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Fumed Silica Synthesis. Influence of Hydrogen Chloride on the Fumed Silica Particle Formation Process

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Summary: Interaction of silicon dioxide molecule up to the small silica protoparticle and primary particle formation, and influence of hydrogen chloride (HCl), water (H_2O) and inert molecules (nitrogen N_2) "under flame condition" and "after cooling" on structure and properties of fumed silica were investigated by quantum-chemical simulations. An attempt to give definition of surface concept on atomic level was made.

Introduction

This work is the part of the series of papers devoted to the influence of small molecules on pyrogenic silica formation [1-6]. It deals with the very first stages of this process. At the very beginning of flame process (point 1 at fig.1) SiO_2 molecules stack into protoparticles in the environment of HCl, N_2 and H_2O.

As it has been shown in previous works [6], HCl by means of specific forces is able to adsorb weakly on SiO_2 primary particle surface, creating active center, which can react with water molecule without chemical barrier. On the other hand, the system of statistically uniformly distributed molecules SiO_2 and HCl in 1:4 proportion doesn't produce protoparticle and doesn't react with water molecules under the same conditions. So the question is: why does silicon dioxide act differently, depending on protoparticle size?

PM3 semiempirical method was used to simulate systems under study [7]. Computations were performed by CLUSTER-Z1 computational toolset [8].

Problem The influence of HCl on fumed silica protoparticle formation, size and properties at the first stages of flame process.

Presumption Since the concept of time doesn't figure in quantum chemistry computations, let us assume that each of models had simulated very quick process in which kinetical properties of particles, related to the thermal motion, didn't act.

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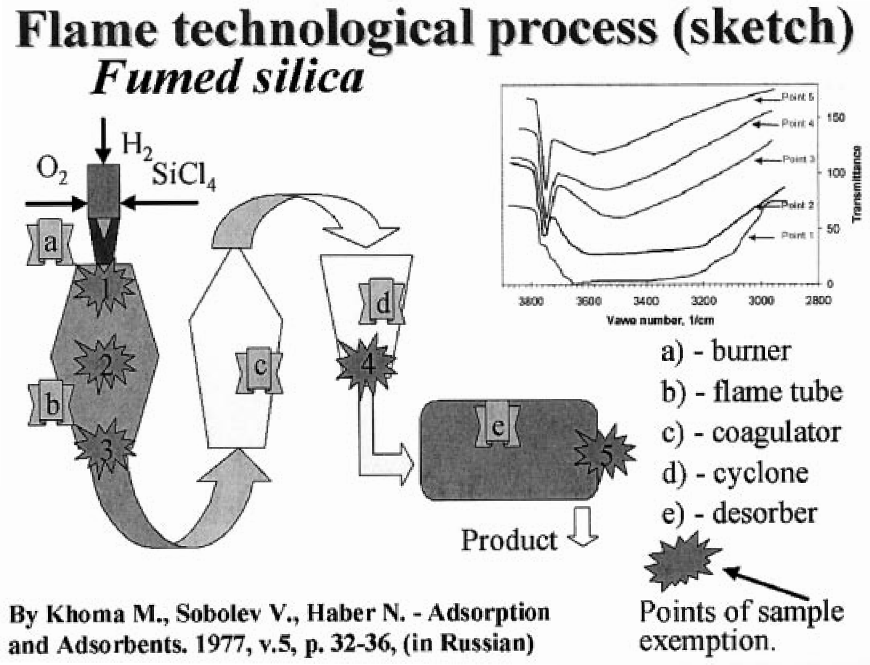
This means that we collect a couple of consecutive points on the pathway of reaction, according to our knowledge on this process, and compute interactions of molecules at that points without time scale - as very quick ones.



Flame technological process (sketch)

Fumed silica

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

Product

Points of sample exemption.

By Khoma M., Sobolev V., Haber N. - Adsorption and Adsorbents. 1977, v.5, p. 32-36, (in Russian)

Fig. 1. Flame technology process.

Objectives

To determine protoparticle's critical size after which the further growth of particle passes without barrier, and to explain the phenomena of formation threshold itself.

To check the difference between protoparticle formed in the environment of small molecules (HCl and N_2) and protoparticle, formed of SiO_2 molecules set only. To check the difference between particles that stack together on different stages of formation.

To examine the catalytic influence of chlorine hydride on the protoparticle hydroxylation.

I. Protoparticle critical size

Problem Does the critical size of protoparticle formation – *formation threshold* – exist? What is its value and origin, if it does?

The general reaction of flame process is:

$SiCl_4 + O_2 + 2H_2 = SiO_2 + 4HCl$.

