Fumed Silica Synthesis: From Molecules, Protoparticles and Primary Particles to Aggregates and Agglomerates

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Summary: Basing on quantum chemical simulations (semi-empirical methode PM3) and vibration spectroscopy (Infrared (IR) and inelastic neutron scattering (INS)) and using other experimental data, a model of the formation of fumed silica particles is proposed, leading from initial molecules, via protoparticles and primary particles up to aggregates and agglomerates. Also, defintions of products in the flame process steps are suggested, from a chemical point of view. This process may be described as a sequence of states:
Molecules => (molecular clusters = protoparticles) => primary particles => aggregates => agglomerates

Introduction

From a chemical point of view, only a small number of atoms, involved into chemical reactions, define the nature of interactions. There are three stages of transformations from molecules to a bulk product. They are defined as: (I) molecular reactions (conversion of silicon tetrachloride to protoparticles), (II) surface cluster reactions between protoparticles and small molecules like water and hydrochloric acid (surface termination) and (III) primary particle interactions up to aggregates and agglomerates. These three stages may be named as molecular reactions, surface reactions and interparticle reaction of mechanochemical colloid nature. The relative number of atoms belonging to this system, included into chemical interaction, dramatically decreases. Therefore these three stages will be discussed separately. Fig. 1 shows a scheme of the technical process of fumed silica production, together with experimental IR-spectra along the production pathway [1]. There are a lot of publications on the amorphicity of the fumed silica structure [2,3], but only recently work has been done in that area on a quantum chemistry level, simulating the formation of amorphous silica, using silicon dioxide molecules as an initial state [4-7].

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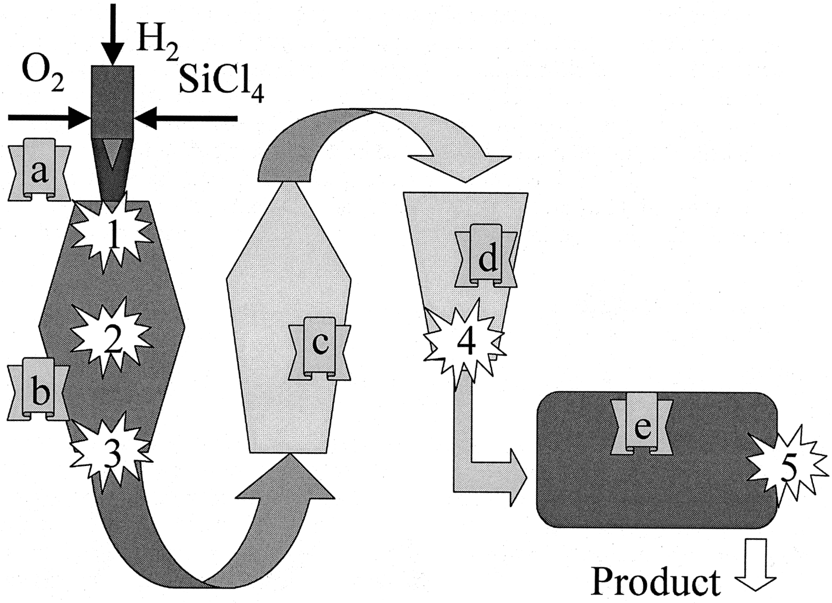

Fig.1. Fumed silica technological process (sketch) [1].

a) - burner
b) - flame tube
c) - coagulator
d) - cyclone
e) - desorber

✷ Site of silica sampling

Molecular reactions and characteristics of fumed silica protoparticles

Molecular reaction between oxygen, hydrogen and silicon tetrachloride leads to silicon dioxide formation mainly, if the reaction condition takes place under a small excess of oxygen to decrease 'oxygen vacancy' concentrations. The same type of reaction between oxygen and silicon tetrachloride is widely used in CVD processes (chemical vapour deposition) to form high purity silicon dioxide for optic fibers. Therefore, in the vapour conditions of the flame, the silicon tetrachloride will be converted to silicon dioxide molecules. At the temperature of 2500 K and atmospheric pressure, the average distance between silicon containing molecules will be about 10-11 Å. The silicon tetrachloride conversion is rather complicated due to a triplet state of oxygen and a singlet state of product after of silicon tetrachloride conversion. This part of is under extended investigation and results are to be discussed in future. Some preliminary results show how the nature and the formation of some special structures in the silica body and its surface may be explained, namely defects of the structure like oxygen vacancy. These defects have been under extended investigations for a lot of years, but only a few data about their structures and the nature of its formation is available. The present study is dedicated to further knowledge to current problems in this field.

