Silica Nanofillers – Preparation and Characterization

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Summary: Studies were conducted on formation of monodisperse silicas from sodium metasilicate and hydrochloric acid solutions in emulsion medium. Non-ionic surfactants were used as emulsifiers. Physicochemical parameters of the precipitated silicas were determined, including particle size, polydispersity, structure and shape of particles. Moreover, specific surface area (BET) and porosity were characterized. Silica of optimum physicochemical parameters, i.e. of the ideally spherical particle shape, monodisperse character was obtained using a homogenization technique during precipitation and Rokafenol N-3/N-6 surfactant mixture as emulsifiers.

Introduction

Nanosubstrate-based composite materials are required by technologists in multiple branches of contemporary techniques. They can secure, first of all, stability of products, their high mechanical strength as well as resistance to chemical and weathering.[1] Highly dispersed monodisperse silicas could be included within this group of compounds. In the traditional techniques, silicas are precipitated from aqueous solutions of lithium group silicates using acidic agents (acids or acid anhydrides).[2] Other methods involve silica formation in the gas phase (the so called flame hydrolysis technique)[3] or employing the technique of Stöber, involving the use of alkoxysilanes.[4] New trends in silica precipitation technology involve the use of emulsions to control particle shape of dispersed silicas (their appropriate shape, uniform character and size).[5-6] Moreover, an organic medium and type of emulsifiers significantly affect formation of silicas in hydrophilic/hydrophobic systems.[7]

Precipitation of nanometric monodisperse silicas was performed in emulsion system in order to obtain materials of a broad application potential, to be used mainly as fillers of polymers and paints. Moreover, the silicas exhibited a strong adsorption capacity and, therefore, could be used as chemically stable carriers and adsorbents of organic compounds, such as organic pigments.

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Experimental

The silicas were precipitated by mixing two emulsions, the first of which contained solution of sodium metasilicate while the other contained hydrochloric acid. Cyclohexane formed the organic phase. Non-ionic surfactants (polydisperse mono(4-nonylphenyl)-polyoxyethylene glycol ethers) of various oxyethylenation extent (Rokafenol N-3, N-5, N-6, N-8, N-9) were added as emulsifiers. Precipitation was conducted in a reactor employing three distinct ways of dispersion of the reactive mix: top mixing, homogenization or ultrasounds. The precipitated silica suspension underwent destabilization. Cyclohexane was distilled off while the silica precipitate was filtered and, in parallel, the surfactants were washed off with acetone. Acetone was distilled off and the silica was dried at 105°C.

Moreover, basic physicochemical parameters of the obtained silicas were estimated. Particle shape and morphology of the formed silicas dispersion were examined using scanning electron microscope (SEM). The observations were conducted using the Philips SEM 515 scanning electron microscope. Studies on zeta potential, polydispersity and particle size distributions were performed in ZetaPlus apparatus (Brookhaven Instruments Co.) using the techniques of electrophoretic (ELS) and dynamic (DLS) light scattering. Specific surface areas (BET) of silica powders were determined by N_2/77 K adsorption (BET method) using ASAP 2010 instrument (Micrometrics Instrument Co.). Volume and size of pores of precipitated materials were also examined.

Results and Discussion

Results of testing principal physicochemical parameters of silicas obtained in emulsions using various techniques of dispersion are presented in Table 1.

On the other hand, values of zeta potential, polydispersity, mean diameter of particles, specific surface area (BET) and pores characteristics of the silicas are listed in Table 2.

The N-3/N-8 emulsifier system induced an evident decrease in bulk density of the precipitated silica (to values below 80 g/dm^3). Moreover, the silicas precipitated in presence of Rokafenol N-3/N-8 mixture or Rokafenol N-9 exhibited the highest capacity to absorb water (450 and 600 cm^3/100g, respectively) and the highest capacity to absorb paraffin oil (800 and 900 cm^3/100g, respectively).

Table 1. Principal physicochemical parameters of silicas.

