Surface properties and chemical modification of hydrated silicas

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Silicas of highly dispersion degree were obtained using the precipitation technique with potassium metasilicate solution and sulphuric acid. This process includes formation of silica particle and their aggregation. Studies on the surface modification of silicas using silane coupling agents are described. Application of these compounds results in the change of the hydrophilic character to the hydrophobic one. The studies on morphology and microstructure using scanning electron microscopy (SEM) were performed. The zeta potential, polydispersity and changes in the tendency to form agglomerates and aggregates of the particles were also described. Moreover, the chemical interactions of silica surface with silane coupling agents using FT-IR spectroscopy were examined. The modified silicas with any of the examined silanes manifest a decreased tendency to secondary agglomerate formation and in many cases uniform silicas were obtained.

1. INTRODUCTION

Colloidal silicas can be obtained in several chemical processes. The most important of them include hydrolysis of alkoxysilane esters [1], combustion of silicon halides [2], formation of nanometric silicas in emulsion systems [3-5], and precipitation from aqueous solutions of lithium silicates. Procedures of precipitation of silicas from sodium metasilicate solutions are also known [6-8].

Highly dispersed, precipitated silicas exhibit a specific affinity to functional groups of organic substances [9-11]. They exhibit an acidic and hydrophilic character. Silica surface modification aims at altering physicochemical properties and inducing hydrophobic transformation of the surface. Consequently, the modification process markedly broadens applicability of

silicas. Various types of compounds can be used for the silica surface modification but silane coupling agents [12-16] and selected surfactants [17, 18] are particularly important.

In the present study we described experiments on silica formation in the course of precipitation from aqueous solutions of potassium metasilicate and of sulphuric acid. In the course of precipitation, the silicas were modified with silane coupling agents.

2. EXPERIMENTAL DETAILS

Materials. Highly dispersed silicas were obtained in the process of precipitation from aqueous solutions of potassium metasilicate ($K_2O*mSiO_2*nH_2O$) using sulphuric acid in presence of: a hydrophobicity-inducing agent, Rokanol K-7 ($C_{18}H_{37}O(CH_2CH_2O)_7H$), and a coagulating agent, sodium sulphate(VI).

For modification, the following silane coupling agents were used: 3-mercaptopropyltrimethoxysilane (A-189), n-octyltriethoxysilane (U-222), N-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D), ureido-N-3--aminopropyltrimethoxysilane (U-17), 3-glycidoxypropyltrimethoxysilane (A-187).

Preparation and modification of hydrated silicas. Potassium metasilicate solution, containing appropriate amount of the coagulating agent (sodium sulphate(VI)), and 5 wt% solution of sulphuric acid were dosed in parallel to a reactor of 0.5 dm^3 in capacity, containing aqueous solution of the hydrophobicity-inducing agent (0.25 weight parts of Rokanol K-7 per 100 weight parts of SiO_2). The system was intensely blended using a rapidly revolving mixer. A thermostate allowed to maintain steady temperature of 85 °C. The precipitation process was conducted until pH of the mixture stabilized at the level of 5 to 7. The reaction yielded a white silica powder, which was washed with water, filtered and heated in a stationary drier for 48 h at 105 °C.

A series of precipitated silica samples was obtained, of specific physicochemical properties, maintaining stable precipitation conditions: silicate modulus $M_S=4.0$, sulphuric acid concentration, c=5wt%, SiO_2 concentration in K_2SiO_3 solution of 5wt%, temperature of 85 °C, rate of dosing sodium metasilicate solution, v=2.2 cm^3/min and rate of dosing sulphuric acid, v=0.23 cm^3/min.

The modification process was conducted basing on the earlier established optimum parameters of silica precipitation. We found technologically proper to

modify highly dispersed silica obtained in the medium of Rokanol K-7 and sodium sulphate(VI). Silane coupling agents, applied at the amounts of 1-10 weight parts per 100 weight parts of SiO_2, were used to modify the precipitation system.

