

Teofil JESIONOWSKI\*

## **INFLUENCE OF N-2-(AMINOETHYL)-3-AMINOPROPYLTRIMETHOXYSILANE ON PHYSICOCHEMICAL AND MORPHOLOGICAL PROPERTIES OF SILICAS OBTAINED IN AN EMULSION SYSTEM**

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Synthesis of monodisperse silica was performed in a precipitation reaction from aqueous solution of sodium metasilicate using hydrochloric acid in an emulsion system. Effect of N-2-(aminoethyl)-3-aminopropyltrimethoxysilane was studied on surface and morphological properties of the precipitated silica. Particle size and polydispersity were measured using the technique of dynamic light scatter (DLS) and scanning electron microscopy (SEM). The extent of surface modification and its type were evaluated using FTIR spectroscopy. Moreover, adsorptive properties were characterised by estimation of specific surface area (BET) and of macroporosity. The XPS technique permitted to quantify the amount of modifier deposited on silica surface. Alterations in surface charge were studied by estimation of isoelectric point by direct testing of electrophoretic mobility and, indirectly, by calculating zeta potential. Aminosilane modification of SiO<sub>2</sub>, formed in emulsion medium, results in extensive changes in surface character and in morphology of the particles. Already at the time of silica preparation surface silanol groups become markedly reduced and, in addition, aminosilane chemisorption results in augmented hydrophobicity. Increased particle homogeneity has also been obtained and a decreased value of polydispersity due to aminosilane interactions with the surface of examined silica.

*Key words: spherical silica particles, surface modification, SEM, DLS, ELS, XPS*

### **INTRODUCTION**

Silicas represent a very valuable research material in several scientific centers of the world (Iler, 1979; Bergna, 1994; Legrand, 1998). Numerous methods of obtaining silicas are known. The most important include flame hydrolysis (Barthel, 1995). Products of the technology exhibit a strictly defined dispersive character but they encounter application restrictions in adsorption processes.

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\* Poznan University of Technology, Institute of Chemical Technology and Engineering  
Pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland  
E-mail: Teofil.Jesionowski@put.poznan.pl, phone:+48(61)6653720, fax:+48(61)6653649

Silicas obtained in the form of a gel represent a vast group of products (Faramway et al., 1997; Goworek et al., 1997). On the other hand, the technique of Stöber allows to obtain silicas in reactions of alkoxy silane hydrolysis and condensation in acidic or alkaline medium (Buining, 1996). Formation of silicas in an emulsion medium represents a new, alternate way of producing monodisperse silica particles, frequently of a nanometric size (Gan et al., 1996; Esquena et al., 1997; Jesionowski, 2001; 2001).

Due to their specific surface structure, reflecting the presence of silanol ( $\equiv\text{SiOH}$ ) groups, almost all types of silica exhibit hydrophilic character. The character can be modified mainly by adsorption of surfactants (Suhara et al., 1995) or by chemisorption of alkoxy silanes (Van der Voort et al., 1996; Jesionowski et al., 2000; 2001).

The studies aimed at obtaining silicas of a strictly defined particle size, spherical shape and exhibiting a stable dispersive character. Alteration of the surface character, i.e., restriction of its hydrophilicity was performed by aminosilane modification of surface hydroxyl (silanol) groups. The so obtained and modified silicas should exhibit high reactivity, in particular with organic dyes and thermoplastic polyolefines, due to their specific surface structure (presence of  $=\text{NH}$  and  $-\text{NH}_2$  groups).

## EXPERIMENTAL DETAILS

### MATERIALS

Aqueous solution of sodium metasilicate, silicate modulus of 3.3 ( $\text{Na}_2\text{O}=8.50$  wt%;  $\text{SiO}_2=27.18$  wt%, density =  $1.39$  g/dm<sup>3</sup>) represented the principal raw material for production of the silica. The precipitating agent involved 5 wt% HCl solution. The organic phase was formed by cyclohexane and the non-ionic surfactant from the group of oxyethylenated fatty alcohols ( $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n$ ,  $R=\text{C}_{16-22}$ , and  $n_{\text{mean}}\approx 7$ ), produced by Chemical Works 'Rokita' S.A., Poland, served as an emulsifier. For silica surface modification, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, technical grade (Witco Co., USA), was used.