In order to investigate the first stages of flame process we have simulated some models, almost all of which contained different quantity of "gas sets" – silicon dioxide and hydrogen chloride molecules in 1:4 proportion. Varying the starting geometry of these "sets", we tried to get required answers.

1.1 Threshold existance

Let us examine two systems: *9si9hcl* and *coresi* (Fig.2).

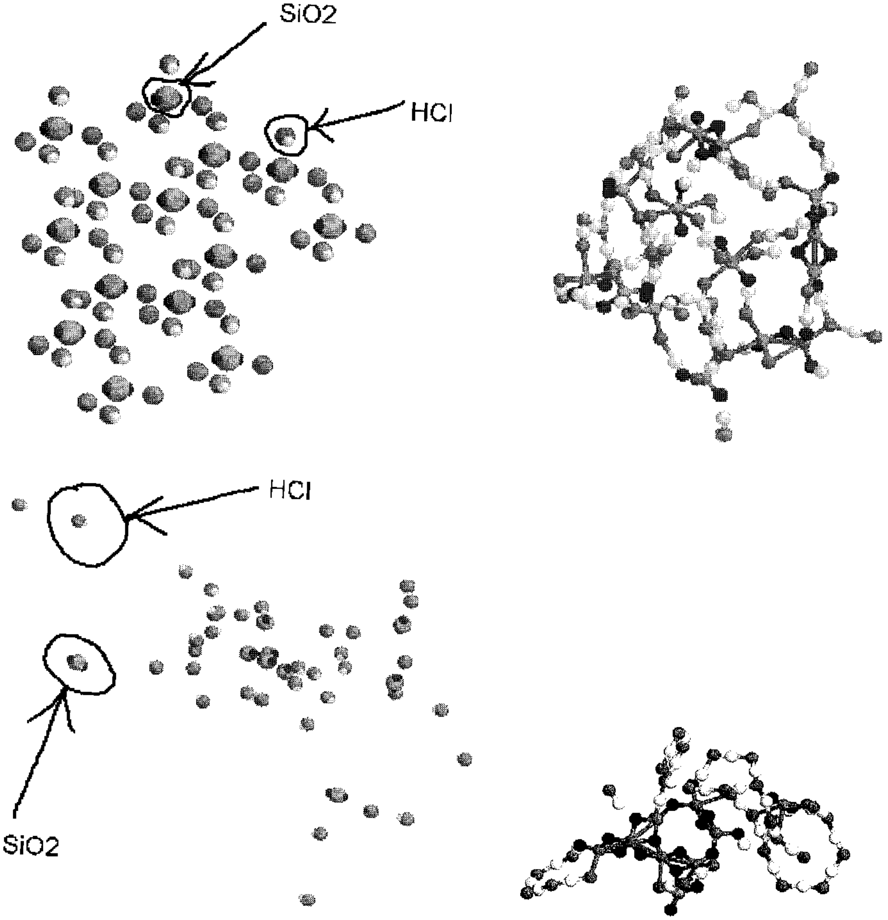


Fig.2. Threshold existence. a) 9si9hcl; b)coresi (a: above; b: below; left: start structure; right: final structure).

9si9hcl is built of 9 "gas sets", each having tetrahedral shape with SiO_2 molecule, surrounded by HCl molecules. Optimization of this system leads almost to the chaotic structure: most of silicon dioxide molecules form particles of 1-3 SiO_2 size, separated by HCl. No protoparticle formation is observed.

Coresi also contains 9 "gase sets", but there is a kind of "core" or "nucleus" of 5 SiO_2 molecules, separated from other SiO_2 molecules by HCl interlayer. Finally, the $8SiO_2$ protoparticle arises. Its form is almost linear. One SiO_2 molecule, surrounded by HCl, is weakly attached to the HCl interlayer (let us note this for the further discussion).

It's interesting to note that HCl form cyclic constructions without legibly certain molecules. This is the result of kinetical properties neglection.

Thus there is some number of SiO_2 molecules in "core" that can be the nucleus of protoparticle formation. Such model can simulate the case, when several SiO_2 molecules appears nearby before being influenced by HCl at the very beginning of flame process. Now, there is the problem: is the border of this phenomena smooth or discontinuous?

1.2 Threshold value

In order to determine the value and the shape of threshold we simulated some series of models: *core3, core4, coresi* and *csi2.* (Fig.3), that differ with the size of "core" SiO_2 molecules – 3, 4, 5 and 12, correspondingly.

