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ZnO-SiO$_2$ OXIDE COMPOSITES SYNTHESIS DURING PRECIPITATION FROM EMULSION SYSTEM

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Abstract. A new method of obtaining a ZnO-SiO$_2$ synthetic composite from emulsion systems is described. The reagents were solutions of sodium silicate and zinc sulphate, cyclohexane was used as an organic solvent and non-ionic surfactants as modifiers. The influence of the mode of reagents dosing and type of emulsifiers on the physicochemical properties, structure and particle size of ZnO-SiO$_2$ was evaluated. The choice of the optimum emulsifier or mixture of emulsifiers and their amounts needed for the process of precipitation and ensuring getting products of uniform particles and the smallest possible size was proposed. The ZnO-SiO$_2$ composite obtained was characterised by micrometric particle size. The oxide composites obtained were subjected to thorough analyses to determine their physicochemical properties, dispersion and morphology. Particle size distributions were evaluated by the NIBS technique and laser diffraction method. The products were also characterised by sedimentation profiles, wettability with water and colorimetric analyses, determination of bulk density or ZnO and SiO2 contents.

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keywords: ZnO-SiO$_2$, precipitation, particle size distribution, surface morphology, wettability, sedimentation, emulsion

1. Introduction

Silica and silica-based materials have found widespread application for industrial, technological and domestic purposes. The demand for improved silica types with specific properties such as mechanical strength, pore volume and size distribution, surface area or reactivity is fueling the search for innovative production of such materials (Sun 2004). For many years, silicates have attracted great attention due to their special physicochemical properties, low cost and abundant supply, and have been widely applied in many fields, e.g. as molecular sieves (Ying 1999), catalyst supports (Fotopoulos 2007), for gas absorption and separation (Kalinkin 2009), and as raw materials for the glass industry (Yang 2010).

In recent years, ZnO nanoparticle embedded SiO_2 composites have attracted extensive research interests. It has been found that these materials have improved luminescence efficiency compared to bulk ZnO materials. Excellent nonlinear optical properties, saturable absorption and optical bistability have also been reported for these composites (Mo 1998, Fu 2003, Chakrabarti 2004, Zhao 2007). ZnO-based nanocomposites are promising materials in ceramic technology for application as varistors, sensor elements, photoconductors in electrophotography (Cannas 1999), and for electroluminescent applications such as in flat-panel displays, photoelectronics integrated devices, and semiconductor lasers. However, the luminescence efficiency of ZnO-based nanocomposites needs to be improved for the above applications (Fu 2003). Yao et al. (2000) have reported band gap luminescence from ZnO in mesoporous silica, and they have found that Zn–O–Si cross-linking bonds that formed at the interface between ZnO and the pore walls of silica had a great influence on the optical properties of ZnO/SiO_2. Much attention has been paid to the UV barrier properties of fabrics modified with $ZnO\text{-}SiO_2$. It has been shown that coating of fabrics with a paste of $ZnO\text{-}SiO_2$ is an effective method of surface modification (Sójka-Ledakowicz 2010).

Recently, intense research has been dedicated to preparation of materials of desired properties (e. g. spherical shape of particles, high adsorption activity) (Jesionowski 2009). In the production of highly dispersed synthetic silicates a particularly important are the technological conditions of the process. They affect the physicochemical properties of the products obtained and surface modification permits improvement of the product properties (Krysztafkiewicz 2004). In conventional methods, uncontrolled nucleation and subsequent growth of the precipitated particles in a bulk aqueous medium finally generates large particles with a wide size distribution (Lee 2006). To overcome these problems, many recent studies have used emulsions to control the size, distribution and morphology of the fine particles (Ganguli 1997). Emulsions consist of droplets of one liquid dispersed throughout another one referred to as the continuous phase (Robins 2002). They are used in a wide spectrum of industrial applications including production of pharmaceuticals, food, cosmetics and textiles. Due to a small droplet size of the dispersed phase, the total interfacial area in the emulsion is very large. Since the creation of interfacial area incurs a positive free energy, the emulsions are usually thermodynamically unstable. Nevertheless, it is possible to make highly stable emulsions by the use of emulsifiers. Emulsifiers accumulate at the oil/water interface and make an energy barrier against flocculation and coalescence of the droplets. The emulsifiers can be ionic, non-ionic or zwitterionic surfactants, proteins or amphiphilic polymers (Somasundaran 2006). Midmore (2001) observed that the addition of non-ionic surfactants, used to flocculate silica dispersions, caused synergistic effects on the stability of oil-in-water (o/w) emulsions containing silica.

In this study $ZnO\text{-}SiO_2$ synthetic oxide composites were obtained by precipitation from emulsion. The reagents were water solutions of sodium silicate and zinc sulphate, cyclohexane (organic solvent) and non-ionic emulsifiers. The effects of different modes of the reagent dosing were analysed. The main aim of the study was to identify an emulsifier or a mixture of emulsifiers needed for the process of precipitation and its or their amounts whose use would ensure getting a product of optimum properties made of uniform particles of the smallest possible diameters.

2. Experimental

2.1. Materials

The reagents used to obtain ZnO-SiO_2 oxide composite were 5% water solutions of zinc sulphate of analytical grade (Chempur) and sodium silicate of technological grade (Vitrosilicon SA). The non-ionic surfactants were nonylphenylpolyoxyethyleneglycol ethers of a medium oxyethylenation degree 3, 5 and 6 (NP3, NP5 and NP6) – Sigma Aldrich. Cyclohexane of analytical grade was used as an organic solvent (POCh SA).