### EMULSION AND SILICA PREPARATION

Two emulsions were prepared. The 'alkaline' one ( $E_1$ ) contained 100 cm<sup>3</sup> 5 wt%  $\text{Na}_2\text{SiO}_3$  solution and 110 cm<sup>3</sup> cyclohexane, supplemented with an emulsifier. The 'acidic' emulsion ( $E_2$ ) consisted of 33 cm<sup>3</sup> 5 wt% of HCl and 35 cm<sup>3</sup> of cyclohexane, supplemented with an emulsifier of the same composition as in  $E_1$  but in appropriately lower amount. The pre-dissolved emulsifiers were diluted in cyclohexane. The aqueous phase (for  $E_1$  5 wt% solution of  $\text{Na}_2\text{SiO}_3$ , for  $E_2$  5 wt% solution of HCl) was dosed in few portions and the mixture was homogenised at 19,000 rpm for 5 min. The so prepared emulsions were used in precipitation reactions.

The precipitation was conducted in the reactive vessel of 0.5 dm<sup>3</sup> capacity. Mixing took place in a homogeniser of ULTRA TURRAX T25 basic type (IKA LABORTECHNIK, Germany) at 19,000 rpm. The  $E_2$  emulsion was placed in the

reactive vessel and subjected to intense mixing. Emulsion E<sub>1</sub> was dosed to emulsion E<sub>2</sub> at a constant rate, using peristaltic pump. As a result of the reaction taking place in the reactive vessel a silica-containing emulsion was obtained. The emulsion was heated to 80°C in order to destabilise it. Subsequently, cyclohexane was separated from it by distillation. The subsequent stage involved filtration of the remaining mixture under a lowered pressure. In this way, the obtained sample was washed with hot water and, then, with acetone in order to wash out the remaining surfactants. Acetone was separated by distillation. Subsequently, the sample was subjected to drying for 48 hours in a stationary drier at 105°C.

#### PHYSICOCHEMICAL EVALUATION

Following the precipitation, the silicas were subjected to physicochemical tests, bulk densities as well as water, dibutyl phthalate and paraffin oil absorbing capacities were estimated.

Examinations of particle shape and morphology were conducted using scanning electron microscopy (SEM). The observations were performed in the Phillips SEM 515 microscope.

Laser Doppler electrophoretic light scattering determinations were performed with a ZetaPlus instrument (Brookhaven Instruments Inc., USA), in the reference beam mode at the wavelength of laser light source of 635 nm, sampling time 256 its, modular frequency 250 Hz and the scattering angle 15°. The zeta potentials were obtained by averaging 10 runs. Each examination were performed in a stable ionic strength (solution of 10<sup>-3</sup> mol NaCl).

The technique of dynamic light scattering (DLS), applied also in the ZetaPlus apparatus, permitted to obtain multimodal particle size distribution pattern on the basis of autocorrelative functions of laser light beam (670 nm) scatter. The most important parameters obtained using the technique included polydispersity and a mean particle diameter. Polydispersity represented a measure of heterogeneity of particle size distribution in the studied system.

Specific surface areas of silica powders were determined by N<sub>2</sub> adsorption (BET method) using ASAP 2010 instrument (Micrometrics Instrument Corporation). Moreover, the volume and size of pores of precipitated materials were examined. Samples were heated at 120°C for 2 hours prior to measurements.

The chemical composition of the obtained silicas was measured with X-ray photoelectron spectroscopy (XPS) on a SPECS ESCA system with Phoibos 100 energy analyser. The spectra were taken with a non-monochromated MgK $\alpha$  X-ray source. The survey scans were recorded using a pass energy of 30 eV and X-ray energy of 100 W, the high resolution spectra were recorded using 5 eV pass energy and 200 W. Charging of the sample surface was neutralised with flood gun with calibrating at 284.6 eV for C 1s peak.

The extent of modification and the character of the reaction between silane coupling agent and the silica were established in the FTIR EQUINOX (Bruker) equipment. In this aim, tablets of KBr with the studied silica were prepared.

## RESULTS AND DISCUSSION

Principal physicochemical parameters of the obtained silica and of the silica following aminosilane modification are presented in Table 1.

Table 1. Basic physicochemical properties of examined silicas.

