Influence of Hydrothermal Treatment on Crystalline Form of SiO_2 Synthesized by Sol-Gel Method

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Influence of Hydrothermal Treatment on Crystalline Form of SiO_2 Synthesized by Sol-Gel Method

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Abstract. The hydrothermal method and traditional sol-gel process for the synthesis of SiO_2 particles were comparatively studied. For the synthesis of SiO_2, tetraethyl orthosilicate (tetraethoxysilane or TEOS) and ammonium chloride (NH_4OH) (as a catalyst) were used. SiO_2 was prepared by the TEOS hydrolysis reaction at room temperature and hydrothermal treatment. Morphology and structure of the final products were characterized by X-ray diffraction (XRD), Fourier transform infrared spectrum (FT-IR) and scanning electron micrograph (SEM). It was found that SiO_2 product synthesized by the TEOS hydrolysis reaction at room temperature has an amorphous phase. XRD analysis shows the presence of an amorphous halo - a strong peak at Bragg angle 21 °-22 °. The hydrothermal treatment leads to crystallization of the material.

1. Introduction

In recent years, silicon dioxide (SiO_2) has been widely used in various industries, such as mechanical engineering telecommunication, micro-electronics, and construction. Silicon dioxide has unique electrical magnetic and optical properties, thermo stability and low flammability [1-4]. Studies have shown that the use of silicon dioxide as filler in composite materials, even in small quantities, significantly improves their original properties [5-7]. SiO_2 exists in many crystalline forms, the most popular ones being quartz, cristobalite, tridymite, stishovite, and coesite, but its best-known form is amorphous silicon dioxide. The SiO_2 nanoparticles are commonly synthesized by means of various approaches, such as precipitation [8, 9], sol-gel [10, 11], and hydrothermal synthesis [12,13]. Other methods that can be used include a plasma-chemical method [14], an electron beam method, and a mechanochemical method [15].

Generally, amorphous SiO_2 can be produced by mixing aqueous solutions of sodium metasilicate with acid. For example, Musić, Filipović-Vinceković and Sekovanić [16] precipitated silica by the reaction of sodium silicate solution neutralization with H_2SO_4 solution. Primary SiO_2 particles were ~ 15 to ~ 30 nm in size, and they are aggregated into bigger particles. Amorphous SiO_2 particles showed a specific surface area up to 130 m^2g^{-1} depending on the parameters of the precipitation process. Wardiyati, Adi and Deswita [17] synthesized SiO_2 by the sol-gel method using a precursor of Na_2SiO_3 and catalyst of H_2SO_4 at a sintering temperature of ≤ 600 °C. The size of the obtained particles was around 20 nm. Meanwhile, the

surface area was 298.31 m^2/g. Qisti, Indurate and Suprihatin [18] used the hydrothermal method in synthesizing SiO_2 to produce nanosilica that was uniform and homogeneous.

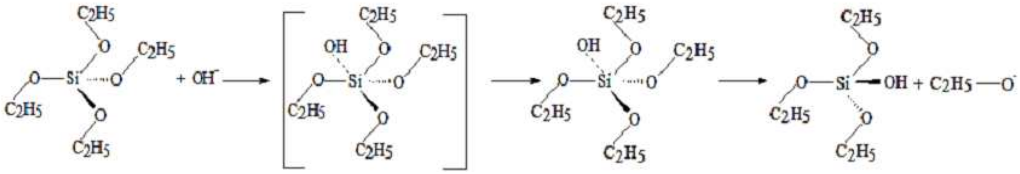
The present paper is aimed to investigate influence of hydrothermal treatment on the crystalline form of SiO_2 synthesized by the sol-gel method.

2. Materials and methods

2.1. Materials

All reagents used were of analytical grade purity. In this synthesis procedure, tetraethyl orthosilicate (tetraethoxysilane or TEOS) was used. It was purchased from Sofex Silicone, Moscow, Russia (99.9 % purity). TEOS is the chemical compound with the formula $Si(OC_2H_5)_4$. TEOS it is a colorless liquid that degrades in water. TEOS is the ethyl ester of orthosilicic acid, $Si(OH)_4$.