2.2. Methods of studies

The process of ZnO-SiO_2 precipitation was performed in a reactor of 0.5 dm^3 in capacity, equipped in a high speed stirrer 1700 rpm (Eurostar Digital, IKA Werke), to which a 5% solution of zinc sulphate or earlier prepared emulsion E1 were introduced. Emulsion E1 was made by mixing 110 cm^3 of cyclohexane and 100 cm^3 of sodium silicate to which NP3, NP5 or NP6 emulsifier or a mixture of two emulsifiers was added. Using a peristaltic pump Ismatec ISM833A the reagents were introduced at a constant rate of 4.2 cm^3/min. Precipitation was performed at room temperature. A scheme illustrating the synthesis of ZnO-SiO_2 composite is presented in Fig. 1.

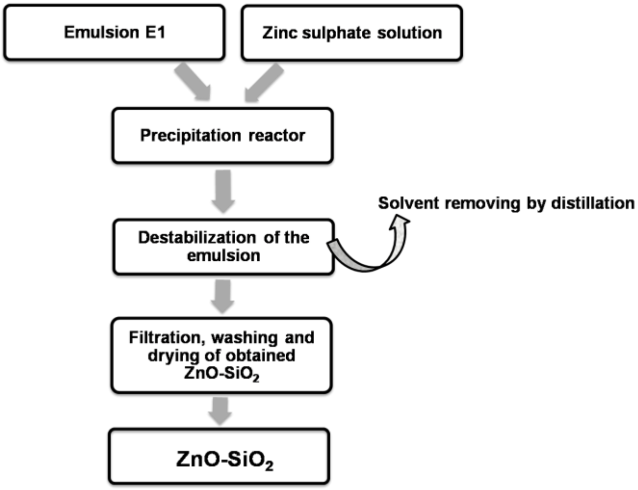


Fig. 1. Synthesis of ZnO-SiO_2 oxide composite from the emulsion systems

The oxide composite ZnO-SiO_2 was characterised by determination of the particle size distribution, surface morphology and wettability with water. The particle size distribution was evaluated by measurements with the apparatuses Malvern Instruments Ltd: Zetasizer Nano ZS (non-invasive backscattering method – NIBS) and Mastersizer 2000 (laser diffraction technique). Surface morphology of the surfaces of the products studied was evaluated by scanning electron microscopy SEM (Zeiss VO40). The colour of the products was classified with the use of a colorimeter Specbos 4000 (JETI Technische Instrumente GmbH). Intensity of the colour was expressed in the CIE L*a*b* system where L* describes lightness, C* colour saturation, h* colour hue and +a informs about the contribution of red, -a – a contribution of green, +b – a contribution of yellow. dE describes total color change which is a resultant of differences in particular components (dL*, da*, db*). The profiles of ZnO-SiO_2 sedimentation and wettability with water were measured with the help of a tensiometer K100 (Krüss) with special equipments. Chemical analysis of the products was made by titration analysis with EDTA solution.

3. Results and discussion

In the first stage the synthesis of ZnO-SiO_2 composites was performed by introducing E1 emulsion in the volume of 210 cm^3 into 200 cm^3 of a 5% solution of $ZnSO_4$. E1 emulsion was made with 110 cm^3 of cyclohexane and 100 cm^3 of a 5% sodium silicate solution with addition of surfactants NP3, NP5 or NP6. Table 1 presents the conditions of precipitation depending on the type of emulsifier and particle size and polydispersity indices obtained at this stage of the study.

The particle size distribution of sample M1 according to intensity (Fig. 2a) reveals three bands. The first covers the diameter range 255 – 295 nm, with the maximum intensity of 4.2% for particles 255 nm in diameter. The second one covers the diameter range 396 – 531 nm, with the maximum intensity of 7.7% for particles of 459 nm in diameter. The third band covers the range of diameters 1280 – 5560 nm and has the maximum intensity of 8.4% for agglomerates of 1990 nm in diameter. For sample M2 only one band is obtained covering the diameter range from 459 nm to 1280 nm, Fig. 2b, with the maximum intensity of 25.8% corresponding to particles of 825 nm. Sample M2 is characterised by a relatively low polydispersity index of 0.476, which means that despite the presence of clusters of secondary agglomerates this composite is rather homogeneous. The particle size distribution of M3 (Fig. 2c) has only one band covering the diameters from 1720 to 3580 nm. Its maximum intensity of 32.4% corresponds to agglomerates of 2300 nm in diameter. Fig. 2d shows the particle size distribution for sample M4 with two bands. The first covers the range 68 nm – 92 nm, with the maximum intensity of 40.6% for particles of 79 nm in diameter, while the second covers the range 4150 – 5560 nm, with the maximum intensity of 20.8% for secondary agglomerates of 5560 nm in diameter. For sample M5 the particle size distribution shows two bands (Fig. 2e), the first covers the diameters from 220 to 396 nm, with the maximum intensity of 26.0% corresponding to particles of

295 nm in diameter, while the second covers the range 531 – 712 nm, with the maximum of 9.3% for particles of 615 nm in diameter.