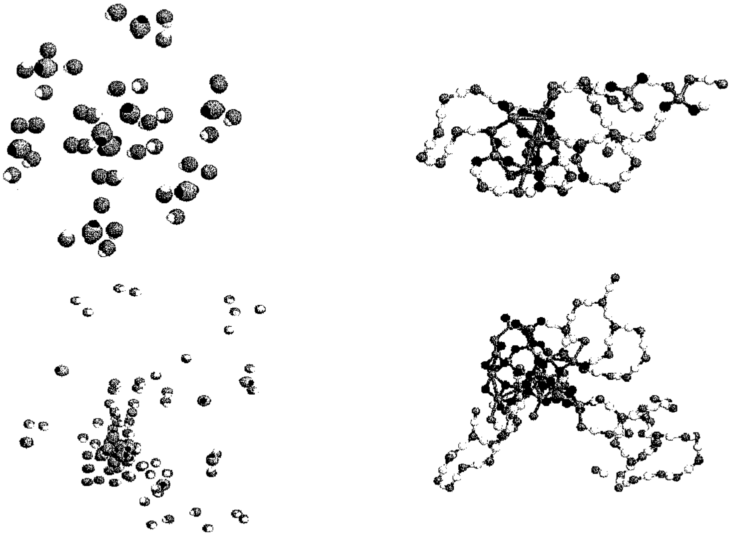


Fig.3. Threshold value. a) core3; b)csi2 (a: above; b: below; left: start structure; right: final structure).

In first two cases protoparticle doesn't certainly arise. 2 or 3 SiO_2 tied with HCl are weakly bonded to the HCl interlayer, and other silicon dioxide molecules doesn't form the "bulk" – there are no double bond between the oxygen and silicon atoms and no cycle formations, typical for SiO_2 particles and protoparticles. In case of *csi2*, protoparticle really arises and certain area of its surface even is not covered with HCl interlayer.

Hence, we conclude that threshold value for protoparticle formation is at least 5 SiO_2 molecules.

1.3 Phenomena origin

There are two reasons for a phenomena of protoparticle formation threshold: chemical – specifical interaction between HCl and SiO_2 molecules, and geometrical - with growth of the protoparticle radius its surface square grows quadratically, and more vacancies for new silica dioxide molecules to attach appear correspondingly. To specify the dominating reason we simulated analogous systems with N_2 molecules instead of chlorine hydride – *core3n4* and *core4nhc*. (Fig.4)

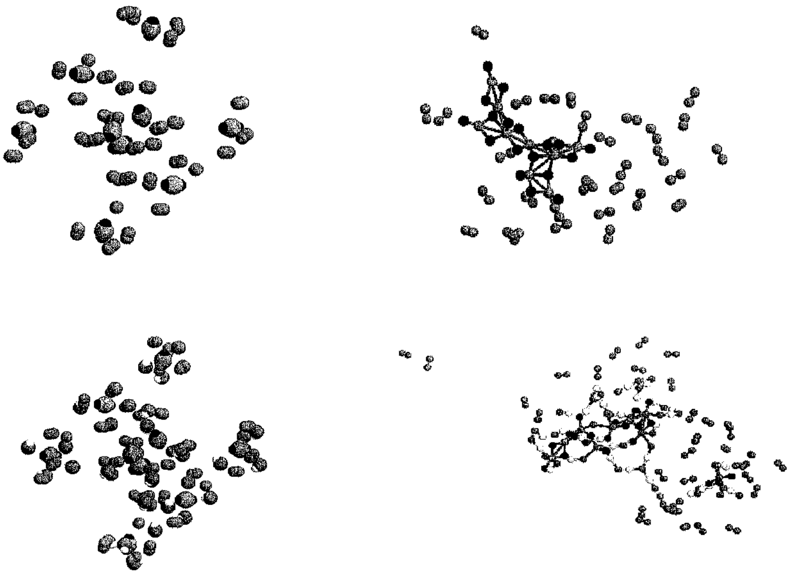


Fig.4. Threshold origin. a) core3n4; b)core3nhc (a: above; b: below; left: start structure; right: final structure).

These systems were acquired by simple substitution of HCl with N_2 molecules. There can be a little chance of nitrogen chemical influence on protoparticle formation process, so, if geometrical reason of threshold phenomena dominated in this process, then nitrogen molecules would prevent "outcore" SiO_2 molecules from attaching to the "core". Otherwise, the chemical reason is dominating one.

As we can see, protoparticle has formed. Hence, the main reason of threshold phenomena is chemical. SiO_2 molecules that can't combine quickly are involved into strong bonding with chlorine atoms of HCl, forming tetrahedron that must be thermally dehydrochlorinated for SiO_2 to attach to the "bulk" of protoparticle.

