

Beata TEPPER*, Teofil JESIONOWSKI*, Andrzej KRYSZTAFKIEWICZ*

COLLOIDAL SILICAS OBTAINED VIA CO-PRECIPIATION METHOD USING CYCLOHEXANE AS AN ORGANIC PHASE

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The process of obtaining colloidal silicas from the emulsion systems with the use of cyclohexane as the organic phase has been studied and the products obtained have been also characterised. The emulsion systems made of water solutions of sodium metasilicate and hydrochloric acid or alternatively sulfuric acid have been used. Non-ionic surfactants have been used as emulsifiers, while a homogeniser has been a dispersing tool. The optimum compositions of the emulsion systems and the optimum parameters of silicas precipitation have been established. The dispersion character of the colloids obtained has been examined and the shapes, size and morphology of the SiO₂ particles formed have been analysed (including a tendency to agglomerate formation and polydispersity).

Key words: silica, emulsions, non-ionic surfactants, particle size, surface morphology

INTRODUCTION

Highly-dispersed silicas show specific structure and properties making them much desired components in many products of modern technologies. They are used as plastomer and elastomer fillers, carriers of therapeutic substances or herbi- or pesticides, auxiliary substances in toothpastes, media regulating the powder liquidity, or densifying or tixotropic agents in construction materials (Bolt et al., 1997, Mathew et al., 2004, Yatsuyanagi et al., 2001).

A number of obtaining methods of SiO₂ have been proposed differing mainly in the type of substrates used, conditions of the process and properties of the product (Schlomach and Kind, 2004; Utting and Macquarrie, 2002).

Traditional methods are based on combustion of silicon tetrachloride vapours (Galarneau 1998), hydrolysis and polycondensation of alkoxy silanes (Stöber 1968), and precipitation of silicas from the water solutions of alkali silicates by an acidic

* Poznan University of Technology, Institute of Chemical Technology and Engineering,
pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland, btepper@interia.pl,

agent (Chen et al., 2005, Gun'ko et al., 2001). Unfortunately, none of the above methods ensures obtaining strictly monodispersed particles of spherical shape. The need for such products has prompted the search for new preparatory solutions leading to high quality materials of target physicochemical properties.

A wide gamut of materials based on highly-dispersed and powdered substances have been produced by chemical, pharmaceutical, food or processing industries. Among them of great importance have been synthetic silicas that can be produced in a number of processes, one of them being precipitation of silicas from the emulsion systems. The main aim of this study is to obtain highly-dispersed silicas of spherical particles in the reaction of precipitation from the emulsion systems made of water solutions of sodium metasilicate and hydrochloric or sulphuric(VI) acid. The compositions of the emulsion system and the conditions of the process have been optimised with respect to reaching this aim.

EXPERIMENTAL

MATERIALS

The sodium metasilicate ($\text{Na}_2\text{O}\cdot m\text{SiO}_2\cdot n\text{H}_2\text{O}$) used contained 8.50% of Na_2O ; 27.18% of SiO_2 ; silicate modulus of 3.3 and had a density equal 1.39 g/cm^3 (VITROSILICON S.A.). The precipitating agent was a 5% hydrochloric acid or a 3% sulphuric(VI) acid (POCh S.A.). The highly-dispersed silica was obtained by precipitation from the emulsion with the organic phase of cyclohexane (POCh S.A.) and a non-ionic surfactant of oxyethylenate unsaturated fatty alcohol (Rokanol K7) as an emulsifier. The Rokanol K7 formula is $\text{C}_{18}\text{H}_{37}\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$ (PCC ROKITA S.A.).