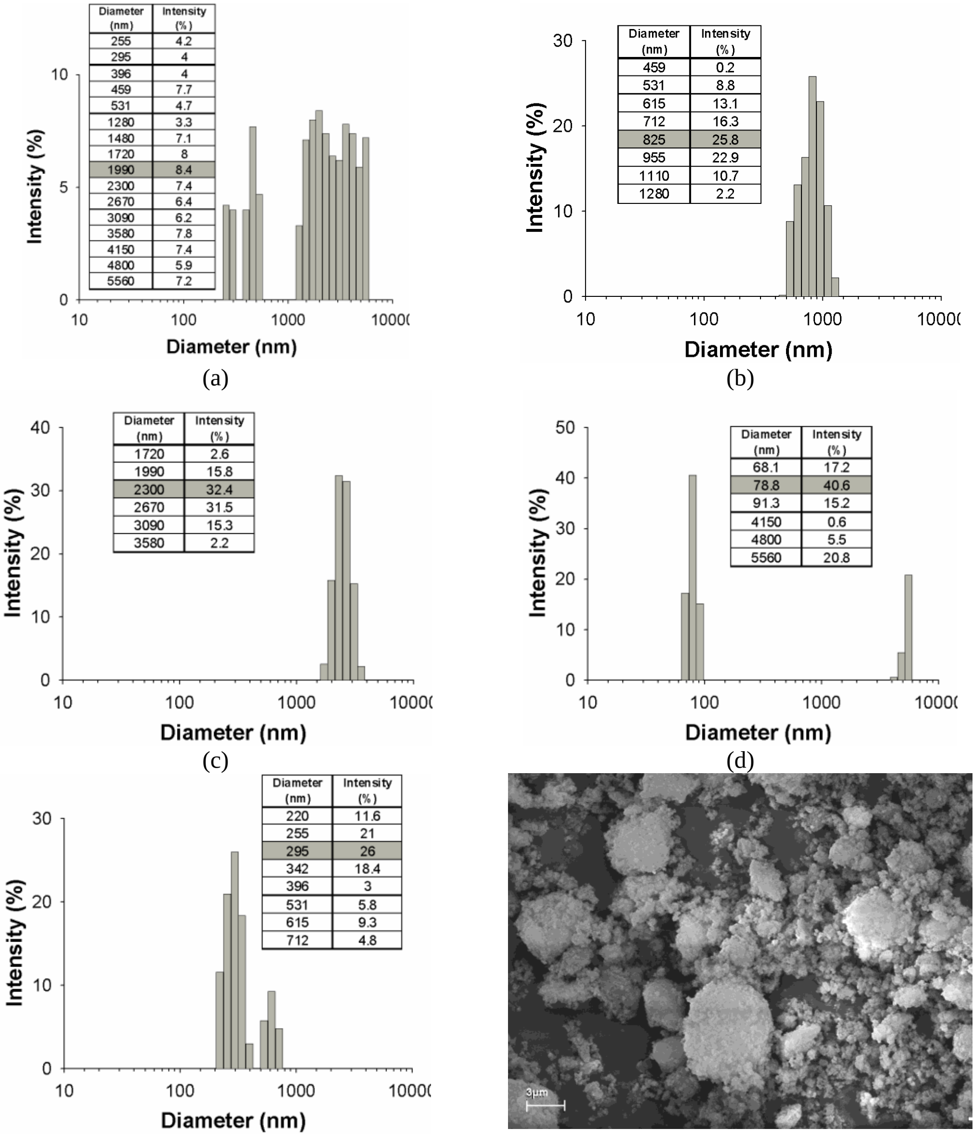
Table 1. Analysis of particle size distribution and PdI versus the type of emulsifier

Sample	Type/amount of emulsifier (g)			Particle diameter (nm)	PdI
	NP3	NP5	NP6		
M1	1.5	-	1.0	255-295 396-531 1280-5560	0.837
M2	-	-	2.0	459-1280	0.476
M3	3.4	-	-	1720-3580	0.807
M4	-	2.4	-	68-92 4150-5560	0.625
M5	1.4	1.2	-	220-396 531-712	0.879

Analysis of morphological and dispersive properties of ZnO-SiO_2 samples synthesised with the use of one ether or a mixture of ethers has pointed to the beneficial effect of using a mixture of non-ionic surfactants NP3 and NP5 on nucleation of the crystal phase and formation of relatively uniform particles of small diameters. In the same sample (M5) a drawback observed was the undesirable tendency towards formation of secondary agglomerations, confirmed by a relatively high polydispersity index PdI= 0.879 (Fig. 2f). In the ZnO-SiO_2 sample precipitated in a water system in similar process conditions, the particle size changes from 225 to 351 nm and from 1350 to 2115 nm (Michalska 2003).

The beneficial effect of a mixture of emulsifiers NP3 and NP5 (sample M5) used in the process of precipitation on the dispersion of ZnO-SiO_2 is best illustrated by the particle size distribution curves recorded by Mastersizer 2000. As follows from Fig. 3, sample M5 shows the presence of ZnO-SiO_2 particles of the smallest diameter of 8.7 μm which in this sample bring the greatest volume contribution (5.7%).

Sedimentation is a phenomenon of free fall of solid particles in liquid and is used to increase a density of suspension under the effect of gravitational field. The rate of fall depends on the diameter and shape of particles and on the material density. Figure 4a presents sedimentation profiles of the ZnO-SiO_2 samples studied as mass increase vs. time. From the profiles the rate of particles fall can be determined. Analysis of the curves shows that the greatest increase in mass over the same period is noted for sample M1. The angle of the curve inclination to the X-axis is the smallest for M1, which corresponds to the fastest sedimentation. For this sample the fast sedimentation is related mainly to large size of particles and their shapes often differ from spherical and can be close to other geometrical figures. Moreover, solid particles of undefined shape can show a tendency to flocculation. The process of sedimentation was the slowest for sample M4, built of very fine particles and few secondary agglomerates whose influence on the process of M4 sedimentation was negligible.