Ammonium chloride (NH_4OH) used as catalyst was purchased from Sofex Silicone, Moscow, Russia (99.9 % purity). To carry out the TEOS hydrolysis reaction, distilled water by GOST 6709-72 "Distilled water - Technical specifications" (pH=6.6) was used. The TEOS hydrolysis reaction (synthesis of SiO_2) was carried out according to the scheme:

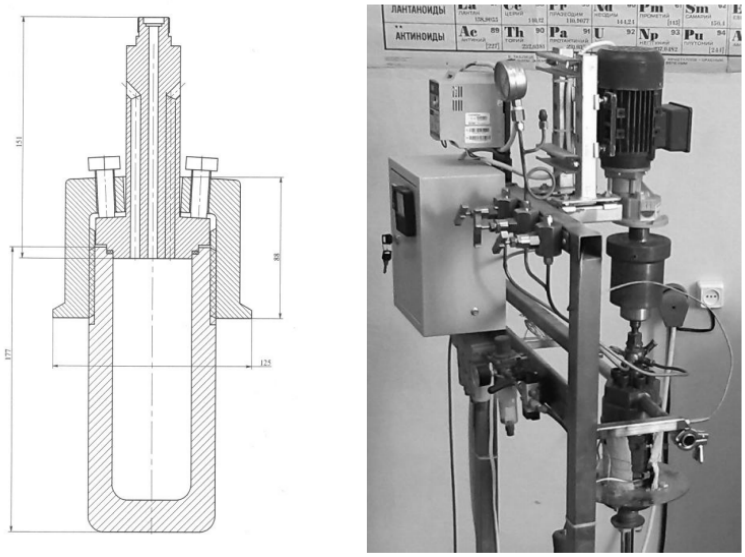


Total reaction:

$$Si(OC_2H_5)_4 + 2H_2O = SiO_2(gel) + 4C_2H_5OH$$

2.2. Hydrothermal synthesis

To carry out TEOS hydrolysis under hydrothermal conditions, the GSA-0.3 high-pressure reactor was used (fig.1). The reactor is designed for scientific and experimental research and chemical reactions in supercritical conditions of high pressure and temperature.



a b

Figure 1. Sketch of reactor capacity (a) and installed installation (b)

Hydrolysis of TEOS in an alkaline medium at room temperature was carried out for 3 days, followed

by drying at a temperature of 110-120° C. Hydrolysis of TEOS in an alkaline medium under hydrothermal treatment was carried out in a high-pressure reactor (temperature 300 ° C, pressure 55 MPa) for 7 hours, followed by drying at a temperature of 110-120 ° C.

2.3. Research Methods

The research was performed with the use of high-tech equipment from High Technologies Center of V.G. Shukhov BSTU (Belgorod, Russia). X-ray phase analysis was performed with the use of the DRON-3 diffract meter (CuKα radiation, Ni filter) according to the standard method. The tube voltage amounted to 20 kV, the anode current was 20 mA, and the detector rotation rate was 2.4 degrees per minute with 1° angular pitch. The measurement rate limit reached 1000–4000 pulses per second. Data analysis and preliminary processing was performed with PDWin software (DrWin, Qual) using the PDF JCPDS database (version 2.02 1999).

Scanning (raster) electronic microscopy was used for the surface morphology identification and microanalysis of the surface layer of the derived bismuth compound. Microphotography was performed using electronic microscope Tescan Mira 3 LMU.

The Fourier transform IR spectrum was recorded using a IR spectrometer VERTEX 70. The specimen was pressed with a spectroscopically pure KBr matrix.

3. Result and discussion

X-Ray diffractometer (XRD) analysis was carried out in the 2θ range of 0°-35°.The result of X-Ray diffraction pattern of SiO_2 synthesized by the TEOS hydrolysis reaction at room temperature and under hydrothermal treatment is shown in Figure 2. Analysis of Figure 2 (a) shows the presence of an amorphous halo - a strong peak at Bragg angle 21 °-22 °. This result indicates that SiO_2 product synthesized by the TEOS hydrolysis reaction at room temperature has an amorphous phase. The diffraction pattern in Figure 2(a) showed only one peak which indicatesthat the SiO_2 product has a high degree of purity.The XRD peak of SiO_2 synthesized by the TEOS hydrolysis reaction at hydrothermal treatment (fig 2,b) becomes sharper at room temperature. It can be concluded that hydrothermal treatment leads to crystallization of the material.