METHODS OF STUDIES

Silicas were precipitated from a water solution of sodium metasilicate by hydrochloric or sulphuric(VI) acid. The process was performed in a system of two emulsions. One of them (E1) contained a solution of sodium metasilicate and cyclohexane, to which the non-ionic surfactant Rokanol K7 (emulsifier) was added. The other emulsion (E2) was made of a selected mineral acid and cyclohexane, to which also Rokanol K7 was added but in a lower amount. For the process of precipitation emulsion E2 was placed in a reactor and vigorously stirred (19.000 rpm), while emulsion E1 was added to E2 at a constant rate of dosing. The resulting product was the emulsion containing the precipitated silica. This emulsion was heated to 80°C to destabilise it, then cyclohexane was distilled off, and the mixture left was filtered under a reduced pressure.

At the first stage of analysis of the silicas obtained the size of their particles was determined, as this parameter is fundamental for evaluation of dispersion of the powders obtained. The particle size distribution was measured by a Zetasizer Nano ZS instrument (Malvern Instruments Ltd.) based on employing the non-invasive back

scattering technique (NIBS). On the basis of the particle size distribution curves also the polydispersity was obtained, which was a measure of homogeneity of a given silica powder. The silica samples were subjected to morphological and microstructural analyses under a scanning microscope SEM (Philips SEM 515). Using a Tensiometer K100 (Krüss) the profiles of sedimentation and wettability in water were determined. The adsorption properties of the silicas were assessed on the basis of nitrogen adsorption/desorption isotherms. The surface area, pore size and volume were measured by an instrument ASAP 2010 (Micromeritics Instruments Co.).

RESULTS AND DISCUSSION

The precipitation of highly dispersed silicas from the emulsion systems was studied for different parameters of the process in order to establish their optimum values. The effect of the amount of the emulsifiers and the type of mineral acid on the physicochemical properties of the final product was tested. Tables 1 and 2 give the quantitative compositions of the emulsions used in the precipitation of silicas with hydrochloric and sulphuric(VI) acid, respectively.

Table 1. The amount of the emulsifier used in precipitation of silicas by hydrochloric acid

Sample No.	Emulsion E1	Emulsion E2	
	Amount of emulsifier Rokanol K7 (g)	Mount of emulsifier Rokanol K7 (g)	Amount of HCl (cm ³)
1	3.0	0.8	33
2	2.5	0.8	33
3	2.0	0.7	33
4	1.5	0.7	33

Table 2. The amount of the emulsifier used in precipitation of silicas by sulphuric(VI) acid

Sample No.	Emulsion E1	Emulsion E2	
	Amount of emulsifier Rokanol K7 (g)	Amount of emulsifier Rokanol K7 (g)	Amount of H ₂ SO ₄ (cm ³)
5	3.0	0.8	33
6	3.0	0.8	70
7	2.5	0.7	390

Figure 1 presents results of the dispersion study of the precipitated silicas for sample 1. The first diagram illustrates the relation between the particles diameter and the intensity, while the other – the relation between the particles diameter and their volume fraction. The curve of particle size distribution in relation to the intensity shows two bands, Fig. 1a. The first corresponds to the silica particles of small diameters ranging from 295 to 459 nm (the maximum intensity of 38.1 corresponds to the diameter of 342 nm). The other band of low intensity corresponds to the presence

of agglomerates of particles covering the range 2300-4150 nm (the maximum intensity of 4.6 corresponds to the agglomerates of the diameter of 3090 nm). The particle size distribution in relation to the volume fraction also shows two bands. The greater volume fraction corresponds to the primary agglomerates (the maximum volume of 22.8 corresponds to the primary agglomerates of the diameter 342 nm).