Sample	Bulk density (g/dm <sup>3</sup> )	Water absorbing capacity (cm <sup>3</sup> /100g)	Paraffin oil absorbing capacity (cm <sup>3</sup> /100g)	Dibutyl phthalate absorbing capacity (cm <sup>3</sup> /100g)
SiO <sub>2</sub>				
A	283	250	300	225
SiO <sub>2</sub> + 3 w/w of U-15D silane				
B	261	250	350	250
SiO <sub>2</sub> + 5 w/w of U-15D silane				
C	221	150	350	275

The silica obtained in the process of precipitation exhibited a relatively high bulk density and high water absorbing capacity. Following modification, the silica altered its physicochemical properties: its bulk density and water absorbing capacity decreased while its paraffin oil absorbing capacity increased. The results have demonstrated increase in hydrophobicity of the silica surface. The increase has depended to a significant extent upon the amount of silane used for the modification.

Particle size distribution and electron micrograph of the unmodified silica are shown in Fig.1. Mean particle diameter amounted to 792.0 nm and the polydispersity was 0.059. The latter value has demonstrated a relatively highly uniform character of silica particles. In the particle size distribution (Fig.1a) two bands could be noted. The more intense band reflected presence of silica particles of smaller diameter and fitted the range of 391.6 to 684.6 nm (maximum intensity of 100 corresponded to the particle diameter of 489.6 nm). The other band within the range of 3,658.7 to 5,905.8 nm was related to particles of much higher diameters and to the formed aggregates and was definitely much less intense (maximum intensity of 5 corresponded to particles with diameters in the range of 4,431.0-5,366.4 nm). SEM micrograph (Fig.1b) confirmed presence of almost absolutely spherical particles of low diameters, which formed larger groups (the so called agglomerates) and the latter represented an undesirable development.

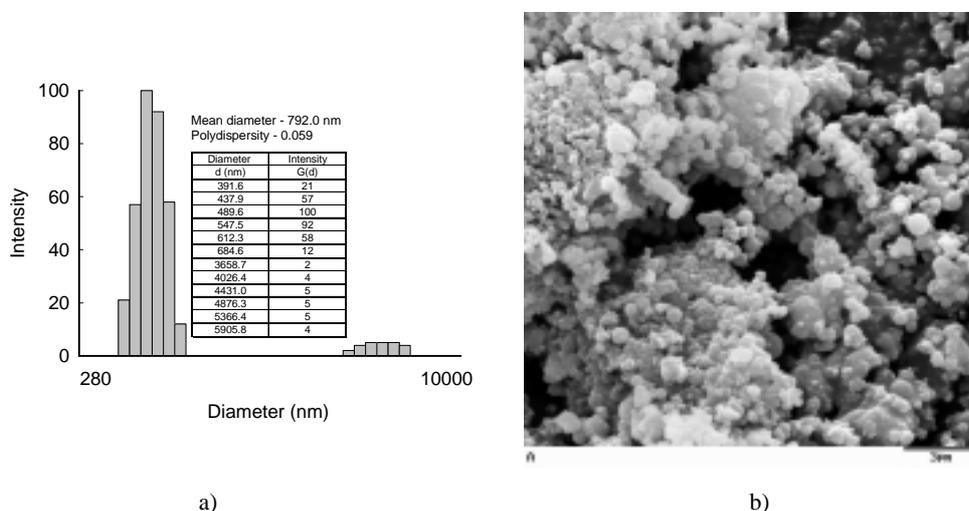


Fig.1. a) Multimodal particle size distribution and b) SEM of unmodified silica.

Particle size distribution and SEM micrograph of silica modified with 3 weight parts of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane are shown in Fig.2. Mean particle size in the silicas was 507.3 nm, while polydispersity was as low as 0.005. This pointed to a most advantageous effect of U-15D silane on silica dispersion. The particle size distribution (Fig.2a) also demonstrated presence of two bands, which have been ascribed to particles of, respectively, smaller and of significantly larger diameters. The more intense band reflected presence of particles of lower diameters (315.9-471.6 nm) and maximum intensity of 100 corresponded to particle diameter of 370.8 nm. Silica modified with 3 weight parts of aminosilane manifested presence of particles within the lower range of diameters as compared to the unmodified silica. The band within the range of 2104.6-2571.3 nm reflected presence of particles of larger diameters and of agglomerates and was decisively less intense (maximum intensity of 7 corresponded to particle diameter of 2249.9 nm). Presence of spherical particles and the highly uniform character of the so modified silica was verified by the microphotogram presented in Fig.2b. Particles of the silica presented much more fine, spherical grains and the system became more uniform.