Physicochemical properties of the obtained silicas. Following the precipitation, studies on morphology and microstructure were performed in order to obtain data on dispersion, particle shape and morphology, structure of individual particles and on silica aggregation and agglomeration type following precipitation. The investigations 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 wavelenght of laser light source of 635 nm, sampling time 256 µs, modular frequency 250 Hz and the scattering angle 15°. The standard error of the zeta potentials, converted from the experimentally determined electrophoretic mobilities according to the Smoluchowski limit of the Henry equation, was typically < 1.0%. The zeta potentials were obtained by averaging 5-10 runs.

Size distribution of silica was also estimated using a ZetaPlus instrument, by the dynamic light scaterring method. In the instrument, the mobility rate was measured of loaded colloid particles, suspensed in a water.

Moreover, the extent of modification was evaluated in FT-IR EQUINOX 55 apparatus (Brucker). Samples for spectrophotometric studies were prepared in the vials, in which the suspensions of original silicas were prepared in carbon tetrachloride. Three wt% dispersions of silica were prepared in CCl_4. Procedures associated with preparation of samples for infrared studies were conducted as rapidly as possible to prevent their exposure to humidity. The studied samples were dried at 105 °C for 2 h or heated at 600 °C for 2 h. In order to demonstrate intensity of individual bands, which characterise silanol groups, silica spectrum was recorded in the range of 3,800-3,000 cm^{-1}.

3. RESULTS AND DISCUSSION

Results of testing zeta potential, polydispersity, effective particle diameter, diameters of aggregates and agglomerates for silicas modified with selected silanes are presented in Table 1. The results were compared to those obtained for the unmodified silicas.

Tab. 1. Zeta potential, polydispersity and effective particle diameter of unmodified and modified precipitated silicas

Amount of silane [w/w]	Zeta potential [mV]	Polydispersity	Effective particle diameter [nm]
no silane			
–	-18.82	0.291	930.2
A-189			
3	-23.53	0.257	594.5
5	-43.54	0.248	570.4
10	-53.26	0.234	756.5
U-222			
3	-56.54	0.286	967.0
5	-23.80	0.348	740.6
10	-27.84	0.349	737.0
U-15D			
3	-13.55	0.241	496.2
5	-17.34	0.288	950.4
10	-32.20	0.244	1224.1
U-17			
3	-21.80	0.252	396.9
5	-45.21	0.233	372.0
10	-11.55	0.265	368.9
A-187			
3	-46.96	0.279	823.2
5	-31.06	0.262	835.4
10	-31.45	0.287	660.7

The unmodified silica, formed in presence of sodium sulphate exhibited a very high zeta potential (-49.86 mV). Supplementation of the system with hydrophobicity-inducing substance (Rokanol K-7) markedly decreased absolute value of zeta potential to (-18.82 mV). Probably, this was induced by a less pronounced effect of electrolyte (sodium sulphate) interaction due to blocking of active centres by the hydrophobicity-inducing agent.

Application of 3-mercaptopropyltrimethoxysilane (A-189), at 3 wt parts per 100 wt parts of SiO_2 , resulted in augmented electrophoretic mobility and, indirectly, in the increase in zeta potential from (-18.82 mV) to (-23.53 mV). Increased amounts of the applied modifier resulted in a further increase in electrophoretic potential of the formed silica suspensions to (-43.54 mV) and (-53.26 mV) for 5 and 10 wt parts of the modifier, respectively. The original silicas and silicas modified with A-189 silane exhibited similar values of polydispersity. Also in the cases of application of A-187, U-15D and U-17 silanes the polydispersity remained stable, manifesting values resembling those for the unmodified silicas.

Particle size distributions established by the dynamic light dispersion technique and appropriate SEM electronograms of the precipitated unmodified and modified silicas are presented in Figures 1 to 7.