Also, model *core4nhc* has been simulated to check the influence of nitrogen on protoparticle formation process. This is *core3* model with 4 N_2 molecules added to each "gas set". Two 4-SiO_2 particles and 1 SiO_2, surrounded with HCl, were the result of optimization. The only significant difference from *core3* system is that surrounded SiO_2 couldn't even reach the interlayer of HCl.

Conclusions

-the threshold exist;

-its value is about 6-7 SiO_2 molecules;

-the formation threshold has mainly chemical origin.

II. HCl influence on protoparticle structure and physicochemical properties

Problem What is the difference in structure and physicochemical properties between protoparticle formed of SiO_2 molecules set only, and protoparticles formed in the environment of HCl in different ways?

In order to solve this problem we have simulated several models, discriminating by level of HCl influence. After optimizing each system was dehydrochlorinated for 4 times, with step-by-step removing of:

1) weakly bonded HCl;
2) HCl under ‘chemical pressure’;
3) H-bonded HCl;
4) all HCl.

For each system the heat of formation (ΔH), dipole moment (D), first ionization potential (I) and specific heat of formation (μ) were defined. Bonds length distribution, angles values distribution, radial distribution function (RDF) and coordination numbers distributions were specified to check the differences in structure.

2.1 Obtaining models

Models under investigated in this chapter can be split into 2 groups:

1) 'HCl-lack' systems (*27SiO2* and *rmw12*) (fig.5 a, e);

2) 'HCl-containing' systems (*2csi1, csi4* and *csi2*) (fig.5 b, c, d).

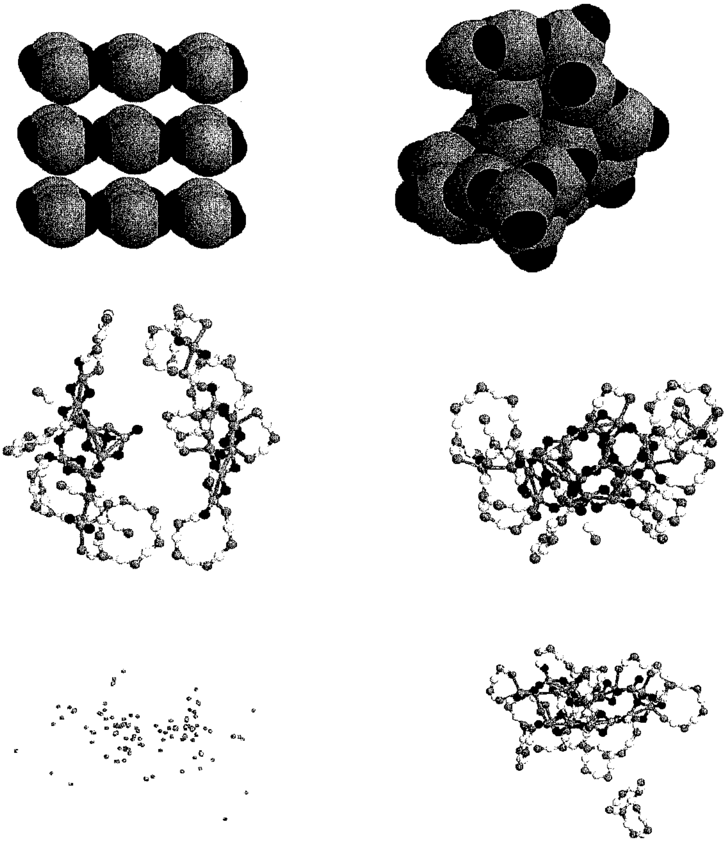


Fig.5. Obtaining models: a) 27SiO2 ΔH= -5412.75 kcal/mol, D= 17.496 Db, I= 6.57052 eV, μ=-200.47 kcal/mol; b) 2csi1, ΔH= -5511.76 kcal/mol, D= 8.586 Db, I= 10.0925 eV; c) csi4, ΔH= -5737.59 kcal/mol, D= 9.359 Db, I= 10.1761 eV; d) csi2, ΔH= -5815.50 kcal/mol, D= 28.452 Db, I= 9.10182 eV; e) rmw12, ΔH= -5471.83 kcal/mol, D= 14.871 Db, I= 5.74801 eV, μ = -202.66 kcal/mol (a: above; b: middle; c: bottom; left: start structure; right: final structure).

Model *27SiO2* was previously described [4]. It is formed by optimization of 27 SiO_2 molecules, placed into cubic lattice with distance of ~7 Å between molecules. Model *rmw12* reflects the process of dehydroxylation of fumed silica primary particle, which leads to the unifying of silica by structure, coordination numbers, bond lenghts and so on (so called coproportionation).

