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PRECIPITATION OF AMORPHOUS SiO_2 PARTICLES AND THEIR PROPERTIES

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Abstract - The experimental conditions were optimized for the synthesis of amorphous SiO_2 particles by the reaction of neutralization of sodium silicate solution with H_2SO_4 solution. Amorphous SiO_2 particles were characterized by XRD, FT-IR, FE-SEM, EDS and microelectrophoresis. The amorphous peak was located at $2\theta = 21.8^{\circ}$ in the XRD pattern. Primary SiO_2 particles were ~ 15 to ~ 30 nm in size and they aggregated into bigger particles. Amorphous SiO_2 particles showed a specific surface area up to 130 m^2g^{-1}, dependent on the parameters of the precipitation process. The EDS spectrum of amorphous SiO_2 particles did not show contamination with sulfate or other ions, which cannot be excluded in traces. pH_{zpc} =1.7 was obtained by microelectrophoresis.

Keywords: Precipitated SiO_2; XRD; FT-IR; FE-SEM; EDS; Microelectrophoresis

INTRODUCTION

Precipitated SiO_2 (silica) has found various applications as filler in rubber and plastics, absorbent, drying powder, substrate for catalysts, anticorrosion agent, etc. Generally, precipitated SiO_2 can be produced by mixing of aqueous solutions of sodium metasilicate and a mineral acid (Winyall, 1984). For example, Schlomach and Kind (2004) precipitated silica by simply adding 50% sulphuric acid into sodium metasilicate solution. The primary silica particles had a uniform size at 22.7 nm. Jesionowski (2002) investigated the precipitation of silica from sodium metasilicate solution using hydrochloric acid. Nonionic surfactants, polydisperse mono(4-nonylphenyl)polyoxyethylene glycol ethers were used as emulsifiers. Spherical silica particles were obtained by using the ultrasonic bath. The precipitated silica had a specific surface area in the interval of 120-260 m^2/g. Also, Jesionowski (2001) investigated precipitation of silica from sodium metasilicate and sulfuric acid in emulsions. Cai et al. (2009) used carbon dioxide to precipitate silica from sodium metasilicate solution. The size of the aggregated SiO_2 particles obtained by dynamic light scattering was about 160 nm. The production of nanofibrillar silica (amorphous) from natural chrysotile asbestos was also investigated. (Wang et al. 2006; Liu et al. 2007).

The properties of precipitated SiO_2 depend strongly on the conditions of its synthesis, such as the synthesis temperature, time of precipitation, pH, addition of coagulant, and modes of washing and drying. These factors influence the size of the SiO_2 particles, their aggregation and specific surface area. The optimization of the properties of precipitated SiO_2 is not an easy task.

In the present work we focus on the precipitation of amorphous SiO_2. The optimization of the synthesis factors was achieved, so that precipitated SiO_2 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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EXPERIMENTAL

Synthesis of Precipitated SiO_2

The commercial aqueous solution of sodium silicate (water glass) having a chemical composition in the range 7.8 – 8.5% Na_2O, 24.8 – 27% SiO_2, 64 – 67% H_2O, and specific weight 1.35 – 1.36 g mL^{-1} was used. After filtration, the sodium silicate solution was diluted in distilled water in the ratio of 1:4 by volume. A concentrated H_2SO_4 solution was diluted in distilled water in the ratio of 1:10 by volume. This H_2SO_4 solution was used to neutralize the silicate component by addition at a constant speed and strong mixing of the precipitation system using a high energy disperser. The speed of adding the dilute H_2SO_4 solution depended on the temperature. In the temperature interval of 80-90°C, the speed of adding H_2SO_4 was 120 - 50 min. The dilute H_2SO_4 solution was added up to pH 9 - 9.5. The pH was measured at room temperature. At this pH and a temperature of 80-90°C, the precipitated system was additionally heated for 42 - 17 min. This was followed by cooling the precipitated system to room temperature. Then, dilute H_2SO_4 solution was added up to pH 5.5. At this pH, NaCl solution was added over 30 min. The concentration of NaCl varied between 1 and 5 g/L of the reaction mixture.

Coagulated SiO_2 was separated from the mother liquor and subsequently washed with distilled water until there was a negative reaction for sulfate ions, as controlled with 0.1 M $BaCl_2$ solution. The separated cake was dried in a cyclone dryer.

Instrumentation

pH values were measured with a pHM-26 instrument and a combined glass electrode with an operating range of up to pH ~ 14, both manufactured by *Radiometer* (Denmark).