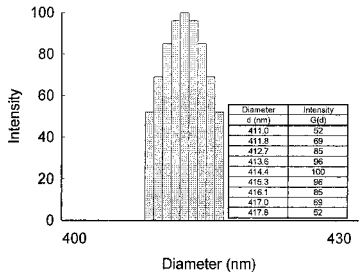
Sample No.	Emulsifiers contents (g)		Bulk density (g/dm^3)	Capacity to absorb: (cm^3/g)		
	E1	E2		water	paraffin oil	dibutyl phthalate
top mixing						
1	N-3 1.5/N-6 1.0	N-3 0.45/N-6 0.3	157	350	400	300
homogenization						
2	N-3 3.75	N-3 2.25	110	350	700	500
3	N-3 0.75/N-5 0.5	N-3 0.45/N-5 0.3	151	200	600	400
4	N-3 1.5/N-6 1.0	N-3 0.45/N-6 0.3	112	350	750	500
5	N-3 0.75/N-8 0.5	N-3 0.45/N-8 0.3	73	450	800	550
6	N-3 0.75/N-9 0.5	N-3 0.45/N-9 0.3	132	300	600	350
7	N-5 1.25	N-5 0.75	133	150	750	550
8	N-6 1.25	N-6 0.75	186	150	450	250
9	N-8 1.25	N-8 0.75	102	450	800	600
10	N-9 1.25	N-9 0.75	97	600	900	750
ultrasonic wave						
11	N-3 1.5/N-6 1.0	N-3 0.45/N-6 0.3	151	250	450	300

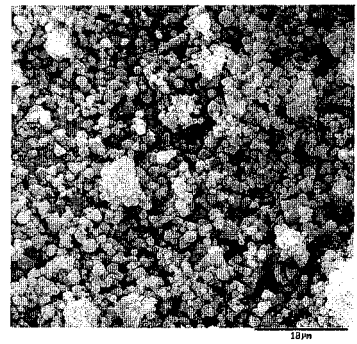
Table 2. Zeta potential, polydispersity, mean particle diameter and adsorption capacity of silicas.

Sample No.	Zeta potential (mV)	Polydispersity	Mean diameter (nm)	BET (m^2/g)	Volume of pores* (cm^3/g)	Mean diameter of pores (Å)
1	-19.56	0.005	414.4	-	-	-
2	-14.65	0.102	661.2	281	0.34	56.61
3	-13.69	0.005	559.1	240	0.28	68.15
4	-46.65	0.005	329.2	165	0.55	94.57
5	-20.66	0.013	736.8	232	0.17	81.47
6	-19.96	0.114	1088.8	86	0.31	52.83
7	-18.67	0.066	696.8	233	0.11	41.87
8	-28.49	0.005	818.5	103	0.77	118.27
9	-21.30	0.131	866.7	260	0.66	108.10
10	-28.82	0.170	623.4	244	0.37	52.33
11	-21.61	0.192	721.4	-	-	-

* pore volume 17 to 3,000 Å

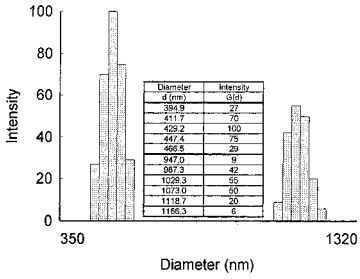
Zeta potential of the obtained silicas showed negative charge and ranged within the limits of (–13,69)-(–46,65) mV. The negative surface charge was typical for precipitated silicas while the applied emulsifiers showed an approximately neutral character or an insignificant charge. Therefore, the studied silicas did not evidently change their surface charge.

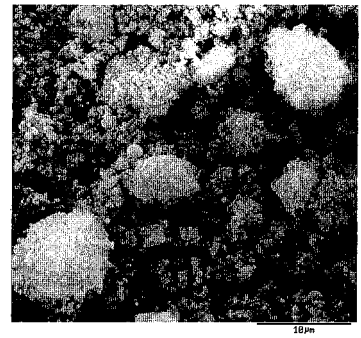




a) b)

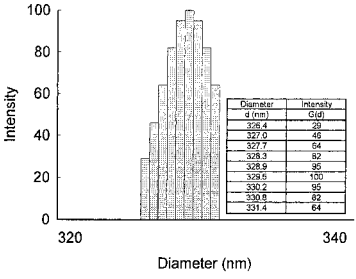
Figure 1. Multimodal particle size distribution (a) and SEM (b) of silica (sample 1).