Therefore, it is possible to assume that the silicon dioxide molecule is a first intermediate product on the way from silicon tetrachloride molecules to fumed silica particles. Data on the conditions of silica flame synthesis are rare, but the temperature in the flame should be higher than the melting point of any forms of silica and may be as high as the boiling point of silica [1]. At this high temperature, silicon tetrachloride should exist as monomolecular gas. Due to the high temperatures in the flame, the ortho-silicon acid or meta-silicon acid should not be the main product of the hydrolysis or/and oxidation of silicon tetrachloride. The silicon dioxide molecule is well known to be stable at such high temperatures or in a matrix-isolated state. Therefore, we consider silicon dioxide molecules to be the initial silicon containing substance, suitable to simulate the formation of silica particles due to its high chemical activity of one-coordinated oxygen and two-coordinated silicon atoms.

Meta-silicon acid molecules are able to react with each other to form cluster, also. Three meta-silicon acid molecules produce cyclic clusters with four-coordinated silicon atoms and two-coordinated oxygen atoms. At high temperatures this cluster may eliminate some water molecules from hydroxyl groups and generate active sites with three-coordinated silicon atom and one-coordinated oxygen atoms. These first steps are followed by a polymerization process, which leads to molecular silica clusters. We suggest calling them ‘protoparticles’. Due to the presence of coordination-unsaturated oxygen and silicon atoms, the surface of molecular silica clusters or protoparticle is highly chemical active.

Quantum chemical simulations of silica ‘protoparticles’ formation, starting from silicon dioxide molecules have been performed. One of the proposed models is shown in fig. 2. The vibration spectrum of this small cluster (27SiO2) is not able to reproduce vibration (IR and INS) spectra of bulk silica, but the spectrum from inner cluster atoms with standard coordination numbers is similar to the experimental data. The band at 400-500 cm^{-1} of O-Si-O angle deformation in the calculated IR-spectrum is not similar to the experimental one due to a high O-Si-O angle dispersion. Fumed silica protoparticles are amorphous silicon dioxide clusters containing from a few silicon atoms up to some thousands silicon atoms. The surface state of silica protoparticles defines their properties. Silica protoparticle surfaces contain very active centers, like one-coordinated oxygen atoms, bonded with silicon atom, and three-coordinated silicon atoms. But the surface concentration of three-coordinated silicon atom is less than the surface concentration of one-coordinated oxygen atoms as a result of the very high chemical activity of the three-coordinated silicon atoms, which are able to react with oxygen atoms in their viccinity, increase their coordination number at least up to four. Therefore, fumed silica protoparticles are covered by active centers like one-coordinated oxygen atoms, double bonded with silicon atoms, and the chemical reactivity of these active sites define the chemical behavior of fumed silica protoparticles.

There are two possible ways to produce nanosize particle: (I) to condense small molecules or (II) to divide a large bulk. Reactions happen in the gas phase, where the process of combining molecules takes place. It was shown recently, that using crystalline models to simulate the amorphous state of a solid is not realistic [8].

Results about the influence of small molecules on silica protoparticle formation are published elsewhere [9].

A set of fumed silica protoparticle simulations with different starting conditions and different number of silicon dioxide molecules has been investigated. The main results of these studies in fact are that, from a chemical point of view, the final structures are independent from the starting conditions. It means that in any case it results an amorphous silica, covered by the same active centers and similar distributions of bond lengths, bond angles and, the principal result, similar distributions of coordination numbers at oxygen and silicon atoms (fig. 3). These results support the modell on the amorphicity and formation of fumed silica structures.