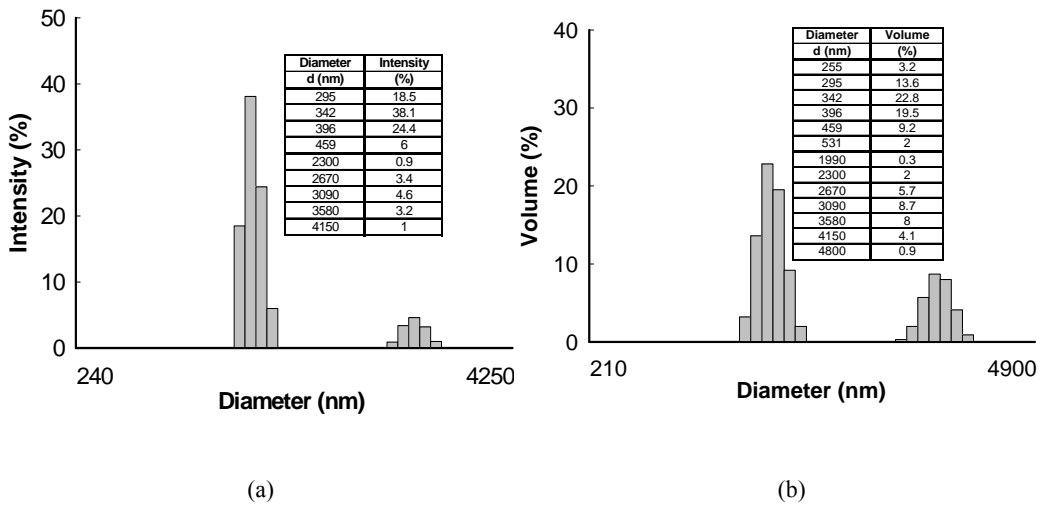


Fig.1. Silica particles size distribution in relation to (a) intensity, (b) volume for silica sample 1

Figure 2 presents the particle size distribution and the SEM photograph of silica sample 2.

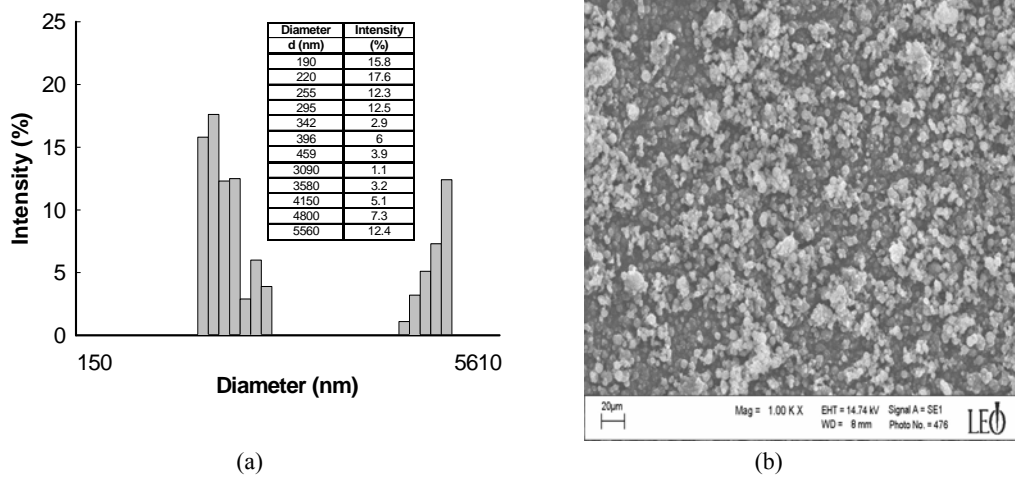


Fig. 2. The particle size distribution in relation to intensity (a) and the SEM photograph (b) for silica sample 2

As follows from Fig. 2a the band assigned to the primary agglomerates (190-459 nm) is dominant and the maximum intensity of 17.6 corresponds to the particles of 220 nm in diameter. The less intense band corresponds to the agglomerates of the diameter from the range 3090-5560 nm and the maximum intensity of 12.4 corresponds to the agglomerates of 5560 nm in diameter. The SEM photo confirms the high quality of the silica sample 2 as the particles are of spherical shape and relatively low polydispersity (0.350). The silica sample 2 is built in 70% of the primary particles whose size varies from 190 to 459 nm.

Figure 3 presents the particle size distribution in relation to volume and the SEM photograph of silica sample 6.

