Fumed Silica Synthesis: Influence of Small Molecules on the Particle Formation Process

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Introduction

Burning silicon tetrachloride in an oxygen-hydrogen flame produces fumed silica. This process is known for at least 50 years [1-5], but some important details are still uncertain. We would like to study several starting steps of fumed silica synthesis on the way from molecules to products. To do this we have performed quantum-level simulations of protoparticle and primary particle formation, from silicon dioxide molecules. Additionally, we have simulated the behavior of silica clusters in the presence of small molecules like water and hydrochloric acid.

The reaction of silicon dioxide molecules leads to a silica cluster, which is covered with chemicaly highly active sites of one-coordinated oxygen atoms and three-coordinated silicon atoms. These clusters interact together and produce silica bulk like quartz glass. Reaction with water terminates the silica particle surface and leads to a complicated structure of the particle surfaces. The hydroxyl shell protects the particle body against the increase in particle size, but leads to aggregate and agglomerate formation.

Results and discussion

Quantum chemical simulation was performed to study the mechanism of hydroxyl shell formation when water reacts with active sites of silica particles. The influence of small molecules like hydrochloric acid and carbon dioxide on this process was studied, too. Reaction with water is described in different articles with silica particle formation process together.

Hydrochloric acid is able to react with the hydroxyl-free surface of silica cluster, as it exists just after formation, (protoparticle) *without energy barrier,* producing a hydroxyl group and weakly bonded chlorine. The distance between the chlorine and silicon atoms for the system under study is 2.417 Å, in comparison to 2.017 Å (experimental) and 2.054 Å (calculated) for the molecule $SiCl_4$. The formal charge of the chlorine atom for the system under study is -0.754 e^-, in comparison to -0.354 e^- for $SiCl_4$. The Wiberg index (bond order) chlorine–silicon of the system under study is 0.3231, compared with the value 0.8468 for $SiCl_4$.

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Very similar results have been received for thr reaction between HCl and the surface of a dehydroxylated silica particle (dehydroxylated primary particle), and after equalization of the coordination numbers. However, the main difference is that the chlorine atom is not strongly bonded to a silicon atom: The HCl molecule is tied to the silica surface only via H-bonding, the formal charge at the chlorine atom is -0.908 e^-, and the Wiberg index for the Cl-H bond is only 0.1104.

A similar phenomena (weakly bonded chlorine) is present for the system with water and hydrochloric acid. The results show that the chlorine atom is bonded to the silica cluster mainly as an ion, and it is proposed to regard the system under study as an ion pair, which may dissociate into free ions. As a result, under thermal fluctuations, charged particles will be formed and may be repulsed if apporaching each other (see fig. 1). Vibration spectra calculations show that all vibrations with significant contribution of chlorine atoms are located below wavenumbers of 400 cm^{-1} and show low infrared (IR) intensities, and, therefore, are difficult for observation.

Comparing Wiberg indexes for the bond of chlorine atoms with silica systems in the series $SiCl_4$ – protoparticle – dehydroxylated primary particle, we can affirm that the strength of bonding decreases significantly with the growth of the system order. That is the reason why the final product – fumed silica – does not contain chlorine.