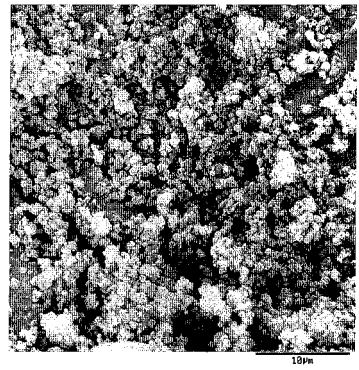




a) b)

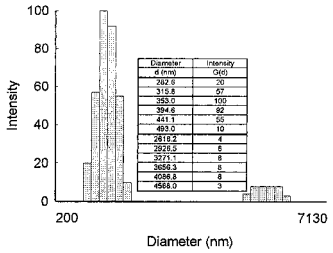
Figure 2. Multimodal particle size distribution (a) and SEM (b) of silica (sample 2).

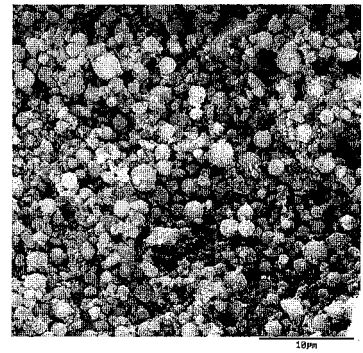




a) b)

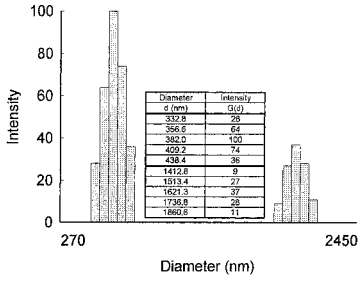
Figure 3. Multimodal particle size distribution (a) and SEM (b) of silica (sample 4).

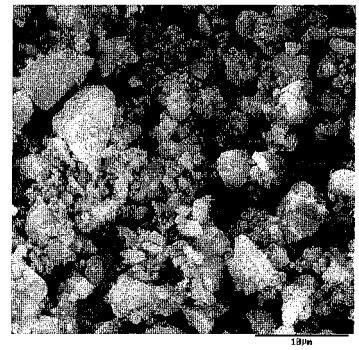




a) b)

Figure 4. Multimodal particle size distribution (a) and SEM (b) of silica (sample 7).





a) b)

Figure 5. Multimodal particle size distribution (a) and SEM (b) of silica (sample 11).

The polydispersity value proves that the formed dispersion are homogenous. The value decreases with increasingly ordered arrangement of silica particles (Table 2, Figs. 1-5). In such cases, silica particles tend to exhibit a single range of particle diameters. Definitely the most uniform was the silica (sample 4) obtained using Rokafenol N-3/N-6 mixture, and the least uniform was the silica formed using ultrasonic waves in the same emulsifier system (sample 11). Moreover, the obtained silicas (Figs. 1b-5b) extensively developed outer surface and specific surface areas for most samples exceeded 200 m^2/g (Table 2).

Particle size distributions and SEM electron micrographs of selected precipitated silicas are presented in Figs. 1-5.

Particle size distributions and SEM micrographs of silicas obtained Rokafenol N-3/N-6 emulsifiers employing various dispersion techniques are shown in Figs.1, 3 and 5. The highest dispersion was manifested by the silica obtained using a homogenizer. Its mean particle diameter was 329.2 nm, and its particle size scatter (Fig. 3a) covered the range of 326.4-331.4 nm (maximum intensity of 100 corresponded to the particle diameter of 329.5 nm). Moreover, the silica showed an almost ideally spherical shape of particles (Fig 3b) and manifested low tendency to form agglomerates, very characteristic for the precipitated silicas. On the other hand, the silica obtained using ultrasonic waves manifested the typical agglomerated particle structure. The particle size distribution (Fig.5a) demonstrated the two typical bands: the first within the range of 332.8-438.4 nm (maximum intensity of 100 corresponded to the diameter of 382.0 nm) and the other of lower intensity within the range of 1,412.8-1,860.6 nm. Mean diameter of the silica particles was 721.4 nm. Also the silicas obtained using other emulsifiers (e.g. Rokafenol N-3, Fig.2, or Rokafenol N-5, Fig. 4) exhibited a highly uniform character and their particles showed evidently spherical shape.

Conclusion

Application of Rokafenol N-3/N-6 emulsifier mixture and of a homogenizer to form a silica permits to obtain uniform spherical silica particles of the approximate diameter of 300 nm. Application of Rokafenol N-3 or N-5 alone also allows to obtain silicas of similar properties. On the other hand, Rokafenols of higher oxyethylenation extent (less hydrophobic ones) exert a completely distinct effect on type and properties of the formed silica dispersions.

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