According to the particle size distribution in Fig. 3a, the dominant band corresponds to the primary particles of 164-295 nm in diameter making 67% of the sample. The band corresponding to agglomerates covers relatively narrow range of their diameters from 3580 to 6440 nm and the agglomerates occupy 33% of the sample volume. The polydispersity of silica sample 6 is close to 0.828 and the SEM photo in Fig. 3b (showing the morphology of the particles) attest to the improved quality of this sample.

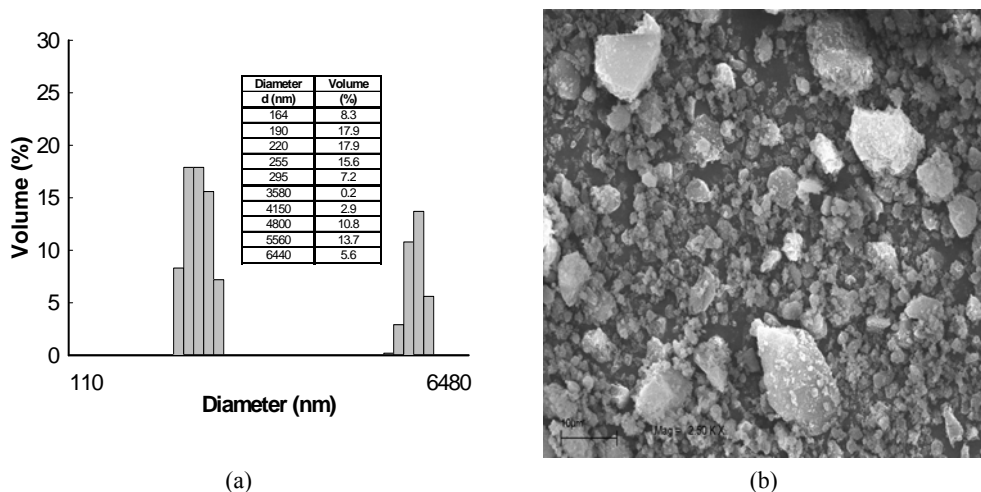


Fig. 3. The particle size distribution in relation to volume (a) and the SEM photo (b) for silica sample 6

Figure 4 presents the particle size distributions in relation to intensity and volume for silica sample 7.

Reduction of the amount of the emulsifier by $\frac{1}{6}$ in emulsion E1 and a considerable increase in the volume of sulfuric acid in emulsion E2 leads to a deterioration of the final product as follows from the volume fraction of the secondary agglomerates being slightly greater than that of the primary particles.

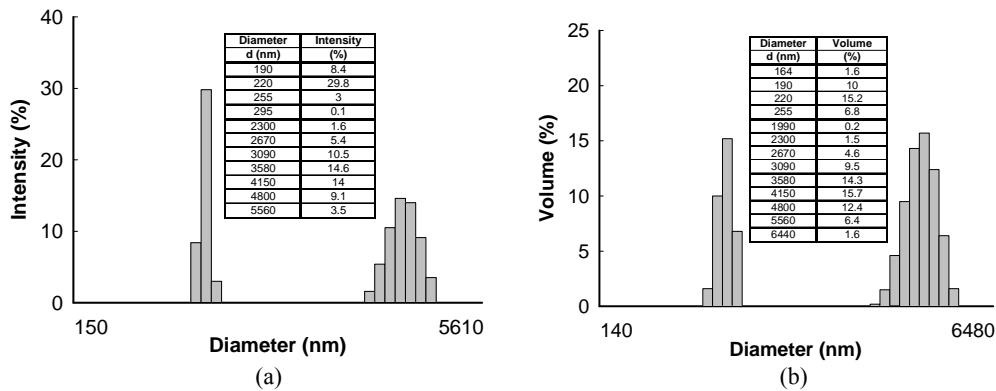


Fig.4. The particle size distribution in relation to intensity (a) and volume (b) for silica sample 7

