispherical heating mantle to dissolve the silica, and to produce a sodium silicate solution. The solution was filtered and washed with boiling distilled water. The filtrate and washing were allowed to cool to room temperature.

2.2.3. Synthesis of silica nanoparticles

Firstly, 10 g of polyethylene glycol was dissolved in the water (90 ml). subsequently, OSA derived sodium silicate was slowly added to the polyethylene glycol water solution that was being sonicated at 50 °C. Then, 0.5 mol/L sulfuric acid solution was added gradually into the solution in order to initiate the hydrolysis-condensation reaction and sonication was continued 0.5 h. The sol was adjusted until the pH value equaled 4. The resulting gel mixture was aged at 50 °C for more than 8 h. The silica gel aged was filtered and washed by distilled water for several times. The filtration cake was distilled with n-butanol, and then calcined at 550 °C for 2 h in atmospheric condition to remove the surfactant. The silica nanoparticles were obtained finally.

3. Results and discussion

The chemical compositions of the OSA before and after the pretreatment and the silica powders were determined by X-ray fluorescence spectroscopy, and the results are presented in Table 1. Unlike conventional organic silicon compounds, the OSA is a industrial waste, which contains several main extraneous components. The thermal and acid treatments are efficient, resulting in a material with a high reduction in the Fe_2O_3, Al_2O_3, CaO and MgO content. The silica

(SiO_2) in the OSA is not attacked by H_2SO_4 solution in the acid treatment. The silica nanoparticles are obtained by the following reactions:

$$NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O. \quad (2)$$
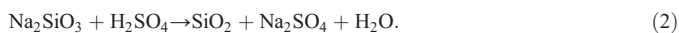
The sodium sulfate (Na_2SO_4) in the silica gel can be washed easily due to its high solubility in water. Table 1 shows that the contents of the extraneous elements are reduced to a low level during the preparation process. The purity of silica nanoparticles is higher than 99.90%.

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku Rotaflex diffractometer equipped with a rotating anode using Cu Kα radiation. The X-ray diffraction scanning angle is from 0° to 80° and rate is 0.01°/s. Fig. 1 shows the XRD pattern of the calcined silica particles. The typical silica characteristic is observed at a broad peak centered at $2\theta = 22.5°$, which indicates the sample is amorphous [22]. The result is accord with selected area electron diffraction. BET analysis was used to determine the total specific surface of silica nanoparticles (Sample was dried at 120 °C for 12 h). BET data indicates that the specific surface area of silica nanoparticles prepared by this method is as high as 697 m²/g.

In order to investigate the action of ultrasonic cavitation during the formation of silica particles another experiment was performed at the same conditions except for ultrasonic irradiation. To find the effect of the sonication time continued, the experiments were performed varying the sonication time continued at a rang 0.5–1.5 h.

Transmission electron microscopy images of silica nanoparticles were obtained with a JEM-2000EX microscope. Silica nanoparticles were dispersed ultrasonically in ethanol, and a drop of suspension was deposited on a carbon coated copper grid. TEM micrographs of silica nanoparticles obtained from the rigorous magnetic stirring (a), and the ultrasonic technique at hydrolysis-condensation periods of 0.5 h (b), 1 h (c) and 1.5 h (d) were exhibited in Fig. 2. Among them, the smallest spherical silica particle size with narrow uniform distribution can be observed in Fig. 2-b, and the average size of particles is about 10 nm. Obviously, the average particle size decreases from 60 nm to 5 nm and the powders are less agglomerated when the rigorous magnetic stirring is replaced by ultrasonic cavitation. However, when ultrasonic periods were increased, serious aggregate silica particles with the larger particle size are obtained (Fig. 2-c,d). Schematic representation of the proposed mechanism for silica nanoparticles formation using ultrasonic is shown in Fig. 3. Comparing with traditional stirring, ultrasonic cavitation is easily achieving microscopic uniform mixing, eliminating partial uneven concentration,
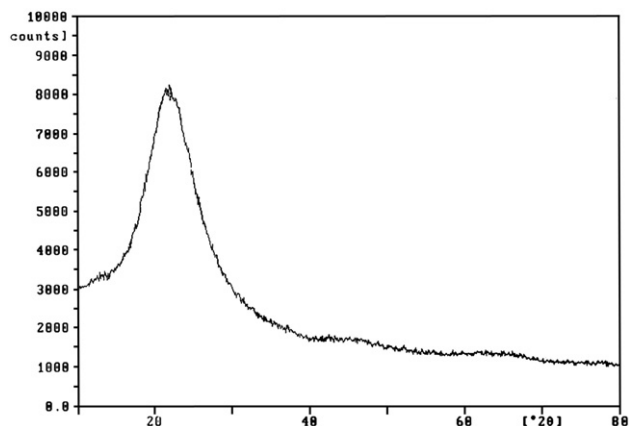
Fig. 1. XRD pattern of the silica nanoparticles.