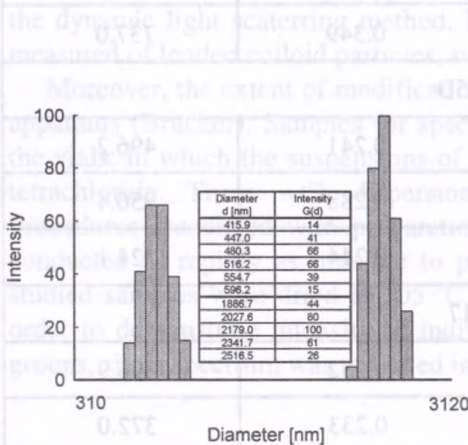| Diameter d [nm]	Intensity G(d)
415.9	14
447.0	41
480.3	66
516.2	66
554.7	39
596.2	15
1886.7	44
2027.6	80
2179.0	100
2341.7	61
2516.5	26

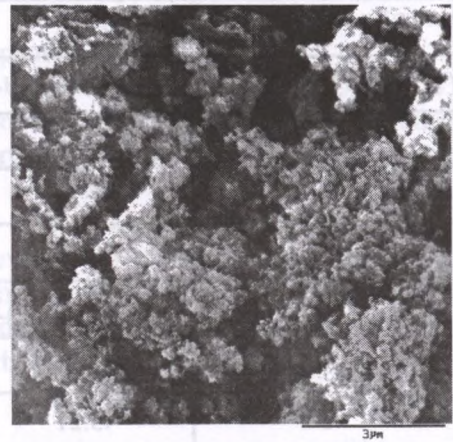Fig. 1a. Particle size distribution of unmodified silica

Fig. 1b. SEM micrograph of unmodified silica

Silica precipitated in the absence of silane agent exhibited strong tendency to form secondary agglomerates, as demonstrated by extensive areas composed of primary agglomerate (aggregate) particles. The silica showed low effective diameter of particles (930.2 nm). The particle size distribution curve (Figure 1a) manifested two typical bands. The band of the highest intensity of 100 in the range of 1,886.7 to 2,516.5 nm was typical for secondary

agglomerate structures while the band of intensity 66 (415.9-596.2 nm) corresponded to primary agglomerate structures. Presence of the two types of existing structures was confirmed by electron micrograms (Figure 1b).

Following modification of silica using n-octyltriethoxysilane (U-222), a tendency was observed for decomposition of secondary agglomerates (Figure 2). For silica modified with 3 wt parts of the silane, agglomerate diameter amounted to 1,578.8 at intensity of 100. As compared to the unmodified silica, the band of primary agglomerates was shifted to the range of 322.7-400.7 nm (Figure 2a). The effect of U-222 could also be observed on respective electron micrograms (Figure 2b).

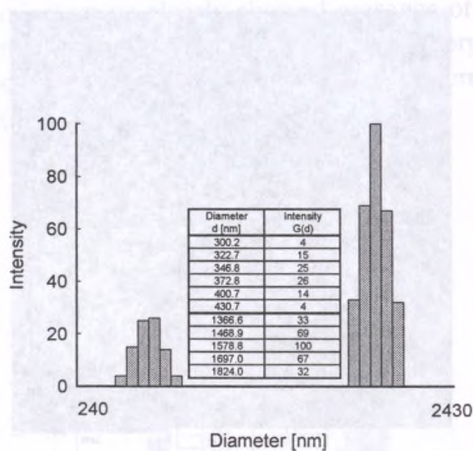| Diameter d [nm]	Intensity G(d)
300.2	4
322.7	15
346.8	25
372.8	26
400.7	14
430.7	4
1366.6	33
1468.9	69
1578.8	100
1697.0	67
1824.0	32

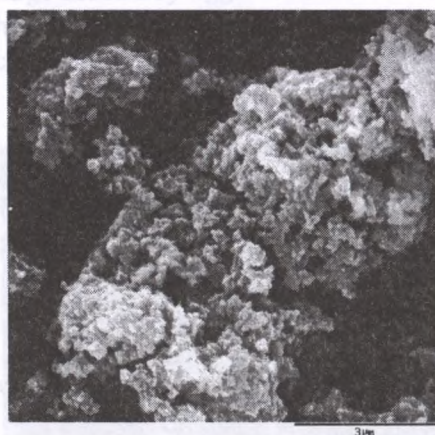Fig. 2a. Particle size distribution of silica modified with 3 w/w of U-222 silane