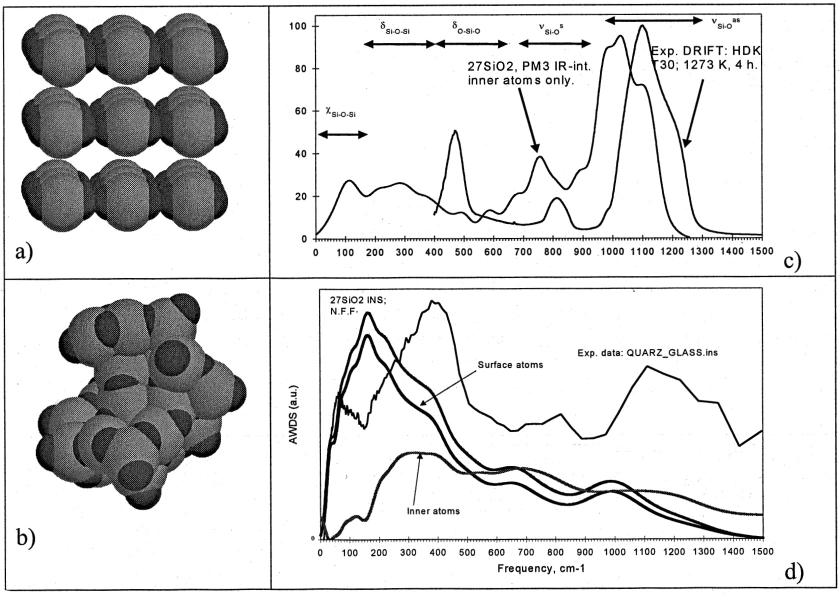

Fig.2. Protoparticle formation from 27 silicon dioxide molecules:

a) starting from a cubic structure; silicon–silicon distance 7 Å.

b) optimized silica cluster 27SiO2,

c) calculated (blue) and experimental (red) IR spectra with assignments; IR-intensity was calculated for the inner atoms of cluster 27SiO2; experimental spectrum: DRIFT, fumed silica Wacker HDK T30, heated at 1273K, 4 h, in vacuum.

d) INS spectra: blue - calculated INS spectrum for cluster 27SiO2; green - calculated INS spectrum for inner atoms of 27SiO2; black - calculated INS spectrum for surface atoms of 27SiO2; red - experimental spectrum of quartz glass.

Simulations of amorphous silica protoparticles show that the first steps of silicon dioxide molecule interactions lead to the formation of very small silica clusters. These clusters consist of several silicon atoms: from two up to five. Afterwards, these small clusters interact together to form larger cluster. As a result of the growth of the clusters the coordination number of silicon and oxygen atoms inside the cluster increase like under high pressure. This may be explained as a result of surface tension of the hydroxyl-free silica particle. The behavior of the small silica clusters during their interaction is very similar to the behavior of small drops of viscous liquids. The viscosity of these drops is approximately proportional to the drop size: the bigger drops are the more viscous they are. It is necessary to point out that the cluster surface is not as viscous as the cluster core. These results are not obtained using crystal-like starting structures for simulations of amorphous silica particles. Hydroxylation-dehydroxylation processes in the flame lead to a decrease of the heat of formation, the number of surface-active centers, a densification of the protoparticle and an equalization of the coordination number to standard values (4 and 2), see fig. 3a through 3e. But this processes also lead to an increase of the amount of silicon atoms with coordination number 5 and oxygen atoms with coordination number 3. It probably means that the fumed silica core contains silicon atoms with coordination number 5 and oxygen atoms with coordination number 3.

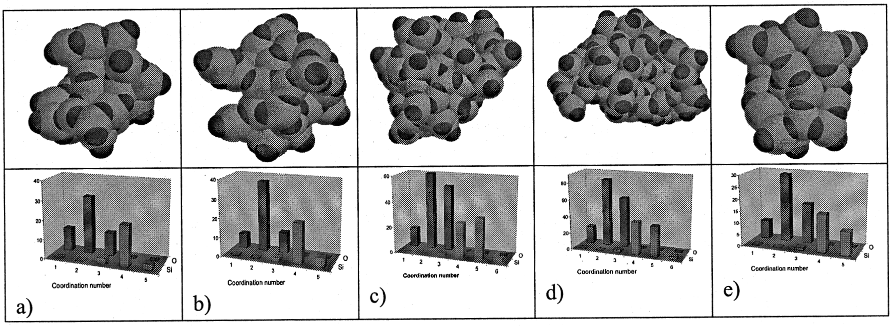

Fig.3. Coordination number distribution for silica protoparticles:
a) cluster 27SiO2, heat of formation -5412.76 kcal/mol.
b) cluster 28SiO2, heat of formation -5735.53 kcal/mol.
c) cluster 64SiO2, heat of formation -13958.87 kcal/mol.
d) cluster 3-27SiO2, heat of formation -18366.63 kcal/mol.
e) cluster 27SiO2 after hydroxylation-dehydroxylation process, heat of formation -5471.83 kcal/mol.

