Korytkova E. N., Chepik L.F., Mashchenko T.S., Pivovarova L.N., Gusarov V.V. Crystallization of ultra-disperse silica in the hydrothermal conditions

I.V. Grebenshchikov's Institute of Silicate Chemistry of RAS, Saint-Petersburg

key words: [silicagel, aerosil, crystallization, dehydration, nonomaterials.

The important factor in the silica geochemistry is its interaction with water, whose intensity depends on many parameters, i.e. temperature, pressure, nature and state of water, content of impurities in it, which catalyzes a dissolution, precipitation and crystallization of silica.

Despite numerous experimental data on the system SiO_2-H_2O, the chemical features of silica, which characterize its interaction with water and aqueous fluids, are not properly understood. The investigation of crystallization of ultra-disperse silica related to the problem of the synthesis of silica-oxide nanomaterials, which are useful for inorganic material science and technique, is very actual now.

Following to these problems, we undertake an investigation of an influence of a pre-history of initial substances and parameters of hydrothermal treatment on phase state and size of particles of synthesized silica. Amorphous silica materials, produced by different methods and differing from each other by water content and microstructural features, were used as precursors.

The initial samples were treated by chemically different hydrothermal solutions (H_2O and aqueous solutions of NaF and NaOH) at temperatures 250-500^{O}C and pressure up to 100 MPa.

Physico-chemical investigation of the products of the hydrothermal treatment of the precursors at given temperatures and pressures showed a gradual dehydration, compaction, and structurization of the initial amorphous compounds with the formation of crystalline SiO_2 varieties: opal-like silica of the different degree of ordering (amorphous A-opal, cristobalite -tridymite CT-opal, cristobalite C-opal), α- cristobalite, keatite, quartz. The character of these modifications, their rate, and size of the particles of the crystallizing phases are not equal for the studied precursors and are defined by both their pre-history and parameters of the hydrothermal treatment, i.e. a composition of the reaction environment, temperature, pressure, run duration (see Table).

The largest differences between the samples with different pre-history are observed at their hydrothermal treatment by water. According to stability, the following sequence is established: silicagels<aerosils<xerogels. For the first and in some extend to the second compounds, the gradual transformation at low temperatures (25-300^{O}C) to opal-like silica followed by α-cristobalite at more durable treatment and/or higher temperatures is identified. Xerogels are exclusively stable in water and transform to α-cristobalite just at high temperature (480-500^{O}C).

Table 1.

SiO_2 varieties	H_2O content, wt. %;	S_{sp}, m^2/	Size of particles, nm
Silicagel			
I	8.3	90	10-12
II	8.4	230-250	4-6
Xerogel	11.6-	-	15-25
Aerosil	13.5		
I		300	8-12
II	14	380	4-8
	20		

Addition into the reaction media of mineralizators (NaF and NaOH) appreciably activates the process of crystallization of the initial phases, resulting in direct transformation to cristobalite in NaF solutions and quartz, in NaOH solutions.

Variations of the phase composition of the samples at their hydrothermal treatment are correlated with a growth of their particles (see Table). The optimal hydrothermal treatment in order to produce ultra-disperse crystalline silica with size of particles of 25-30 nm is the treatment of silicagels and aerosils by water at temperature 250-300^{O}C and pressure 100 MPa.

Table 2. Conditions of the hydrothermal treatment of SiO_2 varieties and characteristics of the synthesized products.

Varieties	Conditions of the hydrothermal treatment			Characteristics of the products			
	T,°C	P, MPa	Time, h	Phase	H_2O content, wt%.	Ssp, m2/g	Size of particles, nm
	SiO2						
I	300	70-100	24-48	A-opal	~3	30	20-30
	300	70	144-168	CT-opal	2,5-2,2	-	25-30
	400	100	48-120	CT-opal	2,2-1,9	-	30-35
	480	100	48	α-cristobalite, traces of quartz	1,4	-	40-50
II	250	100	288	A-opal	4,64	70	15-20
	300	100	144-168	C-opal	4,56-4,16	-	20-35
	350	90	120	C-opal	3,92	-	25-35
	400	90	48	α-cristobalite, traces of keatite	2,2	-	25-40
	Xerogel						
	300-400	70-100	120-144	α-cristobalite, traces of quartz	1,8-1,7	-	45-50
	450	70	24-168	A-opal	5-3,9	6	100-200

Varieties	Conditions of the hydrothermal treatment			Characteristics of the products			
	T,°C	P, MPa	Time, h	Phase	H_2O content, wt%.	Ssp, m2/g	Size of particles, nm
	480-500	70	24-48	A-opal	2,3-2,0	-	200-250
			48	α-cristobalite, traces of cristobalite	1,26	2	300-500
	Aerosil						
I	300-400	70-100	24-120	A-opal	5,5-5,2	80	25-35
	400	100	144	CT-opal	~5	-	30-40
	450-480	70-100	24-48	A-opal	3,5-3,3	-	40-50
II	250	100	288	CT-opal	7,9	-	15-20
	300	100	24-48	A-opal	7,5-7,1	-	20-25
	300	100	144	CT-opal	6,01	-	25-30
	300	100	168	C-opal	4,04	-	25-35
	350-400	100	120	α-cristobalite	2,98-2,55	-	35-40

The study is supported by the Russian Foundation for Basic Research (project no. 00-03-32277).