The X-ray powder diffraction pattern was recorded using an APD 2000 diffractometer manufactured by *ItalStructures* (Riva Del Garda, Italy).

The Fourier transform IR spectrum was recorded using a *Perkin-Elmer* spectrometer (Model 2000). The specimen was pressed using a spectroscopically pure KBr matrix.

The BET measurement was performed using a *FlowSorb* II 2300 surface area analyzer (*Micromeritics*, Norcross, GA, USA).

Electrophoretic mobilities were measured using a microelectrophoresis apparatus manufactured by *Rank Brothers*, Cambridge, U.K.

A thermal field emission scanning electron microscope (FE-SEM, model JSM-7000F) manufactured by *Jeol Ltd.* (Japan) was used. FE-SEM was linked to an EDS/INCA 350 (energy dispersive X-ray analyzer) manufactured by *Oxford Instruments Ltd.* (UK). Sample was not coated with an electrically conductive layer.

RESULTS AND DISCUSSION

Fig. 1 shows an X-ray powder diffraction pattern of precipitated SiO_2. An amorphous peak with the equivalent Bragg angle at $2\theta = 21.8^{\circ}$ was recorded. Martinez et al. (2006) prepared amorphous SiO_2 by the sol-gel procedure, subjected it to thermal treatment, then analyzed it using the Rietveld refinement. In their work, an amorphous peak was centered at $2\theta = 23^{\circ}$. With an increased heating temperature, this peak was shifted to lower 2θ values. Depending on the molar ratio (R) of water to TEOS (R = 5 or 11.66) and the heating temperature, the amorphous structure transformed to quartz-like or cristobalite-like structures. Zhang et al. (2008) also recorded one broadened XRD peak for amorphous silica centered at a 2Θ value close to our measurement. Only this XRD peak, corresponding to the amorphous phase, was present upon heating the starting material up to 800°C. Upon heating amorphous silica at 1000°C, tetragonal α-crystobalite and a small fraction of monoclinic tridymite were obtained.

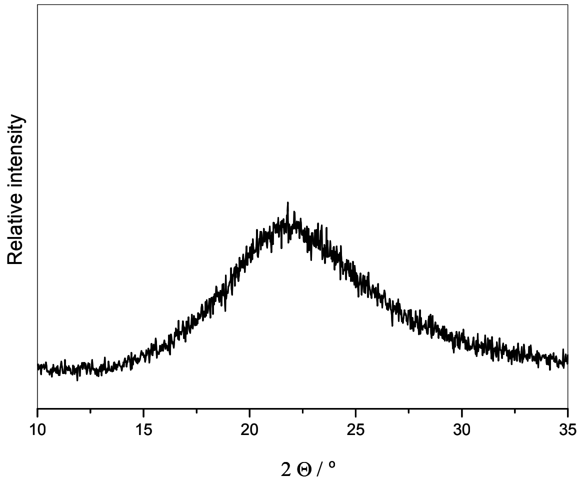

Figure 1: X-ray powder pattern of precipitated SiO_2 with a characteristic amorphous peak

Jesionowski and Krysztafkiewicz (1999) precipitated SiO_2 using the reaction of sodium silicate with dilute HCl, H_2SO_4 or CO_2 in alcohol-containing media. Dispersibility and size of the SiO_2 particles depended on the nature of the alcohol added. In the presence of isopropanol, SiO_2 particles were 525 nm in size, with a tendency to form aggregates 1340 nm in size. The precipitation of SiO_2 in the presence of ethylene glycol yielded particles 112 nm in size, whereas in the presence of glycerine SiO_2 particles 360 nm in size were formed. Pajonk et al. (1995) prepared SiO_2 aerogels using polyethoxydisiloxanes obtained by the reaction of tetraethoxysilane (TEOS) and water in the presence of sulfuric acid. Sol-gel reactions were conducted under acidic, neutral or basic conditions in methanol, ethanol or acetone. Hyeon-Lee et al. (1997) applied the aero-sol-gel procedure to prepare SiO_2 powder with a very high specific surface area, ~ 400 m^2g^{-1}. An inverse microemulsion sol-gel procedure was used to prepare SiO_2 particles of colloidal dimensions (Espiard et al. 1995). The sol-gel procedure was also used to prepare porous and spherical SiO_2 particles (Hirose et al. 1994). Spherical SiO_2 particles showed a tendency to increase in size with an increase of ultrasonic energy during the synthesis of these particles (Enomoto et al. 1996).