Silica protoparticle and primary particle surface reactions

The chemical behavior of fumed silica protoparticles may be represented by chemical reactions with water molecules and with other fumed silica protoparticles. The reaction of active surface centers with water leads to the formation of surface hydroxyl groups. But it is necessary to point out that this reaction goes through a chemical reaction barrier (fig 4). However, the value of the reaction barrier of hydroxylation (24.16 kcal/mol) indicate that at the high temperature of the flame, a main part of active centers will be converted, when reacting with adsorbed water, to form a hydroxyl group shell on the silica particles' surfaces. The energy of the hydroxylation reaction is high enough to enable other adsorbed water molecules to react with the active centers to produce new hydroxyl groups. Water molecules close to hydroxyl groups are slightly hindered to react with the silica particle surface, and therefore, a set of different hydroxyl groups are produced as shown in fig. 5. These groups were obtained as results of complete hydroxylation of the silica cluster 27SiO2 – resulting in a new cluster 27SiO2-12W (fig. 5).

The next important point is when water molecules interact with a surface-active center, a one-coordinated oxygen atom, and if there is no three-coordinated silicon atom nearby available. In this case, the charged hydroxyl group may leave the protoparticle, and the protoparticle becomes electrically charged. This may influence the protoparticle's properties and its also ist chemical reactivity.

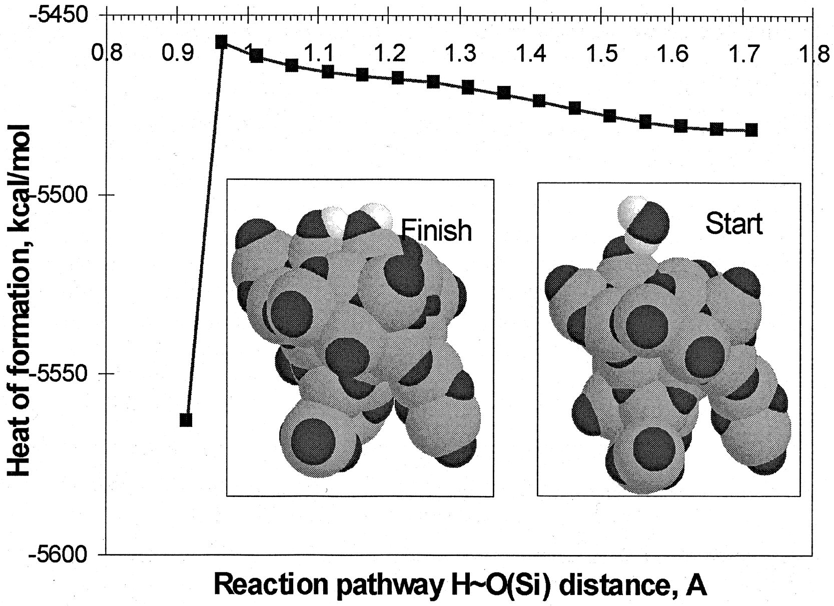

Fig.4. Reaction between an adsorbed water molecule and an active center of a silica cluster.