Fig. 2b. SEM micrograph of silica modified with 3 w/w of U-222 silane

Silicas modified with 3-mercaptopropyltrimethoxysilane (A-189) manifested low tendency to for agglomerates, practically until 3 to 5 wt parts of the silane were used for their modification. The electron micrograms (Figures 3b-4b) documented destruction of agglomerates and presence of exclusively primary agglomerates and even presence of primary particles. The size distribution curve of silica particles modified with 3 wt parts of the mercaptosilane (Figure 3a) demonstrated two bands, corresponding to primary and secondary agglomerates. The first band of a very high intensity included the range of 310.2-479.1 nm (maximum intensity of 100 corresponded to aggregate diameter of 385.5 nm) while the other band of a somewhat lower intensity covered the range of 1,025.5-1,766.0 nm (maximum intensity of 91 corresponded to secondary agglomerate diameter of 1,420.9 nm). The silica precipitated in such conditions demonstrated the effective particle diameter of 594.5 nm. Silica precipitated in presence of 5 wt parts of the mercaptosilane was even more uniform and exhibited the lower effective particle diameter of 570.4 nm

(Figures 4a and b). The particle size distribution for silica modified using 5 wt parts of A-189 silane (Figure 4a) proved that the silica structure included small amounts of secondary agglomerates, within the range of 2,761.2 to 4,706.7 nm (maximum intensity of 15 corresponded to secondary agglomerate diameter of 3,605.0 nm). In the agglomerate structure of the silica primary agglomerates prevailed, present in two ranges: the first, less intense band within the range of lower agglomerate diameters of 267.0-415.9 nm (maximum intensity of 89 corresponded to agglomerate diameter of 372.3 nm) and the other, very intense band within the range of 808.7-1,127.6 nm (maximum intensity of 100 corresponded to agglomerate diameter of 903.5 nm).

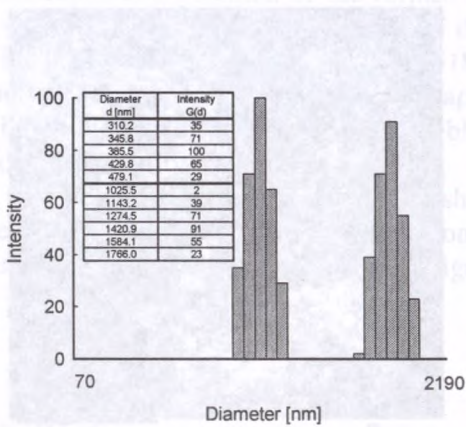| Diameter d [nm]	Intensity G(d)
310.2	35
345.8	71
385.5	100
429.8	65
479.1	29
1025.5	2
1143.2	39
1274.5	71
1420.9	91
1584.1	55
1766.0	23

Fig. 3a. Particle size distribution of silica modified with 3 w/w of A-189 silane

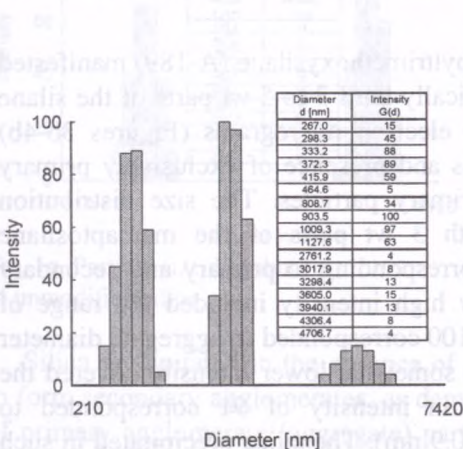Fig. 3b. SEM micrograph of silica modified with 3 w/w of A-189 silane