In the present work, a specific surface area of up to 130 m^2g^{-1} could be obtained. This is important, especially if we consider the relative simplicity of the procedure for the production of amorphous SiO_2 as applied in the present work.

Fig. 2 shows FE-SEM images of the amorphous SiO_2 particles at different optical magnifications. The majority of primary SiO_2 particles were ~15 to ~ 30 nm in size. These primary particles showed a tendency to form bigger particles (aggregates). Fig. 3 shows the EDS spectrum of amorphous SiO_2 particles. This spectrum showed only the presence of silicon and oxygen. An excess of oxygen in relation to the stoichiometric ratio Si:O = 1:2 can be attributed to the presence of water and –SiOH groups. The analysis of precipitated SiO_2 showed that it contained 7.63% of "structural" water and 2.36% of “free water” (moisture). For comparison, the EDS spectrum of precipitated SiO_2 crystallized at high temperature was recorded under the same instrumental conditions and a fully stoichiometric ratio Si:O = 1:2 was obtained due to removal of H_2O molecules and condensation of –SiOH groups. The EDS spectrum did not show the presence of sulfate, chloride or sodium ions, thus indicating that these ions were well removed in the mother liquour. Generally, sulfate ions can specifically adsorb on (hydrous) oxide surfaces, similar to phosphates or chromates (Musić et al. 1986). Their adsorption decreases with a pH-increase, which is opposite to metal cation adsorption, i.e., the adsorption of metal cations increases with a pH-increase (Musić et al. 1988). A good removal of SO_4^{2-} and Cl^- ions can also be due to a low pH_{zpc} of the amorphous SiO_2 particles. Fig. 4 shows the dependence of electrophoretic mobility on the pH of the SiO_2 suspension. The zero point of charge is located at pH = 1.7. Above pH_{zpc} = 1.7 the surface of the amorphous SiO_2 particles is negatively charged.

Fig. 5 shows the FT-IR spectrum of precipitated SiO_2. The IR band at 3437 cm^{-1} is due to the stretching vibration of H_2O molecules. Correspondingly, the IR band at 1632 cm^{-1} is due to the bending vibration of H_2O molecules. The shoulder at 3246 cm^{-1} could be assigned to the stretching vibrations of Si-OH groups in the structure of amorphous SiO_2. The presence of the Si-OH group is proved as bonded water. The very strong and broad IR band at 1111 cm^{-1} with a shoulder at 1188 cm^{-1} is usually assigned to the TO and LO modes of the Si-O-Si asymmetric stretching vibrations. The IR band at 956 cm^{-1} can be assigned to silanol groups. In the case of alkali silicate glasses, this band is assigned to $Si-O^-$ stretching vibrations. The IR band at 800 cm^{-1} can be assigned to Si-O-Si symmetric stretching vibrations, whereas the IR band at 474 cm^{-1} is due to O-Si-O bending vibrations. Murphy and Greytak (1979) assigned the IR band at 380 cm^{-1} to the Si-OH wagging mode. In the present work, the IR band at 380 to 377 cm^{-1} is recorded as a shoulder at 378 cm^{-1}.

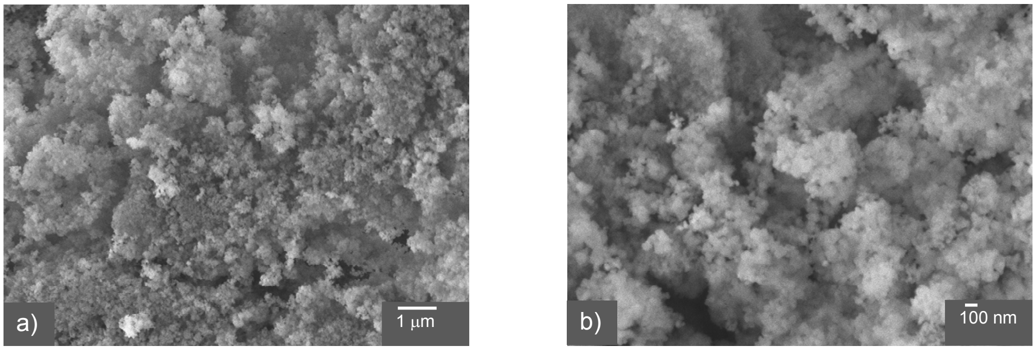

Figure 2: FE-SEM images of precipitated SiO_2 at different optical magnifications (details a and b).