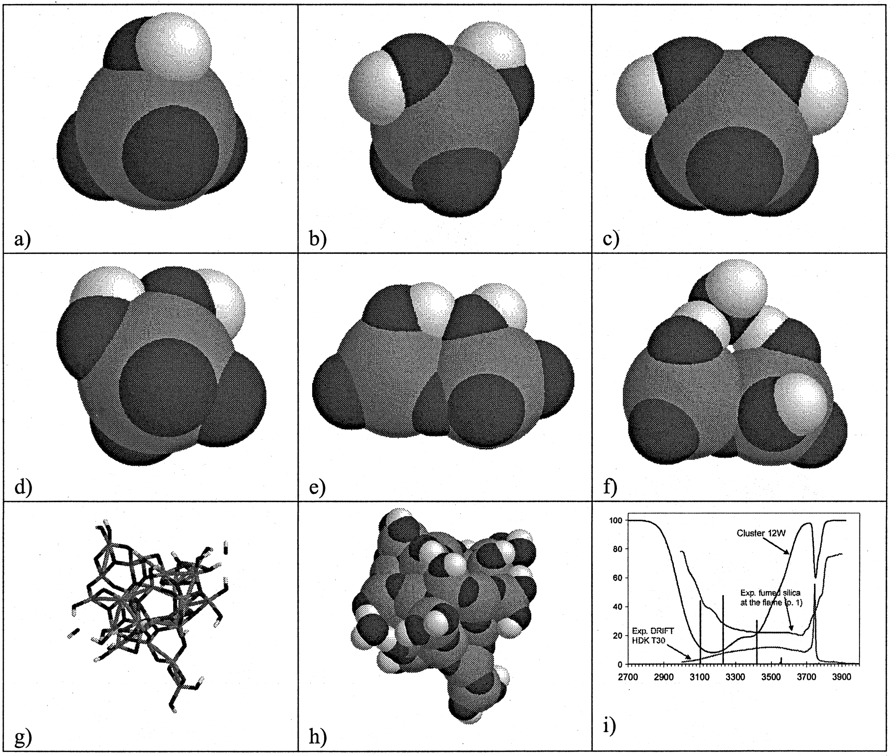

Fig.5. Set of possible hydroxyl groups as a product of an hydroxylation process of a pure silica surface.

a) 'Free' hydroxyl group; Si with c.n. = 4.
b) 'Diol' - two hydroxyl; groups; Si c.n. = 4.
c) 'Diol' - two hydroxyl groups; Si c.n. = 5.
d) 'Diol' - two hydroxyl; Si c.n. = 5.
e) Two H-bonded hydroxyl groups; Si c.n. = 4 and 5.
f) Combined OH-group on 2 groups hydroxyl groups; Si c.n. =4, 5.
g) Complete hydroxylated cluster 27SiO2 – cluster 27SiO2-12W (as sticks).
h) Complete hydroxylated cluster 27SiO2 – cluster 27SiO2-12W (as WdW spheres).
i) Calculated IR-spectrum (blue) and calculated IR-intensity (black) as delta function and experimental data: silica freshly and directly from burner (brown) – point 1 of sample exemption on fig.1 and DRIFT of freshly measured fumed silica Wacker HDK T30 (red). Wave number region 2700-4000 cm^{-1}.

The good agreement between experimental data and calculated IR-spectra for the cluster 27SiO2-12W show that directly in the burner protoparticles like cluster 27SiO2-12W may exist with non-typical hydroxyl shells. Due to the instability of these protoparticles at flame conditions, they are converted to more stable protoparticles like cluster Si18, which is presented in fig. 6, together with ist calculated vibration spectra: IR and INS. Further details of the calculation of vibration spectra and a comparison to experimental spectra will be published elsewhere.