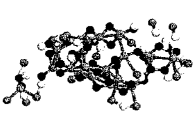
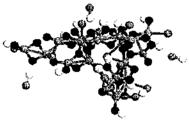
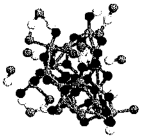
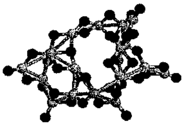
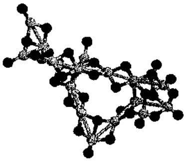
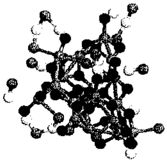
2csi1 model is the system of 2 optimized *coresi* systems (see section 1) - two SiO_2 nuclei reacting after optimization. *Csi4* is the system of two SiO_2 nuclei reacting 'in situ', without preliminary optimization. *Csi2* is the system of 18 SiO_2 molecules with $12SiO_2$ nucleus (fig.3b).

These models were constructed to determine, if HCl influences on the structure of protoparticles themselves or just on further reactions of protoparticles stacking.

2.2 Dehydrochlorination of 'HCl-containing' models

As it's clearly seen from illustrations (fig.5), most of HCl molecules doesn't interact with SiO_2 protoparticles after optimization. Evidently, that in real system such molecules would be detached from silicon dioxide by thermal motions. So, the next step of investigations is dehydrochlorination of 'HCl-containing' models. Wiberg index - the index of covalent bonding - was taken for criterion of interaction. HCl particles which Wiberg index for interaction with SiO_2 was lower than 0.1 were removed from system (fig.6. *2csi1_d1, csi4_d1* and *csi2_d1*), and system was optimized. Then HCl that interacted with SiO_2 under 'chemical pressure' of removed species (electrostatic repulsion between HCl) were removed, too (fig.6. *2csi1_d2, csi4_d2* and *csi2_d2*). On the third step of dehydrochlorination H-bonded HCl was removed and chemicaly bonded chlorine and hydrogen remained only (fig.6. *2csi1_d3, csi4_d3* and *csi2_d3*). And finally, all HCl was removed to investigate SiO_2 protoparticles (fig.6. *2csi1_d4, csi4_d4* and *csi2_d4*).

Each of these stages can take place in real process, because the energy of bonds broken is much lower than energy of thermal motions at 2000°C.

2csi1	csi4	csi2
 2csi1_d1 ΔH= -4353.34 kcal/mol D= 29.160 Db I= 8.2749 eV v(HCl)= 22 molecules	 csi4_d1 ΔH= - 4216.33 kcal/mol D= 17.257 Db I= 8.5921 eV v(HCl)= 17 molecules	 csi2_d1 ΔH= - 4291.18 kcal/mol D= 15.611 Db I= 8.6105 eV v(HCl)= 15 molecules
2csi1_d2 ΔH= -4056.82 kcal/mol D= 14.575 Db I= 7.7511 eV v(HCl)= 10 molecules	csi4_d2 ΔH= - 4172.30 kcal/mol D= 13.099 Db I= 8.4096 eV v(HCl)= 15 molecules	csi2_d2 ΔH= - 4118.83 kcal/mol D= 13.942 Db I= 8.2647 eV v(HCl)= 10 molecules
2csi1_d3 ΔH= -3996.26 kcal/mol D= 15.190 Db I= 7.6499 eV v(HCl)= 8 molecules	csi4_d3 ΔH= - 4105.32 kcal/mol D= 14.335 Db I= 8.2651 eV v(HCl)= 13 molecules	csi2_d3 ΔH= - 4037.31 kcal/mol D= 2.608 Db I= 8.1001 eV v(HCl)= 8 molecules
		

2csi1_d4	csi4_d4	csi2_d4
ΔH= -3583.28741 kcal/mol D= 14.06050 Db I= 7.35185 eV μ= -199.07 kcal/mol	ΔH= -3390.49 kcal/mol D= 13.606 Db I= 7.3786 eV μ= -188.36 kcal/mol	ΔH= -3411.96 kcal/mol D= 15.420 Db I= 6.9669 eV μ= -189.55 kcal/mol

Fig. 6. HCl-containing' systems dehydrochlorination. ΔH – heat of formation, D- dipole moment, I – first ionization potential, ν(HCl) – quantity of HCl molecules, μ – specific heat of formation (per 1 SiO_2 molecule).