Diameter d [nm]	Intensity G(d)
267.0	15
298.3	45
333.2	88
372.3	89
415.9	59
464.6	5
808.7	34
903.5	100
1009.3	97
1127.6	63
2761.2	4
3017.9	8
3298.4	13
3605.0	15
3940.1	13
4306.4	8
4706.7	4
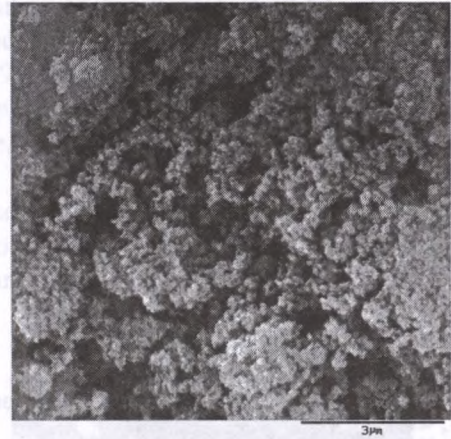
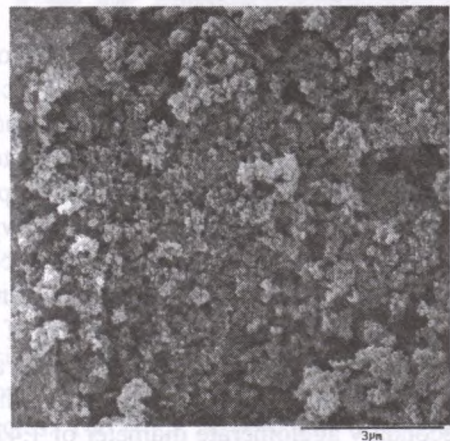Fig. 4a. Particle size distribution of silica modified with 5 w/w of A-189 silane

Fig. 4b. SEM micrograph of silica modified with 5 w/w of A-189 silane

Following modification with 10 wt parts of the mercaptosilane, the silica was less uniform and manifested a tendency to form secondary agglomerates. The effective particle diameter was much higher and amounted to 756.5 nm. In the particle size distribution curve (Figure 5a) two bands could be distinguished, ascribed to primary and secondary agglomerates, respectively. The primary agglomerates were present within the range of 310.9-428.7 nm (maximum intensity of 40 corresponded to the agglomerate diameter of 377.0 nm). Secondary agglomerates formed large clumps within the diameter range of 1,054.1-1,453.5 nm (maximum intensity of 100 corresponded to secondary agglomerate diameter of 1,198.7 nm). The respective electron micrograms clearly showed presence of large secondary agglomerates, formed due to silane adhesion. However, morphology of the so modified silica was quite distinct from that of the silica precipitated in the absence of a modifier (Figure 5b).

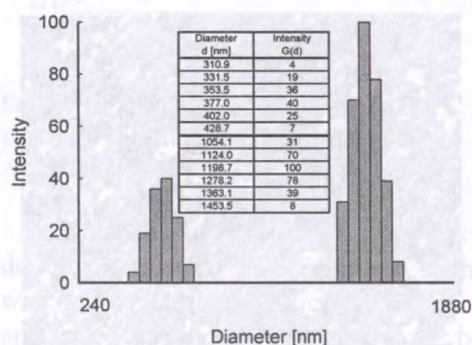| Diameter d [nm]	Intensity G(d)
310.9	4
331.5	19
353.5	36
377.0	40
402.0	25
428.7	7
1054.1	31
1124.0	70
1198.7	100
1278.2	78
1363.1	39
1453.5	8

Fig. 5a. Particle size distribution of silica modified with 10 w/w of A-189 silane
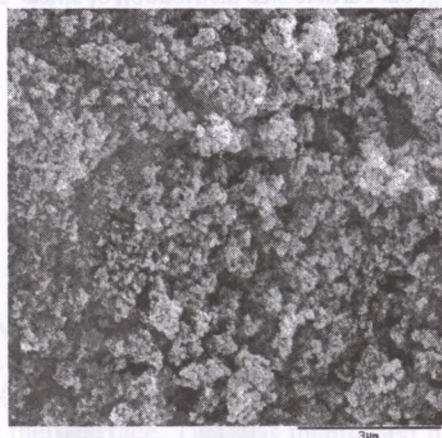
Fig. 5b. SEM micrograph of silica modified with 10 w/w of A-189 silane