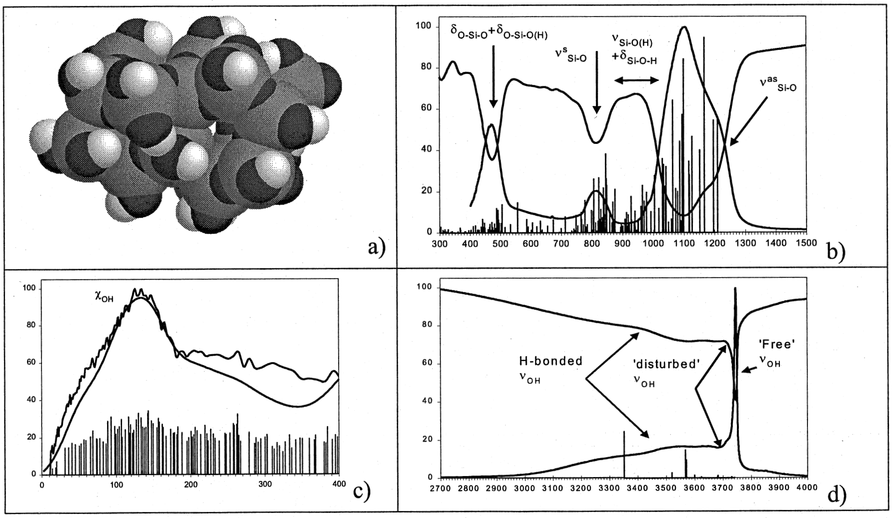

Fig.6. Cluster Si18 and its calculated vibration spectra (IR and INS).

a) cluster model

b) calculated IR-spectrum (blue) and calculated IR-intensity (black) as deltafunction and experimental (red) DRIFT freshly sampled fumed silica Wacker HDK T30. Region 300-1500 cm^{-1}.

c) Calculated INS-spectrum (blue) and calculated INS-intensity (black) as deltafunction and experimental (red) INS-spectrum of freshly sampled fumed silica Wacker HDK T30. Region 0-400 cm^{-1}.

d) calculated IR-spectrum (blue) and calculated IR-intensity (black) as deltafunction and experimental (red) DRIFT freshly sampled fumed silica Wacker HDK T30. Region 2700-4000 cm^{-1}.

Interparticle reaction: Aggregates and agglomerates

There are two pathways for the next steps of reactions of such protoparticles. In the presence of terminating agents, like water, the surface-active centers are saturated and small primary particles are formed. However, the absence of terminating reagents leads to a collapse of protoparticles and the formation of bulk material. Therefore, the main difference between protoparticles and primary particles is not their size, but the chemical structure and degree of saturation of their surfaces. Both possible pathways are shown in fig.7.

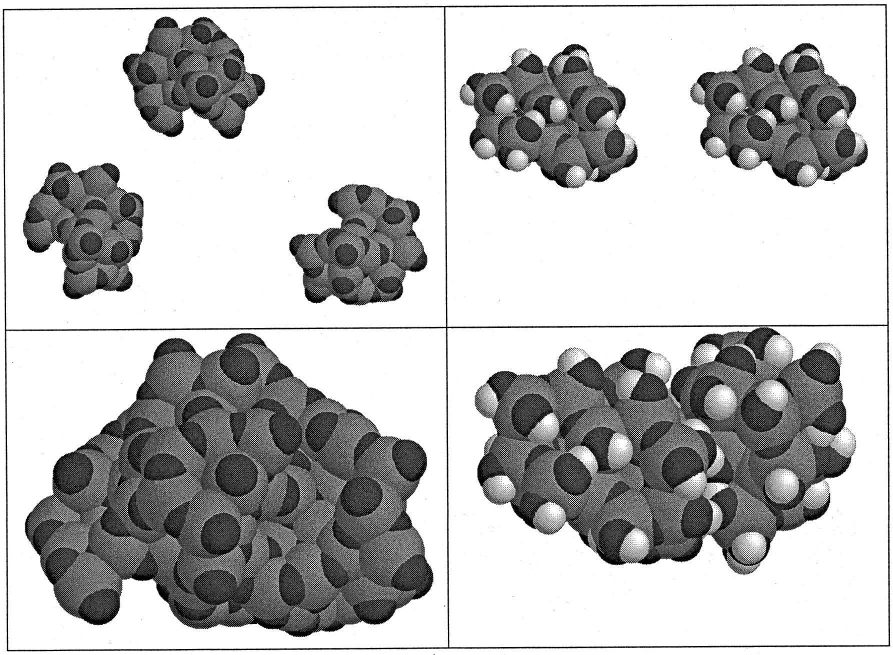

Fig.7. Reaction between protoparticles (left) and primary particles (right). Starting positions in the first row; optimized structures are shown in the second row.

Primary particles can be involved into long distance interactions due to high dipole moments of the particles. This interaction leads to coagulation of primary particles into aggregates. At high temperatures, in the flame, surface hydroxyl groups which are in contact with each other, may react together and produce new ordinary siloxane bonds and water. By this, primary particles are forming aggregates. At lower temperature conditions, after leaving the flame, this reaction does not take place and aggregates will be tied together by weak dipole-dipole interaction and H-bonding, forming agglomerates. Therefore the main difference between aggregates and agglomerates is not the size but the nature of forces which integrate the primary particles into a common system and the energy needed to separate aggregate and/or agglomerate into parts.