2.3 Investigation of structure

In order to investigate differences between systems, statistical methods were used: bond lenghts distribution (fig. 7), radial distribution function - RDF (fig. 8) and coordination numbers distribution (fig. 9). The level of amorphous character was the main objective for analyse.

Such traits are representative for the crystalline state: no bond lenghts dispersion, sharp peaks in RDF, distinct coordination numbers. On the other hand, for amorphous state such traits are representative: broad bond length distribution, smoothed peaks in RDF, dispersion of coordination numbers. There are intermediate characteristics with different level of amorphous or crystalline character in our systems.

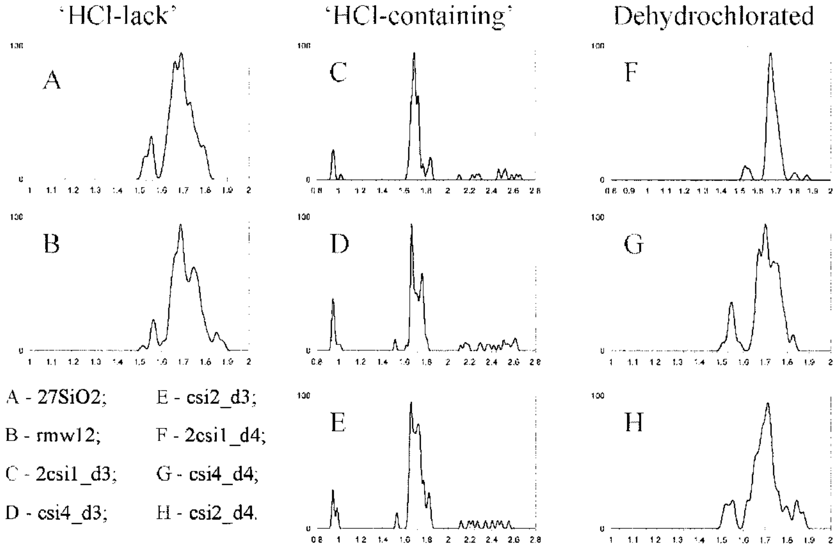


Fig.7. Bonds length distribution.

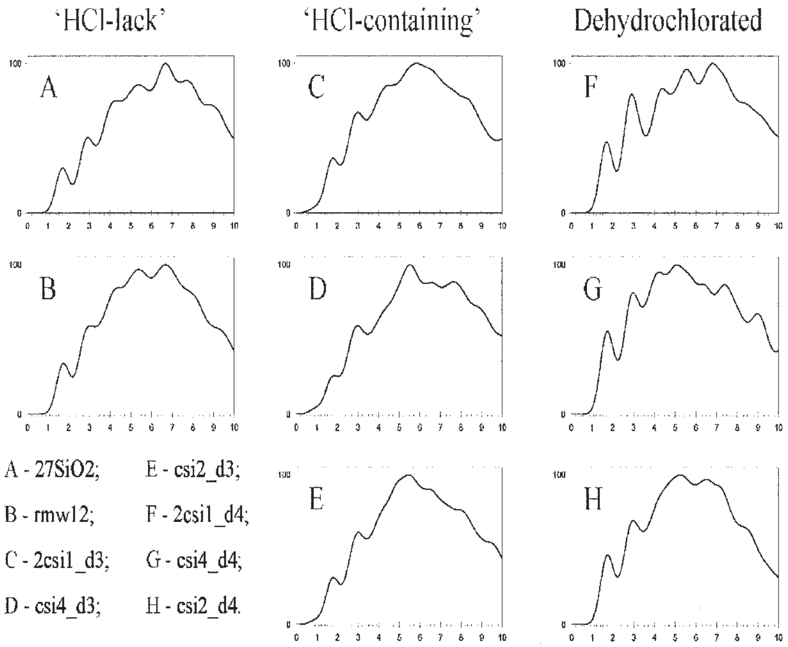


Fig.8. Radial distirbution function (RDF).