Diameter (nm)	Intensity (%)
255	4.2
295	4
396	4
459	7.7
531	4.7
1280	3.3
1480	7.1
1720	8
1990	8.4
2300	7.4
2670	6.4
3090	6.2
3580	7.8
4150	7.4
4800	5.9
5560	7.2

(a)

Diameter (nm)	Intensity (%)
459	0.2
531	8.8
615	13.1
712	16.3
825	25.8
955	22.9
1110	10.7
1280	2.2

(b)

Diameter (nm)	Intensity (%)
1720	2.6
1990	15.8
2300	32.4
2670	31.5
3090	15.3
3580	2.2

(c)

Diameter (nm)	Intensity (%)
68.1	17.2
78.8	40.6
91.3	15.2
4150	0.6
4800	5.5
5560	20.8

(d)

Diameter (nm)	Intensity (%)
220	11.6
255	21
295	26
342	18.4
396	3
531	5.8
615	9.3
712	4.8

(e)

(f)

Fig. 2. Particle size distributions according to intensity evaluated for ZnO-SiO_2 oxide composites obtained on introducing E1 emulsion into zinc sulphate (a) M1, (b) M2, (c) M3, (d) M4, (e) M5, (f) SEM image of M5 sample

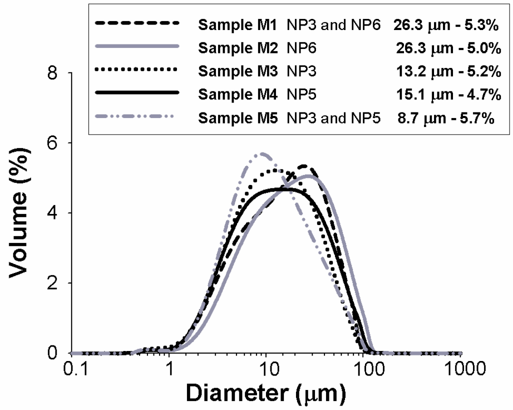
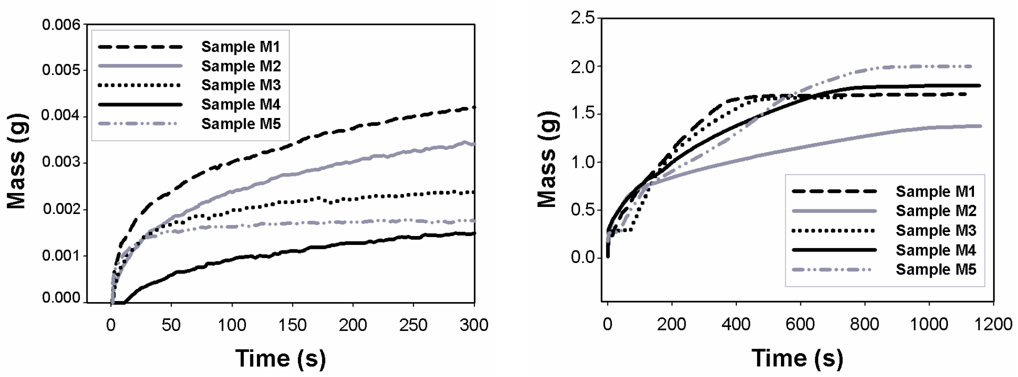


Fig. 3. Comparison of particle size distributions in micrometric range for ZnO-SiO$_2$ composites precipitated on introducing E1 emulsion into zinc sulphate using different types of emulsifiers



(a) (b)

Fig. 4. Profiles of sedimentation (a) and wettability with water (b) for ZnO-SiO$_2$ oxide composites precipitated by introducing E1 emulsion into zinc sulphate

Another important parameter determining the use of materials for certain applications is the ability to absorb water. Much attention at many research centres has been paid to obtain maximally hydrophobic powders by relatively simple and cheap methods. Figure 4b presents the profiles of wettability with water recorded for the ZnO-SiO$_2$ samples studied. The curves illustrate the ability to absorb water by individual samples. The greatest mass increase in time was observed for sample M5, which means that this sample has the greatest wettability. Most probably the presence of relatively small particles showing a tendency to aggregation and their non-uniform morphology are responsible for the high ability to absorb water. The most hydrophobic was sample M2. Its hydrophobicity was related mostly to microstructural differences or partial adsorption of non-ionic surfactants on the surface of ZnO-SiO$_2$ particles.

