COMPUTATIONAL MODELING
OF AMORPHOUS SILICA.

2. MODELING THE INITIAL STRUCTURES.
AEROSIL

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A qualitative algorithm for constructing large clusters of aerosil model structures is used. According to this algorithm and the classification of amorphous silicas, aerosil is classified with tectosilicas, which are characterized by close packing of silicon-oxygen tetrahedra. Two quantitative algorithms for constructing large close-packed clusters are proposed. The structures of the clusters having from 10 to 24 silicon atoms, completely optimized by quantum chemical methods, were obtained. Small, medium, and large clusters for modeling the local and collective properties of atomic and functional group packing in the aerosil structure are distinguished.

INTRODUCTION

Among dispersive silicas, aerosil is of prime importance. First, its production process is the simplest and is effectively controlled, providing good reproducibility of physicochemical properties of the product in different batches. Second, due to stability of its properties, it is widely used to investigate chemical reactions on the silica surface and modify the latter and also to make various products using this modification technology. As a result, good supports for trace amounts of fertilizers and drugs, hemosorbents, looseners, fillers, and other valuable products were obtained.

In previous studies, it was tacitly assumed that the surface of aerosil hardly differs from that of other dispersive silicas, for example, silica gel [1-3]. The choice of aerosil as an experimental object was dictated only by the high stability of its properties.

Our recent investigations of the vibration spectra ("fingerprints") of three dispersive silicas (aerosil, silica gel, and aerogel), demonstrated that they have diverse structures [4-7]. Analysis of the reasons led us to the conclusion that structural polymorphism of amorphous silica is just a manifestation of the high variability common to all solid silicates and that amorphous silicas can be classified analogously to crystal silicates [8]. In accordance with basic crystal chemical principles and the classification of silicates, aerosil should be regarded as amorphous tectosilica, silica gel as amorphous cyclosilica, and aerogel as amorphous polysilica [9]. Thus aerosil ceased to be a model of all silicas and acquired individuality. From this viewpoint, the computational modeling of its structure and adsorption is no longer focussed on elucidating its properties as amorphous silica but is aimed at investigating it as amorphous tectosilica.

Computational modeling of structure and adsorption of aerosil consists of the following steps:
1) constructing the initial structures of polyatomic nanometer-sized clusters for computational modeling;
2) computational modeling of the cluster structure by semiempirical quantum chemical methods;
3) computational modeling of cluster adsorption with respect to water and ammonia molecules;
4) calculating the doubly amplitude-weighted density of vibration states of the clusters and comparing them with experimental values obtained by inelastic neutron scattering.

The main principles of computational modeling and the algorithm for constructing model structures, based on classification of dispersive silicas by analogy with that of crystal silicates, are presented in the first publication of this Institute of Surface Chemistry, Ukrainian Academy of Sciences. Russian University of Peoples' Friendship. Translated from Zhurnal Strukturnoi Khimii, Vol. 35, No. 3, pp. 16-26, May-June, 1994. Original article submitted May 25, 1993.
series [9]. In this paper, the qualitative algorithm is used to construct the initial clusters of aerosil model structures.

INITIAL STRUCTURAL MODELS OF AEROSIL

Before constructing the initial clusters, it is useful to define small, medium, and large clusters, making them compatible with key notions of crystal chemical fragments and their packing types depending on the structural class of the compound under study. The [SiO₄] tetrahedron is the main structural fragment of silicates and silicas. This is just the fragment that is usually considered in computational modeling (see, for example, [10-12]). However, this model structure is absolutely inadequate to describe the properties of dispersive silicas because of their structural polymorphism. Therefore we introduce several definitions which we used earlier in the computational modeling of this class of substances. A small cluster is defined as a structural model of a peripheral (subsurface) functional group. A medium-sized cluster must reproduce the packing of small clusters according to classification of their structure and the short-range distribution of atoms. A large cluster in an ideal case is meant for modeling the correct volume structure of the substance and surface distribution of functional groups. Evidently, these notions are better defined when applied to specific objects.

Since aerosil is amorphous tectosilica, the clusters modeling its framework should have a close-packed framework structure. The close-packed structures of crystal silicas are known to contain siloxane chain cycles with few members: four-membered cycles in quartz [13] and six-membered cycles in cristobalite [14] and tridymite [15].

Structural models of individual small cycles are given in Fig. 1. They were obtained by complete AM1 optimization using quantum chemical programs of the CLUSTER-Z1 package [16]. These and subsequent calculations were performed on a PC AT 386/387 (33 MHz) computer. The clusters are presented in two projections so that the “side view” (A) corresponds to their minimal, and the “top view” (B) to their maximal size.

While in Si₃ silicon atoms lie exactly in one plane, in other clusters silicon cycles are also close to planar. By contrast, large clusters with more than 6 silicon atoms have a distinctly nonplanar structure, which is well seen from their “side view” projections presented in Fig. 2A. Therefore it is clear that the “faceted” planes of a dense volume structure are conveniently constructed from small “rigid” cycles shown in Fig. 1. A structure constructed from large cycles would inevitably be looser. We will consider such structures in the next publication of this series, which deals with model clusters of silica gel [17].

Thus, the model of the volume structure of aerosil represents polyhedra whose edges are formed by small

![Fig. 1. Small cycles of silicon-oxygen tetrahedra Siₙc (AM1). Here n denotes the number of silicon atoms in the cycle. 1) Si₃c (18), 2) Si₄c (24), 3) Si₅c (30), 4) Si₆c (36). The structure optimization method and the number of atoms in the cluster are given in parentheses. A and B are two projections (see the text).](image-url)