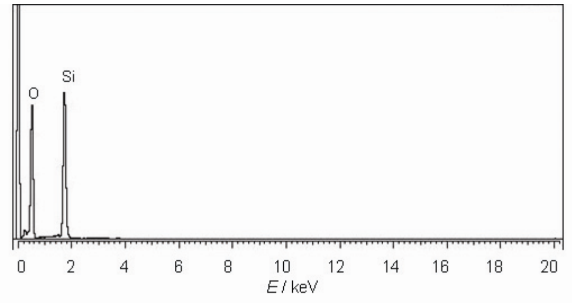

Figure 3: EDS spectrum of precipitated SiO_2.

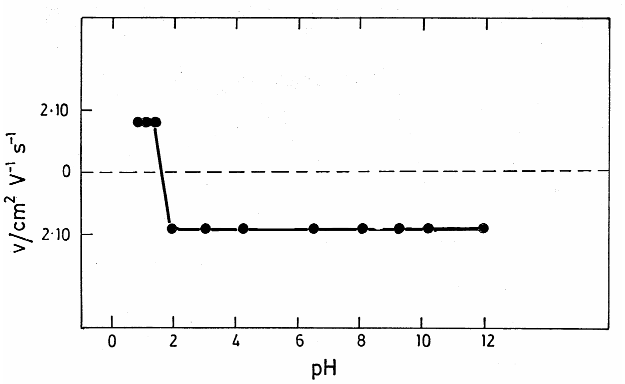

Figure 4: Electrophoretic mobility of amorphous SiO_2 particles as a function of the pH of the suspension.

Bock and Su (1970) recorded the IR spectrum of fused silica and compared it with the results of vibrational calculations. For fused silica, the IR bands at 377, 465, 800, 950, 1100 and 1190 cm^{-1} were recorded. These IR bands also appear in crystalline silica (quartz, crystobalite and tridymite). Of course, the crystalline silicas have more pronounced IR bands with narrower line-widths. Amorphous silica and crystalline silica can really only be distinguished on the basis of measurements in the far-IR region. Vibrational spectra of silica glasses have been studied (Philips, 1987; Tomozawa et al. 2005) and IR spectroscopy used to monitor changes in amorphous SiO_2 during its heating up to 1150°C (Chmel et al. 1990). Innocenzi (2003) used IR spectroscopy to investigate different stages during the sol-gel formation of silica. The FT-IR spectrum shown in Fig. 5 agrees well with the spectrum obtained for amorphous SiO_2 precipitated by the carbonation method (Cai et al. 2009).

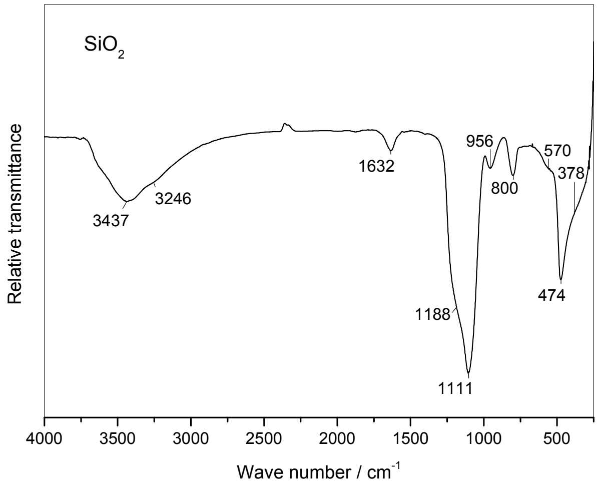

Figure 5: FT-IR spectrum of precipitated SiO_2.

CONCLUSION

- Precipitated silica was produced by neutralization of sodium silicate solution (water glass) with H_2SO_4 solution. The synthesis parameters, such as temperature, time of mixing, pH and the amount of coagulant were optimized. Precipitated silica in the form of powder, as obtained with the optimized parameters, could reach a specific surface area of up to 130 m^2g^{-1}.
- X-ray powder diffraction of precipitated silica showed one amorphous peak located at $2\theta = 21.8^o$ and the FT-IR spectrum was typical of that known for amorphous SiO_2.
- FE-SEM inspection showed primary SiO_2 particles ~15 to ~ 30 nm in size. These particles showed a tendency to aggregate (secondary particles).
- The EDS spectrum did not show a contamination of precipitated SiO_2 with sulfate or other ions. "Foreign" ions could be present at the level of traces. Amorphous SiO_2 particles contained "structural" and “free” water (moisture) which were responsible for excess oxygen in these particles. $pH_{zpc} = 1.7$ was determined by microelectrophoretic measurements.
- Properties of precipitated silica produced at the technological level using the same procedure matched those obtained at the laboratory level.

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