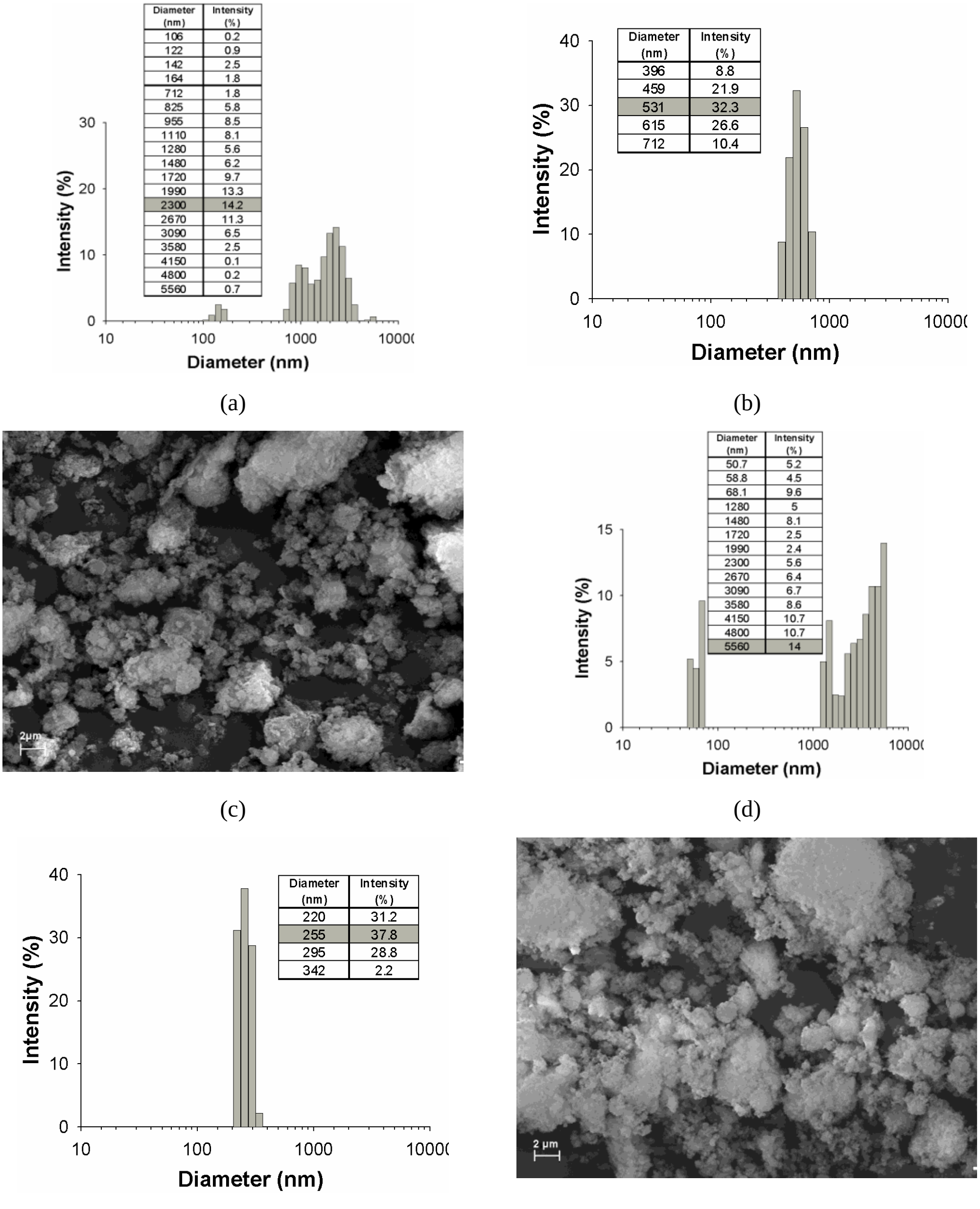
In the second stage of the study, the synthesis of ZnO-SiO_2 composites was performed in a different mode; 200 cm^3 of zinc sulphate was introduced into 210 cm^3 of E1 emulsion. E1 emulsion was made of 110 cm^3 cyclohexane and 100 cm^3 of a 5% solution of sodium silicate with surfactants NP3, NP5 or NP6.

Table 2 presents the dispersion parameters for ZnO-SiO_2 samples precipitated with different amount of emulsifier or a mixture of two emulsifiers.

Table 2. Analysis of particle size distributions and PdI for different surfactants used in the process of ZnO-SiO_2 samples synthesis

Sample	Type/amount of emulsifier (g)			Particle diameter (nm)	PdI
	NP3	NP5	NP6		
M6	1.5	-	1.0	106-164 712-5560	0.598
M7	-	-	2.0	396-712	0.861
M8	3.4	-	-	50-68 1280-5560	0.682
M9	-	2.4	-	220-342	0.910
M10	1.4	1.2	-	164-459	0.317

Figure 5a presents the particle size distribution according to intensity, obtained for sample M6. It shows two bands covering diameters from the ranges 106 – 164 nm and 712 – 5560 nm. In the first band the maximum intensity of 2.5% corresponded to the particle diameter 142 nm. The maximum intensity of 14.2% in the second band corresponds to the particle diameter 2300 nm. Sample M6 is characterised by the low polydispersity index (PdI=0.598), which points to high homogeneity of the particles despite the presence of secondary aggregates. The particle size distribution according to intensity, recorded for M7 is presented in Fig. 5b. It shows one band covering the diameter range 396 – 712 nm, with the maximum intensity of 32.3% corresponding to 531 nm. Figure 5c presents the SEM image of M7 confirming the presence of particles of non-uniform structure. The particle size distribution of sample M8 (Fig. 5d) shows two bands. One of them is relatively narrow and covers the diameters from the range 50 – 68 nm with the maximum of 9.6% corresponding to particles of 68 nm in diameter. The other band covering the range 1280 – 5560 nm testifies to the presence of secondary agglomerates. It maximum of 14.0% corresponds to agglomerates of 5560 nm in diameter. The particle size distribution obtained for sample M9, Fig. 5e, shows one band covering the diameters 220 – 342 nm, with the maximum intensity of 37.8% corresponding to particles of 255 nm in diameter. Besides having single almost spherical particles of small diameter (Fig. 5f), sample M9 shows a tendency to flocculation hence its high polydispersity index of 0.910.