A quite different effect on the tendency to form agglomerates was observed in the case of aminosilane-modified silica (Table 1). Silica modified with 3 wt parts of aminosilane exhibited a distinct surface structure. The particle size distribution curve manifested two bands corresponding to primary agglomerates, one in the range of 147.5-191.3 nm (maximum intensity of 9 corresponded to the particle diameter of 175.4 nm) and the other in the range of 321.7-496.2 nm (maximum intensity of 100 corresponded to the diameter of 382.6 nm). On the other hand, the band of secondary agglomerates (1,082.2-1,669.1 nm) was responsible for the typical "spongious" formation of the precipitated silica (Figures 6a, 6b). Maximum intensity of the band was 56 and corresponded to the particle diameter of 1,403.6 nm.

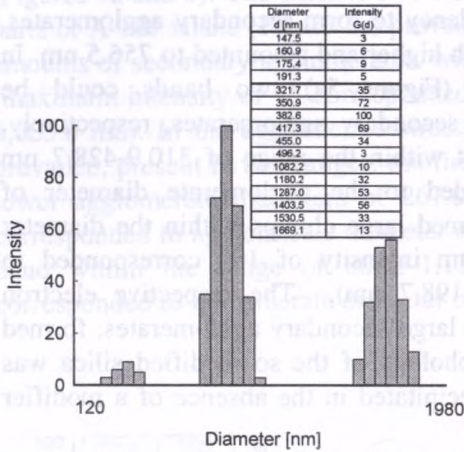| Diameter d [nm]	Intensity G(d)
147.5	3
160.9	6
175.4	9
191.3	5
321.7	35
350.9	72
382.6	100
417.3	69
455.0	34
496.2	3
1062.2	10
1180.2	32
1287.0	53
1403.5	56
1530.5	33
1669.1	13

Fig. 6a. Particle size distribution of silica modified with 3 w/w of U-15D silane

Fig. 6b. SEM micrograph of silica modified with 3 w/w of U-15D silane

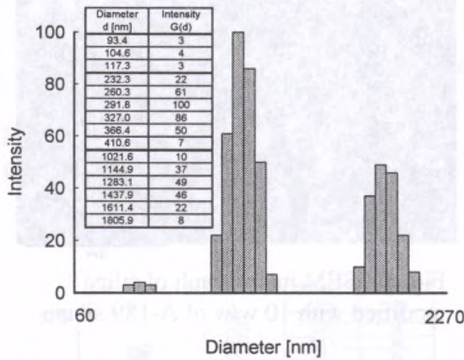| Diameter d [nm]	Intensity G(d)
93.4	3
104.6	4
117.3	3
232.3	22
260.3	61
291.8	100
327.0	86
366.4	50
410.6	7
1021.6	10
1144.9	37
1283.1	49
1437.9	46
1611.4	22
1805.9	8
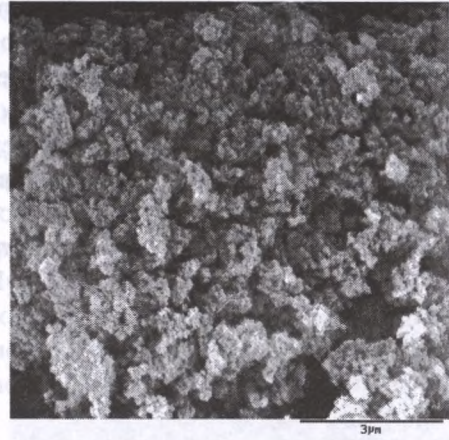
Fig. 7a. Particle size distribution of silica modified with 3 w/w of U-17 silane
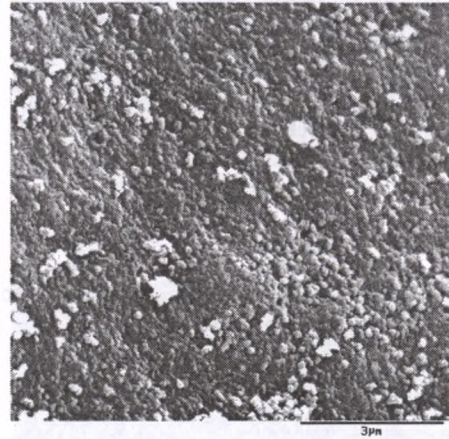
Fig. 7b. SEM micrograph of silica modified with 3 w/w of U-17 silane