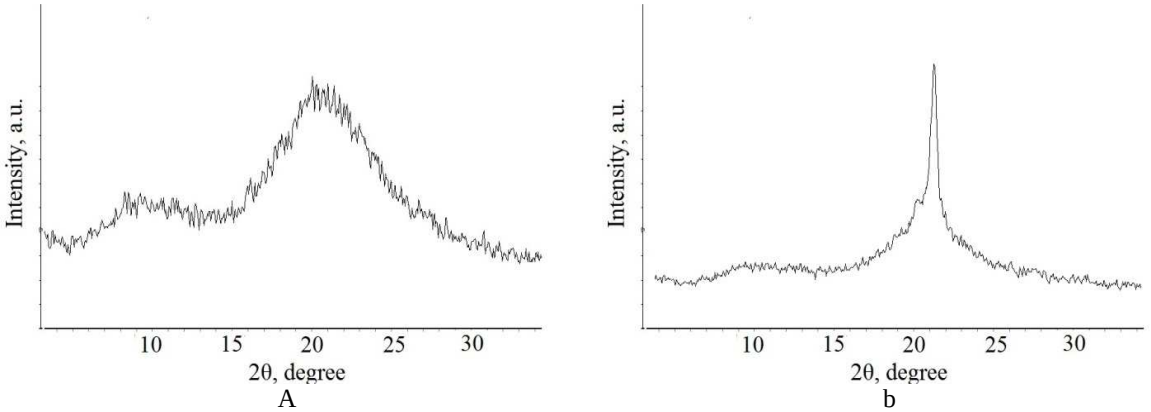
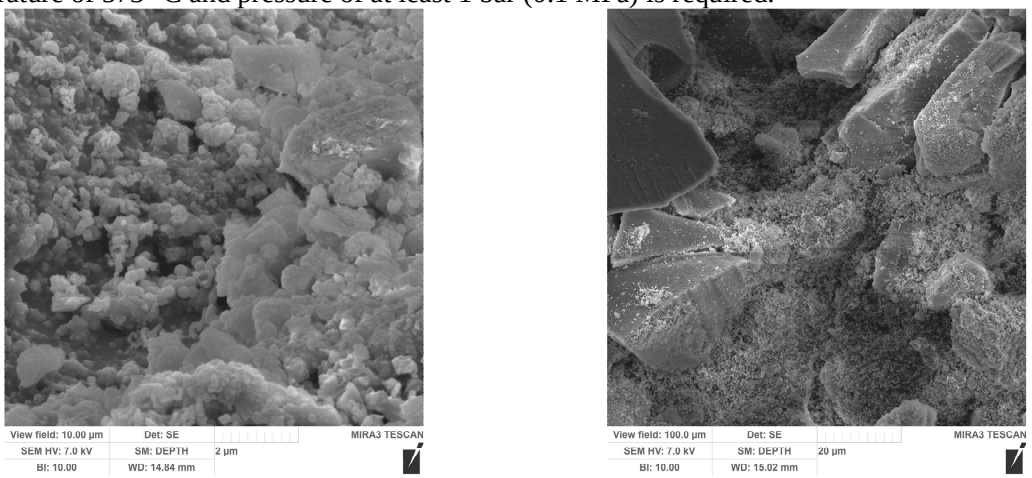


Figure 2. XRD analysis of SiO_2 synthesized by the TEOS hydrolysis reaction at room temperature (a) and hydrothermal treatment (b)