(a)

Diameter (nm)	Intensity (%)
106	0.2
122	0.9
142	2.5
164	1.8
712	1.8
825	5.8
955	8.5
1110	8.1
1280	5.6
1480	6.2
1720	9.7
1990	13.3
2300	14.2
2670	11.3
3090	6.5
3580	2.5
4150	0.1
4800	0.2
5560	0.7

(b)

Diameter (nm)	Intensity (%)
396	8.8
459	21.9
531	32.3
615	26.6
712	10.4

(c)

(d)

Diameter (nm)	Intensity (%)
50.7	5.2
58.8	4.5
68.1	9.6
1280	5
1480	8.1
1720	2.5
1990	2.4
2300	5.6
2670	6.4
3090	6.7
3580	8.6
4150	10.7
4800	10.7
5560	14

(e)

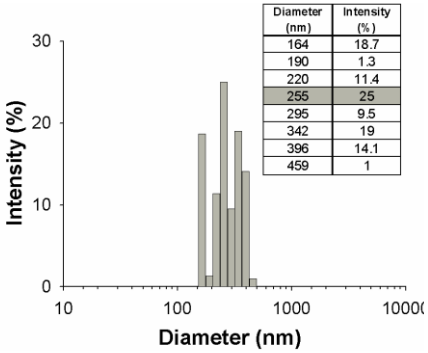
Diameter (nm)	Intensity (%)
220	31.2
255	37.8
295	28.8
342	2.2

(f)

Fig. 5. Particle size distributions according to intensity of ZnO-SiO$_2$ composites obtained by introducing zinc sulphate to E1 emulsion; (a) M6, (b) M7, (c) SEM of M7, (d) M8, (e) M9, (f) SEM of M9, (g) M10

(continued)

Fig. 5. Continued



(g)

The next plot is the particle size distribution of sample M10 (Fig. 5g). It has only one band covering the particle diameters from 164 to 459 nm, reaching a maximum intensity of 25.0% for particles of 255 nm in diameter. The lowest polydispersity index (PdI=0.317) and small sizes of particles illustrate the beneficial effect of a mixture of surfactants NP3 and NP5 on the process of ZnO-SiO_2 nucleation.

ZnO-SiO_2 has also been reported to be obtained from water systems with the use of zinc chloride. The particle size distribution obtained for this sample showed the highest intensities of 15.7% and 15.2% corresponding to particles of 531 nm and 220 nm, respectively. The non-uniform character of its particles and a tendency to formation of aggregates and agglomerates had direct influence on the surface activity of the precipitated ZnO-SiO_2 (Sójka-Ledakowicz 2010).

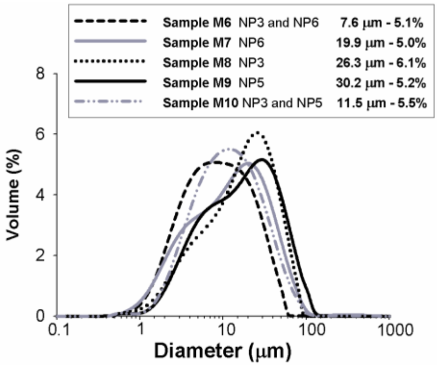
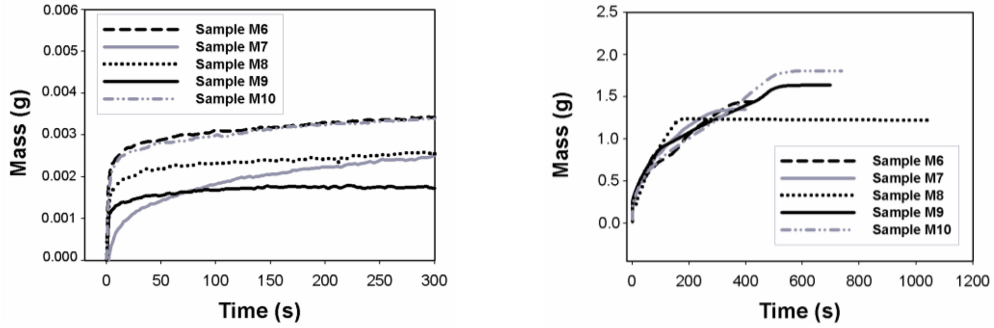


Fig. 6. Comparison of particle size distributions in the micrometric range for the samples obtained by introducing zinc sulphate into E1 emulsion for different emulsifiers or their mixtures

The influence of surfactants on the size of ZnO-SiO_2 particles is best illustrated by the particle size distribution curves plotted on the basis of laser diffraction measurement data. Figure 6 shows the particle size distribution curves for the samples obtained with the use of different emulsifiers. The particle size distribution in the micrometric range according to volume contribution of sample M8 showed that the greatest volume contribution of 6.1% was brought by particles of 26.3 μm in diameter. In the sample M6 the smallest particles of diameters close to 7.6 μm, bring a volume contribution of 5.1%. These results illustrate the beneficial effect of emulsifiers NP3 and NP6 in the process of precipitation

The rate of a particle free fall depends on the physical properties of the liquid and particle, in particular on the difference in their densities, on viscosity of the liquid and size and shape of the particle. As follows from Fig. 7a, the sedimentation profile of sample M6 is inclined at the smallest angle to the Y-axis, which means that in this sample the rate of particles fall is the highest. The addition of a mixture of NP3 and NP6 surfactants in the process of ZnO-SiO_2 precipitation irrespective of its mode, favours the appearance of particles showing a tendency to fast falling. This observation was interpreted as related most probably to a change in the interaction between the solid particles or between the solid particles and the liquid. The lowest sedimentation manifested by the smallest mass increase in time was noted for sample M9. This sample is built of particles of the smallest diameters so their falling can be more uniform. Moreover the use of NP5 emulsifier during precipitation (irrespective of the direction of reagents introduction) influences the hydrodynamic interactions in the systems studied.