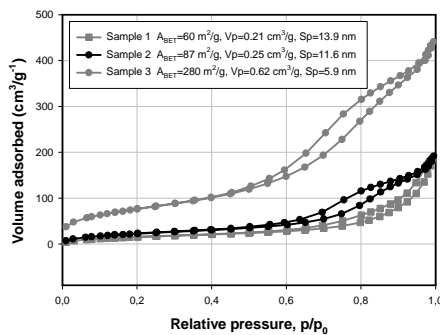


Fig.5. The nitrogen adsorption/desorption isotherms for silicas precipitated from the emulsion system using HCl

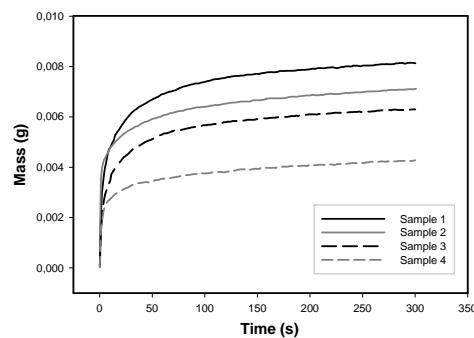


Fig.6. Profiles sedimentation in water for the silicas precipitated applying HCl

Figure 5 presents the nitrogen adsorption/desorption isotherms for silica samples precipitated by a 5% water solutions of HCl in the presence of different amounts of Rokanol K7 in emulsion E1. For samples 1 and 2 starting from low relative pressure the volume of nitrogen adsorbed slightly increases. Starting from the relative pressure of 0.7 the volume of nitrogen adsorbed rapidly increases and reaches a maximum of $200 \text{ cm}^3/\text{g}$ at $p/p_0 = 1$. Sample 3 has a completely different character as indicated by a much greater hysteresis loop. The optimum volume of nitrogen adsorbed of $450 \text{ cm}^3/\text{g}$ (at a relative pressure of $p/p_0 = 1$) indicates that silica sample 3 has the greatest activity. Moreover, the surface area (BET) of sample 3 equal $280 \text{ m}^2/\text{g}$ is significantly greater than those of the other samples. This increase is most probably a result of relatively low content of the emulsifier – close to 2 g – in the alkaline mixture. Despite some differences, each of the samples 1, 2, 3 can be classified as mesoporous on the basis of the nitrogen adsorption/desorption isotherms obtained for them.

Figure 6 presents the profile of sedimentation in water for the silica samples precipitated with the use of hydrochloric acid. The greatest mass increase has been observed for sample 1, characterised by domination of secondary agglomerates over the primary ones. The lowest mass increase has been observed for sample 4, which is characterised by the lowest weight fraction of emulsifiers added to both emulsions E1 and E2, Table 1. A comparison of the results for samples 1, 2, 3 and 4, reveals an inversely proportional relation between the rate of sedimentation and the content of Rokanol K7 in E1, so a decrease in the amount of the emulsifier added to the alkaline emulsion leads to an increase in the rate of sedimentation.

As follows from the plots describing the wettability of silicas precipitated with the use of a 5% water solution of HCl, Fig. 7a, the best wettability has sample 4 obtained from the system with emulsion E1 containing 1.5 g of Rokanol K7, for this sample the total sorption was reached in 1300 seconds. A comparison of the curves presented in Fig. 7a reveals a strict relation between the sample wettability and the amount of the emulsifier in the alkaline emulsion E1; with decreasing amount of Rokanol K7 in E1 the rate of water sorption decreases. Similar conclusions follow from analysis of the wettability curves obtained for the silica samples precipitated using 3% H_2SO_4 (Fig. 7b).