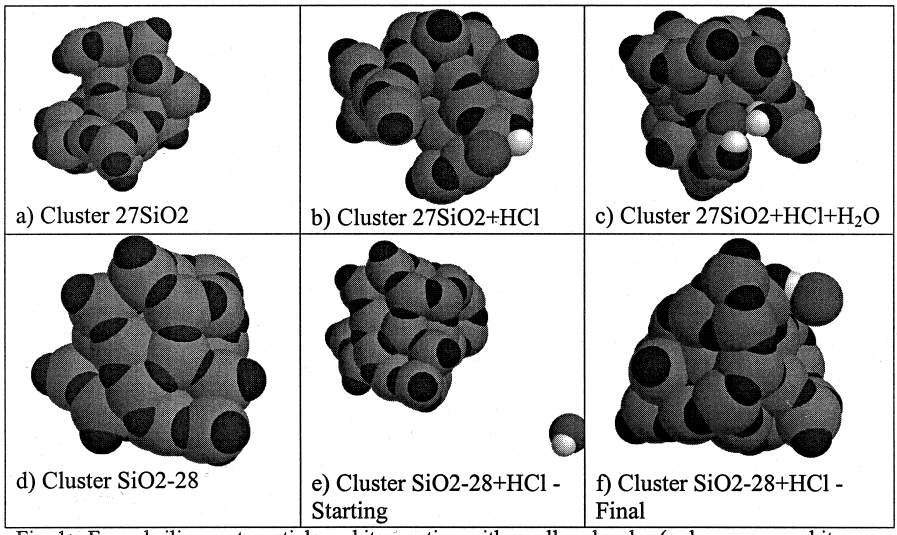

Fig. 1: Fumed silica protoparticle and its reaction with small molecules (red – oxygen, white – hydrogen, light green – chlorine).

a) Products of reaction simulation silica cluster 27SiO2 formation.
b) Product of reaction simulation between silica cluster 27SiO2 and HCl.
c) Product of reaction simulation between silica cluster 27SiO2 and HCl with H_2O.
d) Product of reaction simulation silica cluster 28SiO2 dehydroxylation.
e) Starting position for simulation of reaction between 28SiO2 cluster and HCl.
f) Product of reaction simulation between 28SiO2 cluster and HCl.

As it is well known the second step for the production of fumed silica is desorption of hydrochloric acid under a pressure of water steam. Our simulation shows that this process may be described as a decomposition of weakly bonded complexes of positive charged particles with their discharging and formation of agglomerates.

To simulate the first steps of the formation of fumed silica, the system SiO_2 + HCl + H_2O was studied. The results obtained are shown in fig.2. To check the influence of the absence of hydrochloric acid molecules on the interactions between silicon dioxide molecules and water molecules, during the formation of fumed silica, the system SiO_2 + H_2O was used. The results are shown in fig. 3. It is obvious that without the presence of HCl, water molecules hardly form hydroxyl shells in the silica system.

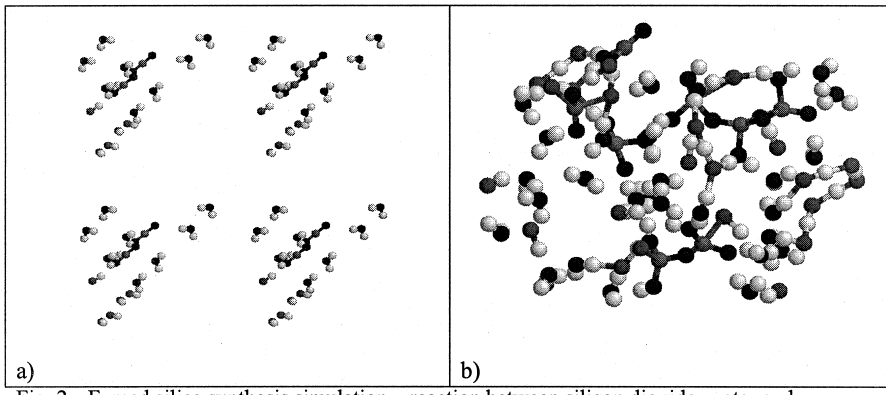

Fig. 2. Fumed silica synthesis simulation – reaction between silicon dioxide, water and hydrochloric acid molecules. Left fig. a) – starting structure, right fig. b) – final structure.