(a) (b)

Fig. 7. Sedimentation profiles (a) and wettability with water (b) of ZnO-SiO_2 samples precipitated on introducing zinc sulphate into E1 emulsion

On the basis of the wettability profiles shown in Fig. 7b the samples tendency to absorb water (in other words their hydrophobic-hydrophilic properties) was characterised. The greatest water absorption ability or greatest affinity to water was observed for sample M10, which testifies to a high free energy of this composite. The smallest mass increase in time was detected for M8, whose surface shows the weakest interaction with water and hence poor water absorption. This behaviour of sample M8 can most probably be attributed by adsorption of NP3 surfactant on the particles of ZnO-SiO_2 leading to changes in the free energy of this composite.

Table 3 presents the properties of $ZnO-SiO_2$ composites obtained, including bulk density and percent contributions of the two oxide components in the appropriate sample.

Table 3. Chemical compositions and bulk densities of $ZnO-SiO_2$ oxide composites

Sample	Chemical composition of $ZnO-SiO_2$ composites (%)			Bulk density (g/dm^3)
	ZnO	SiO_2	H_2O	
M1	25.2	52.8	22.0	25
M2	27.0	54.5	18.5	111
M3	24.8	53.8	21.4	134
M4	26.2	49.5	24.3	112
M5	28.5	51.0	20.5	91
M6	23.5	51.5	25.0	140
M7	24.0	51.4	24.6	149
M8	21.3	57.5	21.2	190
M9	27.8	55.9	16.3	122
M10	26.9	52.2	20.9	109

The greatest content of ZnO in the composites obtained is 28.5% in sample M5 which also shows the lowest bulk density of 91 g/dm^3. The greatest content of SiO_2 reaching 57.5% is determined for sample M8 showing the highest bulk density of 190 g/dm^3.

In $ZnO-SiO_2$ oxide composites obtained from 5% water solutions of zinc chloride and sodium silicate, the greatest content of zinc oxide was 35.0 – 37.3%, while the lowest 28.2 – 28.9%. The greatest percent contribution of silica in the samples precipitated from water solutions was 56.7 – 58.8%, while the lowest was 49.0 – 49.5% (Laurentowska 2010). These data indicate that the percent contribution of particular oxides depends first of all on the concentration of substrates and not on the environment of the reaction.

Table 4 presents the colorimetric data on the $ZnO-SiO_2$ precipitated from the emulsion systems.

Table 4 presents colorimetric properties of $ZnO-SiO_2$ samples ordered according to the type of emulsifier used in the process of precipitation. The reference standard was the $ZnO-SiO_2$ composite obtained upon introduction of a 5% solution of sodium silicate to a 5% solution of zinc sulphate at 20°C. The lightness of all samples, L* takes similar values for all samples. The highest L* (94.32) was observed for M6, which also showed a greatest contribution of yellow, of 4.09. The lowest lightness L* of 92.22 was found for sample M1. The contribution of red varied from 0.04 (sample M8) to 0.42 (sample M9).

Table 4. Colorimetric characterisation of ZnO-SiO$_2$ oxide composites precipitated from the emulsion systems

Sample	Colorimetric properties					
	L*	a*	b*	C*	h*	dE*
M0	93.83	0.26	2.75	2.76	84.53	-
M1	92.22	0.31	2.71	2.73	83.53	1.61
M2	92.76	0.26	2.96	2.97	84.99	1.09
M3	93.08	0.25	2.96	3.03	85.20	0.78
M4	93.96	0.34	3.35	3.36	84.13	0.53
M5	92.58	0.25	2.83	2.84	84.86	1.25
M6	94.32	0.21	4.09	4.10	87.12	1.32
M7	94.28	0.36	3.34	3.36	83.82	0.66
M8	93.43	0.04	3.03	3.03	89.23	0.50
M9	93.42	0.42	3.36	3.39	82.93	0.73
M10	92.39	0.17	2.63	2.63	86.21	1.44

4. Conclusions

The performed reactions of synthesis of ZnO-SiO$_2$ composites from emulsion system gave products of particles whose diameters were mainly in the micrometric range. The particle size analysis by NIBS method showed that the sample of the smallest particles (220 – 342 nm) was obtained by introducing zinc sulphate into E1 emulsion with addition of emulsifier NP5, which proves a beneficial effect of NP5 on dispersion and morphology of the composite. According to the results of the particle size analysis by laser diffraction method, the direction of substrates introduction significantly affects the process of precipitation. The SEM images confirmed the presence of particles of micrometric sizes showing a tendency to formation of agglomerates and aggregates. The hydrophobic or hydrophilic properties of the products obtained were evaluated on the basis of profiles of wettability with water. Differences in the hydrophobic-hydrophilic properties of the products were attributed mainly by microstructural properties and partial adsorption of surfactants on the particle surface. The rates of sedimentation obtained from the sedimentation profiles permitted indirect characterisation of hydrodynamic interactions in the systems studied. Colorimetric analysis provided the information on the colours of the oxide composites studied and in particular confirmed the suitability of using ZnO-SiO$_2$ as a white pigment of high lightness.