As discussed above, agglomerates are formed as a result of dipole-dipole forces, H-bonding and other non-specific forces. During agglomerate formation no ordinary siloxane bonds between particles occur. As a results, agglomerates are less mechanically stable in comparison to aggregates. Agglomerate may be dispersed under simple mixing, but dispersion of aggregates will need markedly more mechanical stress. But, there is no strong border between these three kinds of fumed silica particles – primary particles, aggregates and agglomerates. During heating, agglemerates may lose water due to the condensation of hydroxyl groups, under formation of aggregates. This process finally may lead to the formation of glass. On the other side, under high mechanical stress and/or chemically active media, the ordinary siloxane bonds between particles in aggregates may be broken down, due to mechanically stimulated chemical reactions. In active media like water or proton-donor systems (acids etc.), broken bonds between particles will be saturated and terminated. This leads to conversion of aggregates to agglomerate. From a general point of view, all these transformation may be described as destruction and construction at the small particle level.

All types of surface-active centers can exist on real surfaces in different concentrations. Therefore, real vibration spectra from fumed silica are a sum of vibration of sets of different structural units. This leads to a high sensitivity of vibration spectra to sample history and treatment. Results of quantum chemistry calculation show that all silicon atoms are unsaturated in quantum coordination numbers and they are able to interact with some electrondonor molecules like water. All these data were taken from suitable cluster calculations.

Some other processes on the silica surface were studied. Basing on crystobalit-like type of sets of clusters we have simulated the dehydroxylation process as a result of removing two hydrogen atoms and one oxygen atom from neighboring hydroxyl groups. Step-by-step dehydroxylation processes lead at first to an increase of the quantity of H-bonded hydroxyl groups up to maximum, and later on finally to a decrease of the total number of hydroxyl groups and, according to the dehydroxylation process, to a decrease of the amount of H-bonded hydroxyl groups. The same results were obtained using differ silica clusters (see table 1.)

Table 1. Part of hydroxyl groups, included into H-bonding.

Cluster system	Total number of OH	Number of H-bonds	100%*(H-bonded OH)/(total OH)
Si48	52	6	11.5
Si47-7	38	7	18.4
Si48-11	30	7	23.3
Si48-13	26	4	15.4

The same result have been received from an analysis of H-bonding during agglomerate formation, using different medium sized cluster, type Si18. The data are shown in table 2.

Table 2. Part of hydroxyl group, included into H-bonding, as a function of the number of clusters in agglomerates.

Cluster system	Total number of OH group(s)	Number of H-bonds	Number of H-O-H chain(s)	100%*(H-bonded OH)/(total OH)
Si18	24	2	0	8
2*Si18	48	13	0	27
3*Si18	72	22	5	37.5
4*Si18	96	29	7	37.5

The amount of H-bonded OH-groups was taken as the number of isolated H-bonds plus the number of H-O-H chains.

Tables 1 and 2 show clearly that at least one third of the hydroxyl groups are involved into H-bonding. For cluster systems 3*Si18 and 4*Si18, H-O-H chains were observed. For cluster system 4*Si18 the maximal length of this H-O-H chains was of about 4 atoms. That means that OH-groups are able to form large strcutures with collective systems of H-bonds. That means that fumed silica surfaces will be micro-heterogenous from a chemical point of view.

Conclusion

The following definitions for the flame process producing fumed silica are proposed:

- **Protoparticle** - molecular cluster of silica (10-200 silicon atoms), covered by active groups, which are not stable in chemical point of view.
- **Primary particle** - product of reordering and unification of coordination numbers to standard values, of atoms inside protoparticles due to hydroxylation of its surfaces.
- **Aggregate** - product of the formation of chemical bonds between primary particles by the reaction of neighboring hydroxyl groups at particle-particle interfaces, under formation of ordinary siloxane bonds.
- **Agglomerate** - product of H-bonding and unspecific forces interacting between aggregates and primary particles.

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