Silica modified with 5 weight parts of aminosilane also exhibited a highly uniform character of particles (Fig.3). In this case, mean particle diameter was 442.2 nm and its polydispersity was 0.005. The particle size distribution (Fig.3a) demonstrated only one typical band within the diameter range of 438.5-444.3 nm. Maximum intensity of 100 corresponded to particles of 442.6 nm in diameter. The pronounced homogeneity of particles could also be confirmed by SEM micrograph (Fig.3b).

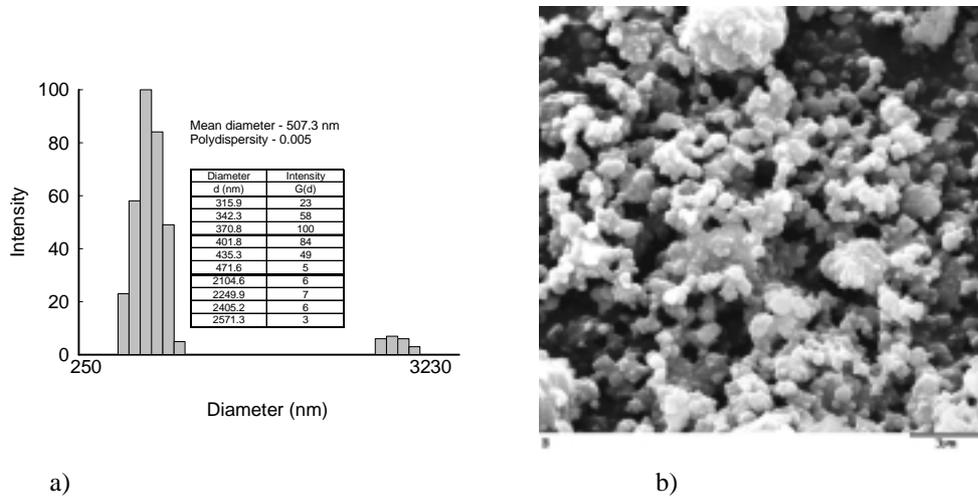


Fig.2. a) Multimodal particle size distribution and b) SEM of silica modified with 3 w/w aminosilane

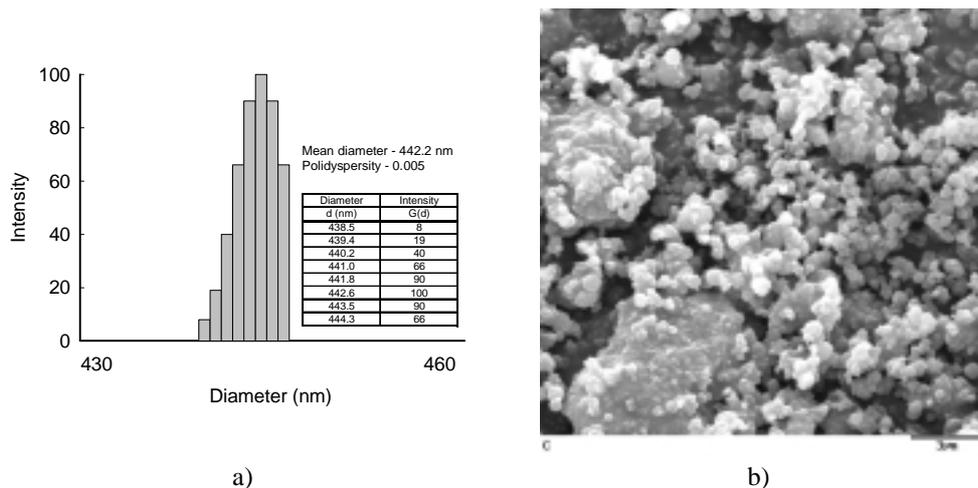


Fig.3. a) Multimodal particle size distribution and b) SEM of silica modified with 5 w/w aminosilane

Results of studies on specific surface area (BET) and on the volume and diameter of pores are shown in Table 2.

