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The influence of synthesis conditions on the packing of the spherical particles of silica in a supramolecular structure

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The mechanism of silica sphere formation according to the principle of hierarchical aggregation is demonstrated.

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The problems of silica permolecular matrix synthesis arouse recently a certain interest. It is connected, on the hand, with the fact that such structures can be used in the synthesis of noble opal analogues, on the other hand they are the most convenient examples for modeling the processes of permolecular crystallization (since they are known and easy to generate). The problems of study of permolecular structures generation arouse a certain interest, since recently they find a more broad application in different spheres of chemistry, physics, including their application as matrices for nanocomposites materials that make more strict and specific demands both to the sizes and the form of the particles. The available data on the mechanism of formation of permolecular structures and their components is insufficient which connected with certain difficulties of their analysis.

In the present work, on the basis of experimental data, we considered the influence of different physical and chemical conditions of permolecular structures synthesis on the sizes and morphology of resulting silica particles, and also the features of their precipitation into well-ordered structure. On the basis of the obtained results we suggested the model of spherical particle structure.

In this connection we conducted series of experiments regarding silica spheres synthesis under different conditions. We derived monodisperse silica spheres in size range 235-765 nm by the Stober-Fink method [1] that we improved [2, 3] which let us greatly extend the size range of derived monodisperse spheres. The first series of experiments was conducted under 18 ºC, all the preparation of tetraethyl ortosilicate came to its preliminary purification through distillation (166-170ºC). The second series was conducted like the first one but under 8ºC. The third series was conducted using tetraethyl ortosilicate processed with combined method [2], in concentration interval (0.04÷4.75) mole/dm^3 for NH_3 and (1.5÷31.8) mole/dm^3 for H_2O, with the constant concentration of tetraethyl ortosilicate of 0.28 mole/dm^3 (Fig. 1). Just in this series we were able to obtain monodisperse silica spheres in the wide ratio of the system components: (0.2÷0.8) mole/dm^3 for NH_3 and (2.75÷6.4) mole/dm^3 for H_2O and hence in the wide size range of 235-765 nm.

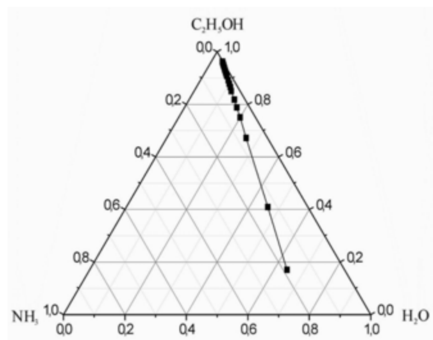

Fig 1. The synthesis area of monodisperse silica spheres at C(TEOS) = 0.280 mole/dm^3

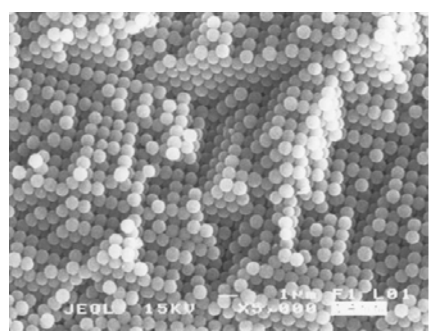

Fig. 2. The fragment of SiO_2 matrix resulting from sedimental precipitation of derived monodisperse silica spheres.

The absolute sizes of the particles were determined by scanning electron microscope JSM-6400, however at H_2O and NH_3 concentration below 0.190 and 2.50 mole/l respectively stable sols formed; for measuring their relative sizes the method of diffusing was used.

As a result we determined relations of derived sphere sizes from NH_3 and H_2O concentration in the system. The attention is drawn to the oscillating character of this relation, which is revealed irrespective of formation conditions.