The use of ureidosilane (U-17) for silica modification exerted a completely distinct effect on surface structure and morphology of the formed dispersions (Figure 7b). Application of 3 wt parts of the silane resulted in formation of a silica particle film. The effective particle diameter for silica modified with 3 wt parts of ureido-N-3-aminopropyltrimethoxysilane was 396.9 nm (Table 1). It was twice as low as that for the standard unmodified silica. Silica modified with 3 wt parts of U-17 silane (Figure 7a) manifested two bands of particle

aggregates; the first of lower intensity in the range of 93.4-117.3 nm (maximum intensity of 4 corresponded to the diameter of 104.6 nm) and the other within the range of 232.3-410.6 nm (maximum intensity of 100 corresponded to aggregate diameter of 291.8 nm). Moreover, a band of secondary agglomerates was present for which the agglomerate diameter was 1,283.1 nm, corresponding to intensity of 49.

FT-IR spectra within the range of 3,000-3,800cm^{-1} for the unmodified silica and for silicas modified with 3 wt parts of A-189 mercaptosilane, after drying at 105 °C or heating at 600 °C, are presented in Figures 8a and 8b, respectively.
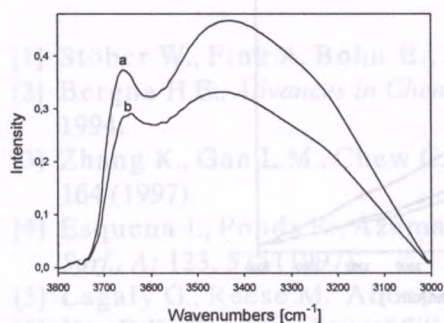

Fig. 8a. FT-IR spectra of (a) unmodified silica and (b) silica modified with 3 w/w of A-189 silane (heated at 105 °C)
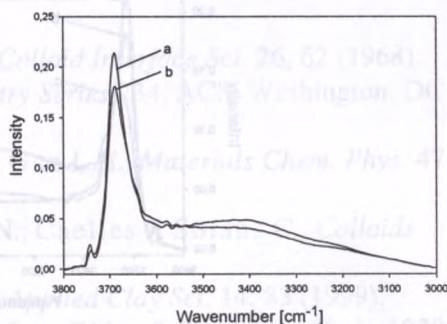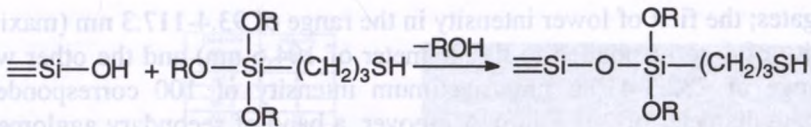
Fig. 8b. FT-IR spectra of (a) unmodified silica and (b) silica modified with 3 w/w of A-189 silane (heated at 600 °C)

As evident from Figure 8a, it was very difficult to define silanol group deficit (at intensity of 3,748 cm^{-1}) at the silica surface following modification with mercaptosilane. Silicas dried at 105 °C continued to carry significant amounts of physically adsorbed water on their surface. This was manifested by the diffuse bands within the range of 3,800-3,450 cm^{-1}. For this reason, samples heated at 600 °C were used to determine silanol group concentration on silica surface. As shown in Figure 8b, very sharp bands were obtained, corresponding to silanol group presence on the silica surface (at 3,750 cm^{-1}). Intensity of the band was clearly lower in the case of silica modified with 3 wt parts of mercaptosilane as compared to the intensity observed for the unmodified silica. This proved that the modification resulted in a lowered number of silanol groups on the silica. This provided a direct evidence for condensation of silica surface silanol groups with alkoxy groups of the modifying compound in the course of chemical modification of silica surface (e.g., with mercaptosilane). The reaction might proceed as follows:

$$\equiv Si-OH + RO-\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{Si}}-(CH_2)_3SH \xrightarrow{-ROH} \equiv Si-O-\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{Si}}-(CH_2)_3SH$$

