Gas-Phase Synthesis and Structure of Needle-Shaped Silica Nanoparticles

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Silica received by combustion of steam of silicon-containing substances ($SiCl_4$, CH_3SiCl_4) in hydrogen-air flame is an important product used as a thickener for liquid media, filler of polymers, abrasive material for chemical-mechanical polishing of monocrystals of electronic equipment, drug absorption of medical supplies etc.

Currently well-known methods of fumed silica synthesis allow receiving an aerogel-like product with a specific surface area of 50-400 $m^2 \cdot g^{-1}$, in which the fractal structure of the oxide material is formed from spherical nanoparticles.

Investigating the dependence of aerogel structure and the size of its primary particles on silica synthesis conditions (the components ratio in the reaction mixture, its homogeneity and outflow velocity from nozzle burner, flame temperature, and its turbulence), we concluded that turbulence and flame temperature are the main factors, which determine a morphological structure of the product and the degree of primary particles dispersion.

At the first stage of the fumed synthesis the origin and growth of proto-particles were carried out by the fleeting heterolytic reactions of siloxane bonds formation at condensation, for example, chlorine siloxane $SiCl_{3-n}(OH)_{n+1}$ (n = 1-3) and further condensation of hydroxide oxide oligomers $–[Si(OH)_2 – O – Si(OH)_2]_m–Si(OH)Cl$ (m = 5-10).

It should be noted, that protoparticles and primary silica particles formed at flame temperature of 1400-1650 K have too large surface energy, it causes a decrease of melting point of the oxide material on 250-400 K. Therefore they are in a molten state at those temperatures.

High turbulence of flame leads to rapid protoparticles coalescence and formation of SiO_2 primary particles. The primary particle of 6-14 nm in size has at those conditions a higher viscosity compared to protoparticles, therefore their adhesion occurs only at the collision.

The calculation of characteristic time of particles coalescence in the flame has shown that it is the same at the synthesis of silica with different specific surface area and is about 10^{-3} s, and turbulent diffusion coefficient is in the range of 10^{-3}-10^{-2} $m^2 \cdot s^{-1}$ that is in 2-3 times higher than the molecular diffusion coefficient.

In turbulent flame with Reynolds number (Re) less than 15000 small-scale pulsations provide a formation of aerogel-like structures formed mainly from linear clusters (fractals). The pulsations enhance diffusion processes in the flames at the large turbulence ($Re \geq 40000$), which leads to an increase in the degree of volume concentration of primary particles and the formation of secondary gel-like structures.

Decisive influence of turbulence of reaction medium on the morphology of the secondary structures in a flame caused to seek ways of volume flame filling by ordered "tornado" type vortices, with the help of which the formation of SiO_2 two-dimensional nanoparticles would occur.

To ensure the necessary turbulent regime the flaming reactor diameter at the widest place was chosen such that the Reynolds number for this zone was 44000-50000, and the energy of the heat flux in the core of the flame was 1400-1700 $kW \cdot m^{-3}$. The temperature in the core of the flame reaches 2773 K at this energy, and the local flow velocity is accelerated almost to the sound speed. However, outside the core of the flame on the distance from the axis equal to two diameters of the burner nozzle, the flow reaction velocity decreases in 4-5 times, and the temperature of the flame reduces to 1400-1600 K due to leak of air. Significant gradient of speed change and temperature of the cross section of the flame results in the formation on the surface of its core a cascade of toroid-like vortices that break down into smaller cylindrical ones with virtually no energy loss. The process of such successive bifurcations stops when the forces of molecular viscosity in media are beginning to affect the structure of small-scale vortices and their energy is converted into heat.

Thus, smaller "tornado" vortices formed from toroid-like ones are oriented in the direction of flow, straightened, and involve in their volume SiO_2 primary particles and submitted to the zone of lower temperatures and speeds. "Tornado" vortices are enough stable and the time of their existence is sufficient for the concentration of primary particles along their axes and forming of monolithic needles as a result of sintering.

The needles formed in the flame have a diameter of 10-15 nm and their length is 1-3 microns. Small clusters of vortices are concentrated at the ends of the needles, namely in places where the entering of spherical particles into a vortices volume occurs. Synchronous process of vortices crushing and the formation in their bulk of the needle-shaped particles leads to the formation of the original product as a two-dimensional grid with rhombic windows.

The specific surface area of fumed product is 370-420 $m^2 \cdot g^{-1}$, and the contents of needle-shaped nanoparticles is 40-80 %.

The study of atomic structure of the needle-shaped SiO_2 particles using TEM and IR-spectroscopy allowed to find out that short openly branched chain clusters of 0.6-2.4 nm in length are the structural motifs of silica. Two SiO_4 tetrahedrons, with tops directed alternately down and up and connected to each other via a common oxygen atom, are in a one repetitive fragment of chain cluster. Intertetrahedral SiOSi angle along the chain is close to 180°. Due to the short length and spatial off-orientation of chain clusters needle-shaped particles are amorphous.