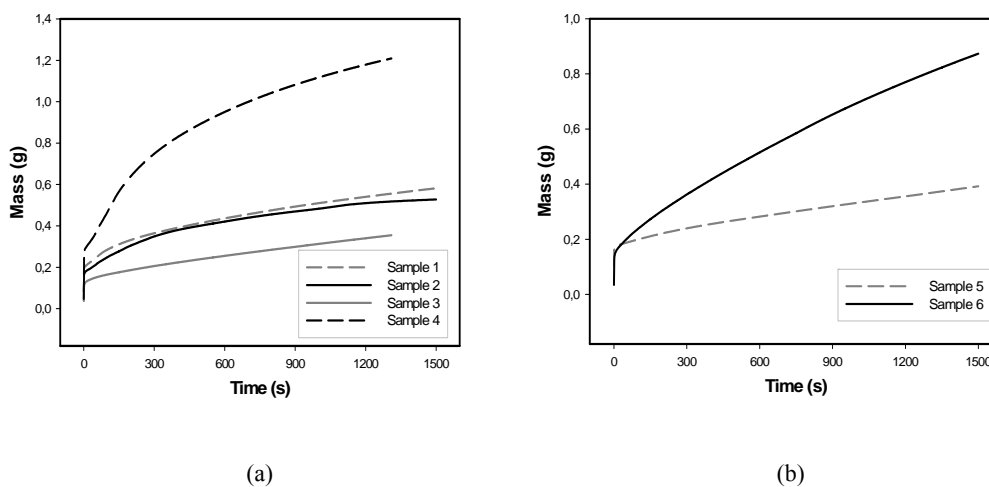


Fig. 7. The wettability of silica samples precipitated from the emulsion system in the presence of (a) HCl and (b) H_2SO_4

Much higher wettability was observed for the silica sample precipitated from the system with a doubled amount of sulphuric(VI) acid in emulsion E2. For this sample a significant increase in the sorption was observed at the end of the measurement (the mass determined reached 1 g).

CONCLUSIONS

The main aim of the study was to obtain highly-dispersed silicas of spherical shape particles and monodisperse nature in the reaction of precipitation from the emulsion systems containing water solutions of sodium metasilicate and hydrochloric or sulfuric acid. As follows from analysis of the silica samples obtained, the precipitation with a 5% solution of hydrochloric acid gives highly-dispersed silicas with particles of spherical shape and homogeneous character. The silica samples precipitated with the use of a 3% sulfuric(VI) acid do not show the characteristics desired. The rate of sedimentation of the silica samples precipitated with a 5% water solution of hydrochloric acid depends on the content of the emulsifier in emulsion E1; the less Rokanol K7 added to E1 the higher the rate. The water sorption by the silica samples precipitated with HCl depends on the weight fraction of Rokanol K7 in emulsion E1. A low content of Rokanol K7 in E1 leads to an increased rate of water sorption, which indicates the hydrophilous character of the samples surface. For the silica samples precipitated with H₂SO₄, the water sorption rate is determined by the presence of the acid in emulsion E2 and a considerable amount of Rokanol K7 in emulsion E2.

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W pracy prowadzono badania ukierunkowane na otrzymywanie cząstek krzemionki z układów emulsyjnych z zastosowaniem cykloheksanu jako fazy organicznej. Badania prowadzono z wodnymi roztworami metakrzemianu sodu i kwasu solnego lub kwasu siarkowego. Stosowanymi emulgatorami były niejonowe związki powierzchniowo czynne. Jako ośrodek dyspergujący zastosowano homogenizator. Ustalono optymalne składy emulsji i parametry strącania krzemionek. Oceniono charakter dyspersyjny otrzymanych koloidów oraz zbadano kształty i morfologię formowanych cząstek SiO₂ (m.in. tendencję do tworzenia aglomeratów, polidispersyjność). Podstawowym celem badań było otrzymanie wysoko zdyspergowanych krzemionek o sferycznych cząstkach i monodispersyjnej naturze w reakcji strącania z układów emulsyjnych zawierających wodne roztwory metakrzemianu sodu oraz kwasu odpowiednio solnego bądź siarkowego(VI).