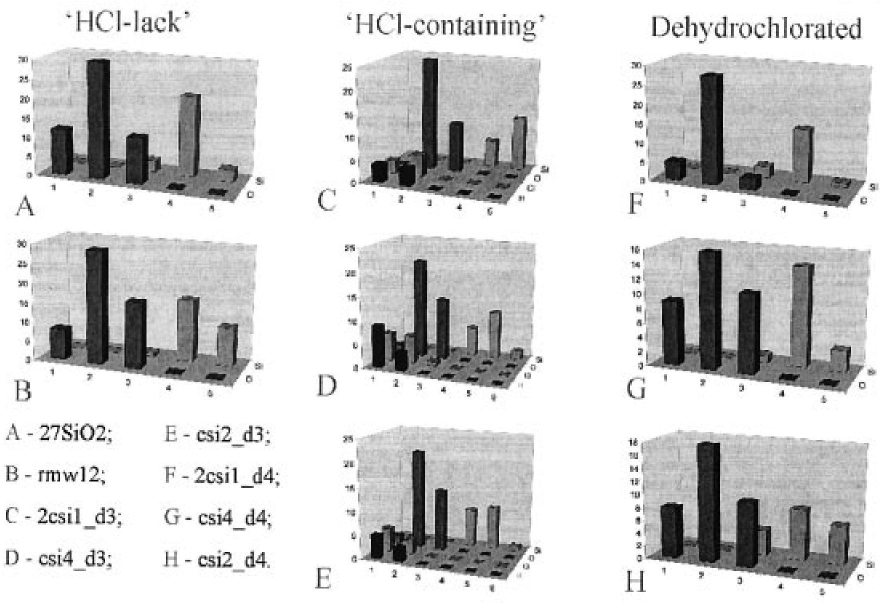


Fig.9. Coordination numbers distribution.

Without going into details of analysis we can point on several conclusions. Firstly, as we have seen, systems formed under influence of HCl differ from 'HCl-lack' systems in structure: they have different shapes of peaks, coordination numbers distribution and so on. Secondly, systems with chemically bonded chlorine and hydrogen are more amorphous (fig. 7). Thirdly, system *2csi1_d4* is much more crystalline then all other - it means that the reaction of relaxed nuclei leads to more crystalline structure.

Conclusions

- Systems formed under influence of HCl differ from ‘HCl-lack’ systems
- Interaction of two already formed protoparticles in HCl environment leads to more crystal-like structures
- HCl may promote both coproportionation (unifying by coordination numbers) or disproportionation, depending on conditions of interaction

III. Chemical properties of protoparticles

Problem Do chlorine atoms bonded to protoparticle possess specific properties? What defines catalytic properties of HCl: specific character of HCl-protoparticle interaction or protoparticle surface energy? What is the meaning of ‘surface’ term on atomic level?

3.1 Types of bonded chlorine

First of all we would like to classify types of chlorine bonded to the bulk of small silica protoparticle (Fig. 8) and investigate their reaction with water molecules. These types of chlorine were observed in different protoparticle models and possess similar properties.

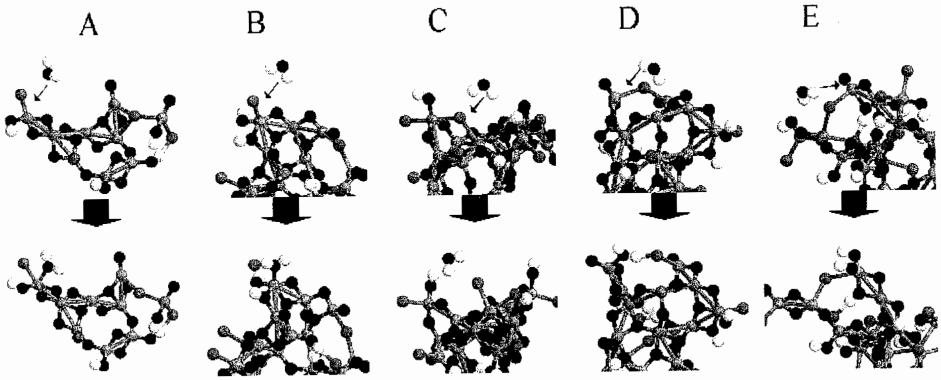
1) One-coordinated "tentacle" chlorine (Fig. 10a) – Almost every protoparticle has a "tentacle" or $=Si-(O)_2-Si=O$ group. Coordinationaly unsaturated silicon atom can attach chlorine atom, and this bond is very strong. Water can only attach to such a group through a chemical barrier. This type of chlorine cannot be eliminated by interaction with water.

2) One-coordinated "bulk" chlorine (Fig. 10b) – Chlorine bonded to an almost coordinationaly satisfied silicon, oftenly upgrading it to coordination number 5. It can be substituted by water through a chemical barrier, forming OH-group and chemically adsorbed HCl.

3) Two-coordinated "bulk" chlorine (Fig. 10c) – Chlorine bonded to 2 coordinationaly satisfied silicon atoms. Such chlorine is hard to be reached by water molecule. Usually it doesn't react with water and is degraded to coordination number 1 only.

4) Three-coordinated "bulk" chlorine (Fig. 10d) – Chlorine bonded to 3 coordinationaly satisfied silicon atoms. It can attach water molecule through a chemical barrier, producing OH-group.