Due to wide application of nanostructure materials and also to the lack of the unified hypothesis of ultradispersed material formation, the study of structure and formation mechanism of monodisperse silica spheres (MSS), which are the most appropriate example of well-ordered structures, arouses a certain interest. In the present time the following opinion is widely spread that regular structures were formed as a kind of permolecular crystallization; otherwise the change of phase of the first type in unordered suspension of interacting colloidal particles [4]; according to this, spheres are heterogeneous and consisted of globules which sizes are about 10 nm. The noble opal structure experimental data, received by transmission electron microscope methods, also speaks well of this hypothesis. However in the present time the issue of sphere inner nature and permolecular crystallization mechanism remains still open resting to a greater extent on empirical level.

On the basis of available written and experimental data we suggested the following permolecular structure formation mechanism. According to the concept of cluster self-organization of matter at nanolevel [5] ultradispersed particles of the size, typical for opal balls, are composed of much smaller particles than mentioned above 10 nm. Accordingly all the compact amorphous formations can be formed as a result of their hierarchical aggregation. In the first case, when clusters are located around the central one, cluster aggregation of the 1st hierarchical level is formed. In the same way the cluster of the 2nd level is formed, etc. (Fig. 3).

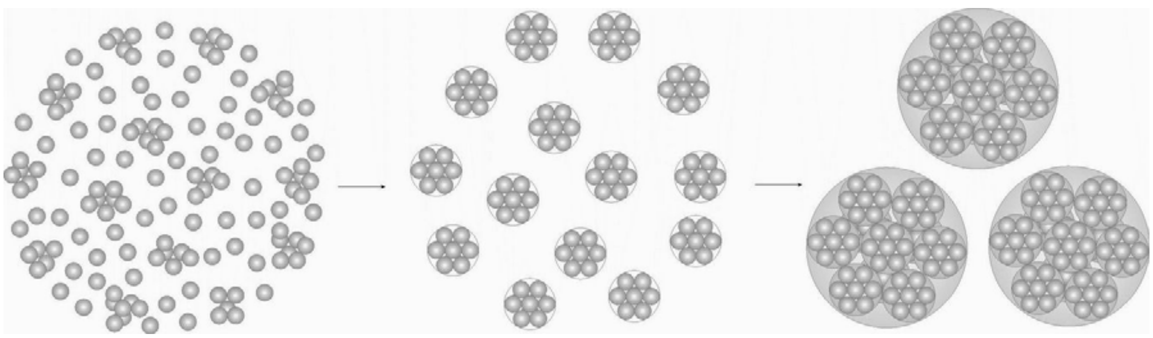

Fig. 3. The mechanism of silica spheres formation according to the principle of hierarchical aggregation.

Since derived opal matrices lack crystallinity it is reasonable that the diameter of initial cluster is less than 8δ (2.4 nm). As a result the observed size range is attained for MSS already at the 6th hierarchical level.

Thus, the discovered oscillating character of relation of sphere diameter from ammonia and water concentrations in the system, together with the discreteness of derived sphere sizes, let us interprete their formation mechanism as the process of hierarchical self-organization of matter at nanolevel.

As a result of the conducted experiments on the synthesis and precipitation of monodisperse spherical silica particles (100-800 nm) in different conditions we have determined a direct relationship between the packing type of particles and pH, water concentration, ammonium ions, size and precipitation speed of the globules.

In fact, at high pH values we have spherical silica particles surrounded by a dense shell of gegenions that results in their electrostatic repulsion. As a result, during precipitating of particles on the surface of a supramolecular crystal, their position in the structure is conditioned by the repulsion of precipitating particles from the surface analogous to charged globules in the structure. It results in maximal filling of space. The situation is changed at low pH values and low sizes (less 400 nm) of particles which results in reducing their surface and the greater reduction of the concentration of gegenions, and as a consequence, of the force of their electrostatic repulsion. Forming here hydrogen bonds prevent the precipitation of the particles in the most favorable positions which results in reducing the filling ratio of the particles.

In the framework of the experiment conducted by us, the packing type of spherical particles in opal matrixes depends on the sol pH and silica sphere sizes. At pH 7.5–8.0 a primitive cubic packing of particles is realized. The increase of pH up to 8.5-9.0 results in the formation of hexagonal packing with a corresponding increase of particle sizes. At a higher pH values the closest packing is formed which is characteristic for natural noble opal.

Acknowledgement

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