EXPERIMENTAL RESEARCH OF PERMOLECULAR CRYSTALLIZATION BY THE EXAMPLE OF AMORPHOUS SILICA

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In the present time, due to increasing interest to permolecular structures, the synthesis of materials, which components have greater size than molecules, wins special attention. The best known representatives of such structural units are silica spheres. The intense research of their formation was connected above all with their application to synthesis of synthetic analogues of noble opal. A considerable attention is given, together with the study of thermodynamic and kinetic formation parameters, to practical recommendation on their synthesis.

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 18ºC; 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.

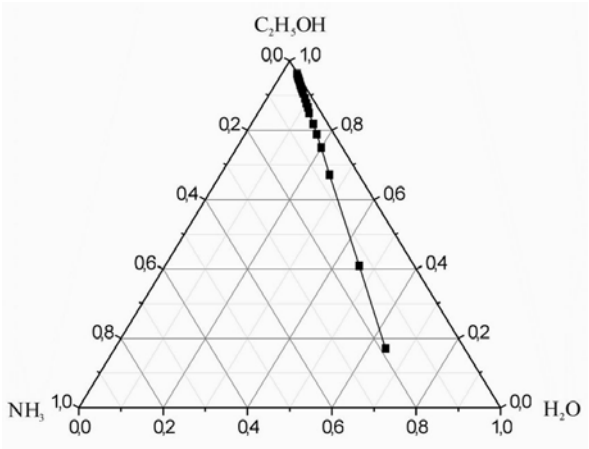

Fig. 1. The synthesis area of monodisperse silica spheres at C(TEOS) = 0.280 mole/dm^3

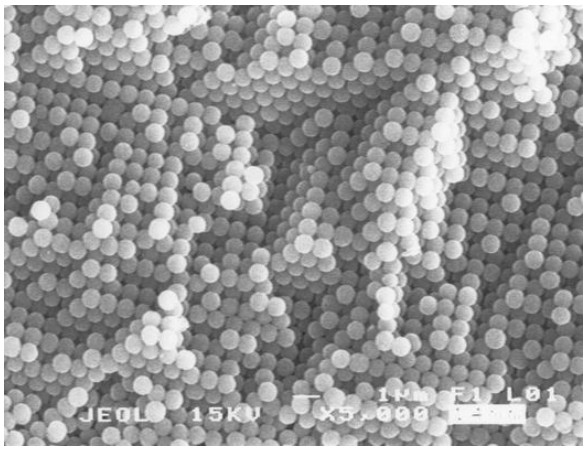

Fig. 2. The fragment of SiO_2 matrix resulting from sedimental precipitation of derived monodisperse silica spheres

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 ultradisperse 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] ultradisperse 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).

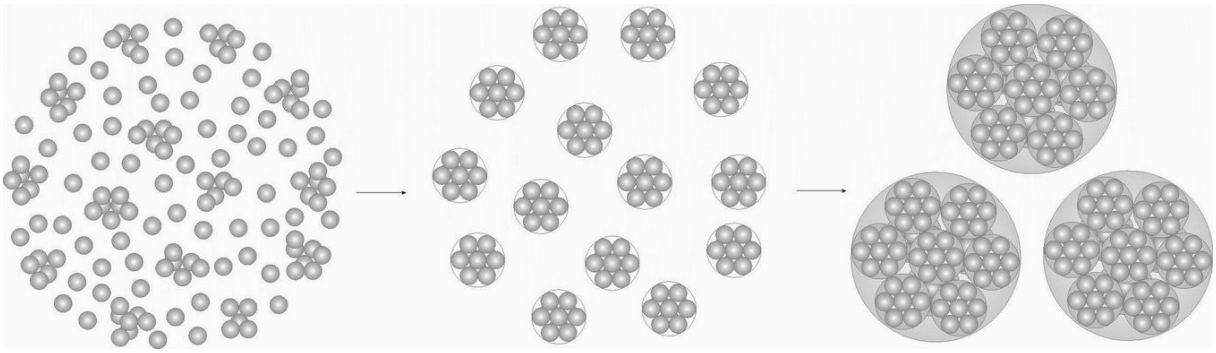

Fig. 3. The mechanism of silica spheres formation according to the principle of hierarchical aggregation

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.

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