Figure 3 shows the microstructure of SiO_2 synthesized by the TEOS hydrolysis reaction at room temperature (a) and hydrothermal treatment (b). Figure 3a shows images of the amorphous SiO_2 particles. As can be seen, primary particles show a tendency to form bigger particles (aggregates). Particle size does

not exceed 2μm. Microphotography shows that the powder obtained has high levels of porosity. Analysis of micrographs of silica powder obtained using hydrothermal treatment (fig 3,b) also shows that the received substance has a crystalline structure (the crystal size in transverse dimension reaches 20 μm). The analysis of electron microscopy confirms the results of X-ray phase analysis in terms of the crystallinity of the obtained substances. However, the microphotography (fig 3,b) shows a significant amount of the substance with an amorphous structure. For a complete polymorphic transformation into β-quartz, higher temperature of 573 °C and pressure of at least 1 bar (0.1 MPa) is required.



a b

Figure 3. Microphotography of SiO_2 synthesized by the TEOS hydrolysis reaction at room temperature (a) and hydrothermal treatment (b)

Figure 4 shows the IR-spectrum of SiO_2 synthesized by the TEOS hydrolysis reaction at hydrothermal treatment. As presented in Figure 4, band corresponding to 3460 cm^{-1} is the stretching vibrational absorption of silicon hydroxyl and physic adsorptive water (H_2O), and 1620 cm^{-1} corresponds to the bending vibrational absorption of physic adsorptive water (–OH bending vibrations of H_2O molecules). A very strong and predominant absorbance peak corresponding to 1080 cm^{-1} can be assigned to Si–O–Si asymmetric stretching vibrations. The IR band corresponding to 457 cm^{-1} is due to O–Si–O bending vibrations. The IR band corresponding to 788 cm^{-1} is assigned to Si–OH group. Presence of physic adsorptive water indicates that the material has an amorphous phase, i.e. that complete crystallization of SiO_2 during hydrothermal treatment did not occur.

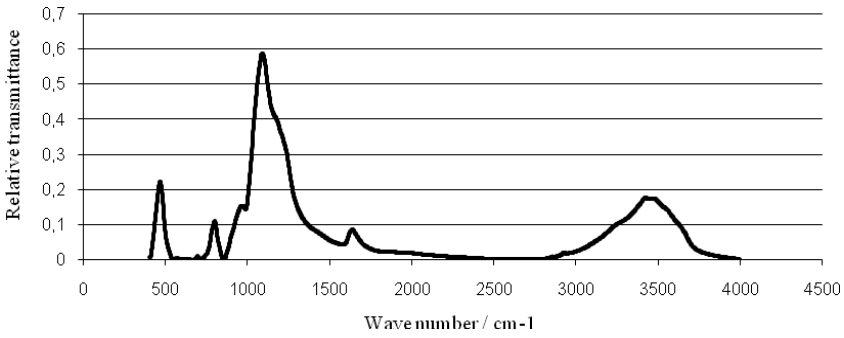


Figure 4. FT-IR spectra of SiO_2 synthesized by the TEOS hydrolysis reaction at hydrothermal treatment

Bands corresponding to 1078, 788 and 457 cm^{-1} are the characteristic adsorptive peaks of SiO_2, and the IR-spectrum diagram of the samples matches the standard diagram of hydrated SiO_2.

4. Conclusion

SiO_2 particles have been synthesized successfully both by hydrothermal method and traditional sol-gel process. It was found that SiO_2 product synthesized by TEOS hydrolysis reaction at room temperature has an amorphous phase. XRD analysis shows the presence of an amorphous halo - a strong peak at Bragg angle 21 °-22 °. The XRD peak of SiO_2 synthesized by the TEOS hydrolysis reaction during hydrothermal treatment becomes sharper at room temperature. It can be concluded that hydrothermal treatment leads to crystallization of the material.

The microphotography of SiO_2 synthesized by TEOS hydrolysis reaction at room temperature also shows images of the amorphous SiO_2 particles. The microphotography of SiO_2 synthesized by the TEOS hydrolysis reactionat hydrothermal treatment shows that the obtained substance has a crystalline structure. However, it shows a significant amount of the substance with an amorphous structure. For a complete polymorphic transformation into β-quartz, higher temperature and pressure are required.

5. Acknowledgments

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