5) Two-coordinated "bridge" chlorine (Fig. 10e) – Chlorine connecting 2 "tentacles" of silica. Such group is very reactive and can react with water molecule, producing 2 OH-groups. This reaction is still passing through a chemical barrier.



1-coordinated Tentacle chlorine => Attach with a barrier!!!

1-coordinated 'Bulk' chlorine => Substitute with a barrier!!!

2-coordinated 'Bulk' chlorine => Doesn't react!!! Degrades chlorine.

3-coordinated 'Bulk' chlorine => Attach with a barrier!!!

2-coordinated Bridge chlorine => Reacts with a barrier!!!

Fig.10. Types of bonded chlorine and their interaction with water.

3.2 Dependance of HCl catalytic abilities on silica protoparticle size

As we have seen, none of chlorine groups on a tiny protoparticle (up to 18 SiO_2) can react with water without chemical barrier. Adsorbed or H-bonded HCl can't do this also.

On the other hand, in previous works [6] HCl catalytic ability for $27SiO_2$ protoparticle was observed. In the presence of hydrochlorine molecule one water molecule can react with silica surface without chemical barrier producing 2 OH-groups. The rest of water molecules react only through a barrier.

Simulation were performed for $64SiO_2$ protoparticle interaction with 7 (H_2O + HCl) sets, and all water molecules reacted without barrier.

The tendance is easily seen. For monomeric SiO_2 molecule HCl prevents both stacking with other silicon dioxide molecules and reaction with water. The same situation is observed up to the threshold of silica protoparticle formation – 6-7 SiO_2 molecules. For tiny protoparticles (7-18 SiO_2) HCl doesn't catalyze hydroxilation. Starting from $27SiO_2$ protoparticle phenomena of HCl hydroxilation catalysis arise and the quantity of water molecules that react without barrier grows with growth of silica protoparticle size.

From our point of view these properties of HCl are closely bound with phenomena of "surface energy" for dispersed matter, and they can reveal the border of surface existence. We believe that further investigation of chemical barriers values for silica hydroxylation will prove this statement.

3.3 Definition of body surface concept on atomic level

Finally, we will try to give the definition of 'body surface' concept on an atomic level, using investigated material, and to illustrate it.

Conceptions introduced:

1) **Body** – system of investigated atoms, which can be considered as model of investigated substance under condition (ideal) of another particles absence (body is defined separately from investigated model, and it is embedded into model after that);

2) **Environment** – system of atoms (particles) of defined model, which don't belong to the body

3) **Atom (particle) sphere of influence** – sphere with a centre in certain atom (particle), in which radius the interaction between defined atom (particle) and every other atom (particle) can not be neglected (taking into account nowadays computing possibilities, this border can be taken for 1 kcal/mol);

4) **Bulk atom (particle)** – atom (particle) of body, in which sphere of influence only other body's atoms are found;

5) **Surface atom (particle)** – atom (particle) of body, in which sphere of influence not only other body's atoms are found;

6) **Neighbouring groups (atoms)** – groups (atoms), which are found in mutual spheres of influence of each other.

Definition:

2 conditions are to be kept for atom (group) to be the part of surface:

1) **surface atoms are to be present**;

2) **neighbouring group/s (atom/s) of environment is/are to be present**.

All atoms of surface form the body surface in totality if bulk atoms (particles) exist.

For example, let's examine system *csi2*.

The concept of surface doesn't have a sense for fully dehydrochlorinated *csi2_d4* system, because no environment is defined. Let's define *csi2_d4* as a *body* and H_2O and HCl molecules as *environment*. The energy of hydroxylation is taken for a criterion of interaction (for *sphere of influence* definition). In this case *csi2_d4* protoparticle doesn't have a surface, because there are no body atoms which interaction with water can't be neglected (water molecule doesn't include to the sphere of influence of any body atom).

For the system $27SiO_2$ with HCl and H_2O molecules (under the same criteria) silicon and oxygen atoms that reacted with water molecule are *surface atoms*.

As we can see, appearance of surface depends not only on body but on environment, too.

Conclusions

– some types of protoparticle-bonded chlorine are comparatively inert and are hard to eliminate by chemical reasons;

– chlorine and HCl don't catalyze hydroxylation on tiny protoparticles;

– the greater protoparticle is the better hydroxylation passes.

General conclusions

– HCl molecules act both as the catalyst and the preventor of silica primary particles formation, depending on silica 'nucleus' size;

– HCl-catalyzed hydroxylation is a well-turned illustration for defining a 'body surface' concept on atomic level.

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