The mechanism of surface condensation of silica silanol groups with alkoxysilanes was confirmed by modification of silica using various amounts of aminosilane (U-15D). FT-IR spectrum of the unmodified silica and aminosilane-modified silica is presented in Figure 9.
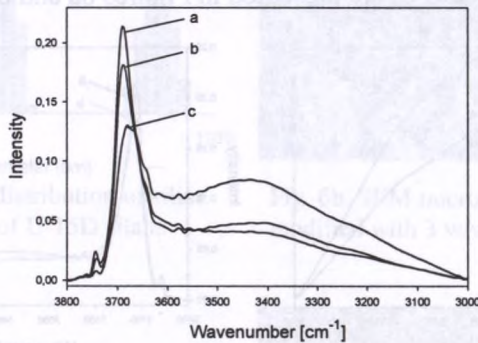

Fig. 9. FT-IR spectra of (a) unmodified silica, (b) silica modified with 3 w/w of U-15D silane and (c) silica modified with 10 w/w of U-15D silane (heated at 600 °C)

The spectrum for the silica, particularly following modification with 10 wt parts of the aminosilane, demonstrated a clearly decreased intensity of the 3,750 cm^{-1} band, confirming progress of the surface condensation. A size of the deficit in surface silanol groups permitted to appraise increasing condensation of the groups.

4. CONCLUSIONS

In the course of precipitation from solutions of potassium metasilicate, highly dispersed silicas were obtained of very interesting physicochemical properties. In their parameters, the silicas did not differ from silicas obtained by classical techniques using solution of sodium metasilicate.

The silica precipitated in the absence of silane modifiers exhibited strong tendency to form secondary agglomerates, which resulted from extensive hydrophilicity of its surface.

Hydrated silicas, modified with most of silanes (except of aminosilane and ureidosilane), showed a much lower tendency to form secondary agglomerates and in many cases the obtained silicas proved highly uniform.

Silica surface modification in the course of the precipitation exhibited character of a chemical reaction, as proved by the deficit in silanol groups observed in FT-IR spectra. The effect was noted following modification with either aminosilane or mercaptosilane coupling agents.

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CURRICULA VITAE
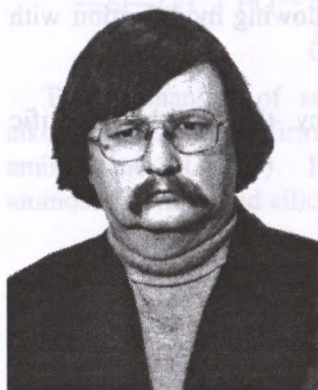
Andrzej Krysztafkiewicz was born in 1947. Graduated from the Faculty of Mathematics, Physics and Chemistry, Adam Mickiewicz University in Poznan and received the degree of Master of Chemistry in 1970. Defended his doctoral thesis in the Institute of Chemistry, Adam Mickiewicz University in 1978. Employed in the Institute of Chemical Technology and Engineering, Faculty of Chemical Technology, Poznan University of Technology since 1970. Defended his habilitated doctor's thesis in 1991.

Teofil Jesionowski was born in 1970. In 1995 graduated from the Faculty of Chemical Technology, Poznan University of Technology, receiving the degree of Master and Engineer of Chemistry. Moreover, defended his doctoral thesis in the Institute of Chemical Technology and Engineering, Poznan University of Technology in 1999. Employed in the Institute of Chemical Technology and Engineering, Faculty of Chemical Technology, Poznan University of Technology since 1999.

Jolanta Żurawska was born in Poland in 1976. In 2000 graduated from the Faculty of Chemical Technology, Poznan University of Technology, receiving the degree of Master and Engineer of Chemistry. She is Ph.D. student in the Poznan University of Technology, Faculty of Chemical Technology since 2000.