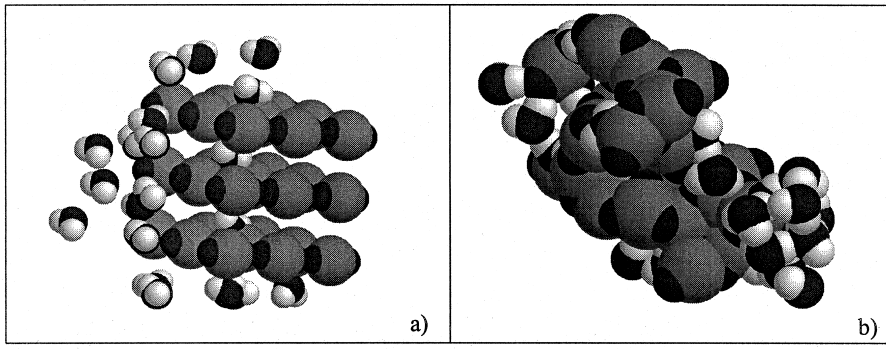

Fig. 3: Fumed silica synthesis simulation – reaction between silicon dioxide and water molecules. Left fig. a) – starting structure, right fig. b) – final structure.

The analysis of these four systems shows that hydrochloric acid molecules play an important role during the synthesis of fumed silica: They catalyze the hydroxylation

process of the silica surface. Without hydrochloric acid molecules, the finale structure of fumed silica will contain only H-bonded water molecules, at one-coordinated oxygen atoms or coordinated to silicon atoms. In the presence of hydrochloric acid molecules the barrier of hydroxylation reaction decreases, and there is no need for a chemical reaction pathway method to simulate the hydroxylation reaction of the fumed silica surface. Therefore, hydrochloric acid promotes partial hydroxylation of silica protoparticles. Other unsaturated parts of silica protoparticles may react together to form primary particles with fully hydroxylated surfaces. This idea was supported by experimental data, showing that changing silicon tetrachloride to tetraethoxysilane, at the same flame conditions, leads to a decrease of the specific surface area by a factor of three. Without a catalyst like hydrochloric acid two water molecules can be adsorbed only by H-bonding on a silica protoparticle as it is presented in fig. 4a. A hydroxonium ion H_3O^+ with three additional water molecules does not react with a silica protoparticle and no surface hydroxylation occurs. The water molecules are adsorbed on the surface by H-bonding, only (fig. 4b). A set of hydrochloric acid and water molecules can react without chemical reaction barrier leading to partial hydroxylation of silica protoparticle surface (fig. 4c).

Carbon dioxide adsorbs on the surface (fig. 4d) with a heat of adsorption of -6.24 kcal/mol and carbon monoxide adsorbs on the surface with a heat of adsorption of -1.94 kcal/mol. Both molecules are bonded by nonspecific forces, mainly local dipole-dipole interactions, an therefore do not terminate (and stabilise) the silica surface and are easily removed. That's why the use of an oxygen-natural gas (mainly methane) flame to heat the desorber unit (removal of byproducts) in the fumed silica production process is possible.

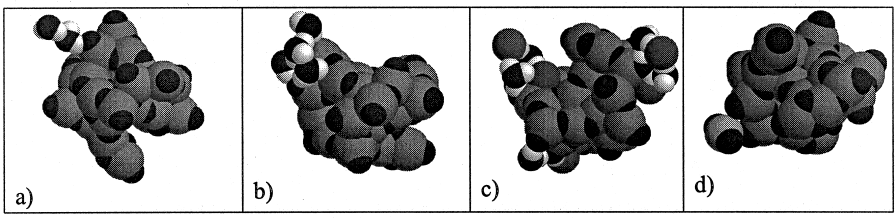

Fig. 4: Fumed silica protoparticle with different set of adsorbed molecules.
a) silica protoparticle and two adsorbed water molecules.
b) silica protoparticle and adsorbed three water + hydroxonium ion H_3O^+ molecules.
c) silica protoparticle and adsorbed six water + six hydrochloric acid molecules.
d) silica protoparticle and adsorbed carbon dioxide molecule.

Similar results have been obtained for silica clusters, which simulate crystobalit-like, but amorphous, structures. The simulations of fumed silica particle behavior have been verified using vibration spectroscopy, namely infrared (IR) and inelastic neutron scattering (INS). Details of the vibration spectra and their assignment are published elsewhere [6].

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