As evident in the Table 2, the unmodified silica exhibited a relatively extensive development of specific surface area, amounting to 182 m<sup>2</sup>/g. Following modification with 3 weight parts of aminosilane BET area decreased to 119 m<sup>2</sup>/g, which was confirmed by the data of Fig.2b, documenting absence of large groups, the so called agglomerates. Increased amount of the modifier (sample C) resulted in enhanced tendencies for particle-particle interactions and this was accompanied by a pronounced

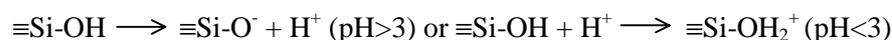
increase in the area, which reached the value of 208 m<sup>2</sup>/g. The alterations in specific surface area were accompanied by altered desorptive-adsorptive properties, expressed by the volume and size of pores.

Table 2. Specific surface area, volume and average size of pores of obtained silicas.

Sample No.	Specific surface area BET (m <sup>2</sup> /g)	Total pores volume (cm <sup>3</sup> /g)	Pores volume 17 do 30000Å (cm <sup>3</sup> /g)		Average size of pores* (Å)
			from adsorption curve	from desorption curve	
A	182	0.45	0.4987	0.4996	99.24
B	119	0.34	0.3907	0.3913	114.16
C	208	0.39	0.4534	0.4525	74.95

\* calculated from BET equation (4V/A)

Dependence of zeta potential on pH (the so called isoelectric point) was demonstrated both for the unmodified and the modified silicas (Fig.4). Numerous studies (Kosmulski et al., 2000; Spange et al., 2000) demonstrated that altered protonisation in the reaction of:



induced alterations in zeta potential and, indirectly, also in the isoelectric point. In this study effect of aminosilane protonisation was analysed on the course of electrokinetic curves and, thus, on values of isoelectric point. In the acidic range of pH, evident differences in surface charge can be noted between silicas modified with aminosilane and the unmodified silica (Fig.4). Almost within the entire acidic range of pH zeta potential manifested positive values and the highest stability was reached at pH ranging between 2 and 6. A completely distinct surface character could be ascribed to the unmodified silica, in which the range of pH = 2 to 6 determined a negative charge of zeta potential. In the range of pH = 8 to 9.5 the studied silicas manifested similar values of the potential. Moreover, the modified silica manifested a definitely higher value of the isoelectric point as compared to the unmodified silica. The value amounted to 1.5 in sample A, 6.2 in sample B, 6.7 in sample C.

The studies performed by XPS technique demonstrated to which extent silane modification affected the atomic composition (%) of the silica (Table 3). Modification with 3 weight parts of silane introduced 1% nitrogen, and the nitrogen content increased to 2% following modification with 5 weight parts of the silane. The nitrogen originated from =NH and -NH<sub>2</sub> groups of the applied aminosilane.

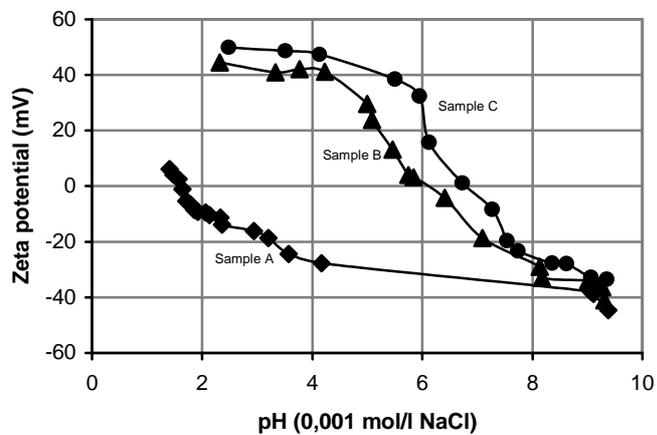


Fig. 4. Zeta potential as a function of pH for unmodified silica and amino-silane modified silicas

Table 3. Surface elemental composition from XPS analysis.