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References

CANNAS C., CASU M., LAI A., MUSINO A., PICCALUGA G., 1999, *XRD, TEM and ^{29}Si MAS NMR study of sol-gel ZnO-SiO$_2$ nanocomposites*, J. Mater. Chem., 9, 1765–1769.

CHAKRABARTI S., GANGULI D., CHAUDHURI S., 2004, *Excitonic and defect related transitions in ZnO-SiO$_2$ nanocomposites synthesized by sol-gel technique*, Phys. Status Solidi, 201, 2134-2142.

FOTOPOULOS A. P., TRIANTAFYLLIDIS K. S., 2007, *Ethylene epoxidation on Ag catalyst supported on non-porous, microporous and mesoporous silicates*, Catal. Today, 127, 148–156.

FU Z., YANG B., LI L., DONG W., JIA C., WU W., 2003, *An intense ultraviolet photoluminescence in sol-gel ZnO-SiO$_2$ nanocomposites*, J. Phys. Condens. Mat., 15, 2867–2873.

GANGULI D., CHATTERJEE M., 1997, *Ceramic Powder Preparation: A Handbook*, Kluwer, Boston.

JESIONOWSKI T., 2009, *Preparation of spherical silica in emulsion systems using the co-precipitation technique*, Mater. Chem. Phys., 113, 839–849.

KALINKIN A. M., KALINKINA E. V., ZALKIND O. A., 2009, *Mechanosorption of carbon dioxide by Ca- and Mg-containing silicates and alumosilicates sorption of CO$_2$ and structure-related chemical changes*, Colloid J., 71, 185-192.

KRYSZTAFKIEWICZ A., LIPSKA L. K., CIESIELCZYK F., JESIONOWSKI T., 2004, *Amorphous magnesium silicate – synthesis, physicochemical properties and surface morphology*, Adv. Powder Technol., 15, 549–565.

LAURENTOWSKA A., CIESIELCZYK F., JÓŹWIAK K., JESIONOWSKI T., 2010, *Syntetyczne kompozyty tlenkowe typu ZnO-SiO$_2$ o dużym stopniu zdyspergowania*, Przem. Chem., 89, 1351–1356.

LEE S. G., JANG Y. S., PARK S. S., KANG B. S., MOON B. Y., PARK H. C., 2006, *Synthesis of fine sodium-free silica powder from sodium silicate using w/o emulsion*, Mater. Chem. Phys., 100, 503-506.

MICHALSKA I., KRYSZTAFKIEWICZ A., BOGACKI M. B., JESIONOWSKI T., 2003, *Preparation and characterisation of precipitated zinc silicates*, J. Chem. Technol. Biot., 78, 452-460.

MIDMORE B. R., 2001, *Interaction between colloidal silica and a nonionic surfactant hexagonal liquid crystalline phase*, Colloids Surf. A, 182, 83–92.

MO C. M., LI Y. H., LIU Y. S., ZHANG Y., ZHANG L. D., 1998, *Enhancement effect of photoluminescence in assemblies of nano-ZnO particles/silica aerogels*, J. Appl. Phys., 83, 4389–4391.

ROBINS M. M., WATSON A. D., WILDE P. J., 2002, *Emulsions – creaming and rheology*, Curr. Opin. Coll. Interface Sci., 7, 419–425.

SOMASUNDARAN P., MEHTA S. C., PUROHIT P., 2006, *Silicone emulsion*, Adv. Colloid Interface Sci., 128–130, 103–109.

SÓJKA-LEDAKOWICZ J., OLCZYK J., WALAWSKA A., LAURENTOWSKA A., KOŁODZIEJCZAK-RADZIMSKA A., JESIONOWSKI T., 2010, *Modyfikacja wyrobów włókienniczych przy wykorzystaniu tlenku cynku o cząstkach nanometrycznych oraz kompozytu tlenkowego ZnO-SiO$_2$*, Przem. Chem., 89, 1648–1652.

SUN Q., VRIELING E. G., VAN SANTEN R. A., SOMMERDIJK N. A. J. M., 2004, *Bioinspired synthesis of mesoporous silicas*, Curr. Opin. Solid St. M., 8, 111–120.

YANG Y., ZHUANG Y., HE Y., BAI B., WANG X., 2010, *Fine tuning of the dimensionality of zinc silicate nanostructures and their application as highly efficient absorbents for toxic metal ions*, Nano Res., 3, 581–593.

YAO B. D., SHI H. Z., BI H. J., ZHANG L. D., 2000, *Optical properties of ZnO loaded in mesoporous silica*, J. Phys.: Condens. Matter, 12, 6265–6270.

YING J. Y., MEHNERT C. P., WONG M. S., 1999, *Synthesis and applications of supramolecular-templated mesoporous materials*, Angew. Chem. Int. Edit., 38, 56–77.

ZHAO S., JI Z., YANG Y., HUO D., LV Y., 2007, *Nano-ZnO embedded SiO$_2$ glass with intense ultraviolet emission*, Mater. Lett., 61, 2547–2550.