Sample	Surface composition (at%)	
A	C	22.3
	O	55.0
	Si	22.6
	N	0.0
B	C	33.4
	N	1.0
	O	46.7
	Si	18.9
C	C	17.8
	N	2.0
	O	56.4
	Si	23.9

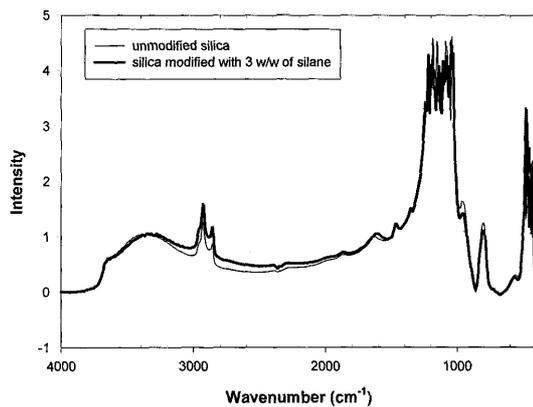


Fig. 5. FTIR spectra for unmodified and 3 w/w of U-15D silane modified silica

Character of the modification was evaluated by FTIR spectroscopy. As can be noted in Fig.5, the studied silicas exhibited no intense  $3,748\text{ cm}^{-1}$  band, responsible for the presence of isolated silanol groups. Traces of the band could only be noted. Most probably, thus resulted from blocking of silanol groups by organic emulsion components in the course of silica precipitation. On the other hand, the band in the range of  $2,965\text{-}2,850\text{ cm}^{-1}$  corresponding to distracting oscillations could be clearly noted. Its presence reflected production of the silica in an organic medium (in the case of the unmodified silica) and modification of the silica with silane coupling agent. Therefore, intensity of the band was higher in aminosilane-modified silica.

### CONCLUSIONS

Following modification with aminosilane extensive changes were noted in silica surface hydrophilicity (e.g., the decrease in water absorbing capacity from  $250\text{ cm}^3/100\text{g}$  to  $150\text{ cm}^3/100\text{g}$ ). Moreover, the studied silicas demonstrated a highly monodisperse character, which was confirmed by SEM microphotographs and particle size distributions. Silica surface modification, particularly with 3 weight parts of aminosilane, induced a pronounced increase in particle homogeneity. On the other hand, spectroscopic studies and laser light scattering provided evidence for the chemical character of N-2-(aminoethyl)-3-aminopropyltrimethoxysilane with the silica surface. Chemical interaction of silane with silica surface induced evident changes in isoelectric point and in the surface composition.

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**Jesionowski T.**, *Wpływ n-2-(aminoetylo)-3-aminopropylotrimetoksylanu na właściwości fizykochemiczne i morfologiczne krzemionek otrzymanywanych w układzie emulsyjnym*, Fizykochemiczne Problemy Mineralurgii, 36, (2002) 243-252 (w jęz. ang.)

Przeprowadzono syntezę monodispersyjnej krzemionki w reakcji strącania z wodnego roztworu metakrzemianu sodu kwasem solnym w środowisku emulsji. Badano wpływ N-2-(aminoetylo)-3-aminopropylotrimetoksylanu na właściwości powierzchniowe i morfologiczne strąconej krzemionki. Wielkość cząstek i polidispersyjność mierzono stosując technikę dynamicznego rozpraszania światła (DLS) oraz skaningową mikroskopię elektronową (SEM). Stopień powierzchniowej modyfikacji oraz jej charakter oceniano wykorzystując spektroskopię w podczerwieni. Ponadto charakteryzowano właściwości adsorpcyjne przez wyznaczenie powierzchni właściwej (BET) i makroporowatości. Technika XPS umożliwiła wyznaczenie ilościowe obecnego modyfikatora na powierzchni krzemionki. Zmiany ładunku powierzchniowego badano wyznaczając dla poszczególnych krzemionek punkt izoelektryczny przez bezpośredni pomiar ruchliwości elektroforetycznej, a pośrednio przez wyliczenie potencjału zeta. Modyfikacja SiO<sub>2</sub> formowanej w środowisku emulsji aminosilanem powoduje duże zmiany charakteru powierzchniowego i morfologicznego. Następuje wyraźne ograniczenie grup silanolowych na powierzchni już w chwili preparatyki krzemionki, a dodatkowo zwiększenie hydrofobowości na skutek chemisorpcji aminosilanu. Uzyskano również wzrost homogeniczności cząstek i zmniejszenie wartości polidispersyjności na skutek oddziaływań aminosilanu z powierzchnią badanej krzemionki.