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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The research performed in this contract was aimed at applying the MD computer simulation technique to the study of the interaction of water molecules with vitreous silica surfaces in order to determine the effect of local substrate structure on adsorption of water molecules, silanol formation, and clustering.

Interaction of Water with the Vitreous Silica Surface
An Atomic Level Description

FINAL REPORT

Stephen H. Garofalini

DECEMBER 20,1990

DAALO3-86-K-0047

RUTGERS UNIVERSITY

The interaction of water with oxide glass surfaces is important in a number of areas such as optical fiber technology, fracture behavior, glass corrosion, and sol-gel technology. Although there have been many experimental studies of water/glass interactions, all of these studies gather data over large number and time averages and molecular level behavior must be inferred. Quantum chemical calculations provide atomic level descriptions of molecular behavior, but are limited to static assemblies of very small numbers of atoms. Molecular dynamic (MD) computer simulations provide a bridge between the small static systems used in the quantum chemical calculations and microscopic, averaged properties observed in experimental studies.

The research performed in this contract was aimed at applying the MD computer simulation technique to the study of the interaction of water molecules with vitreous silica surfaces in order to determine the effect of local substrate structure on adsorption of water molecules, silanol formation, and clustering.

SUMMARY OF IMPORTANT RESULTS:

A new multibody potential for describing silica was developed during this work. This provided the correct description for the silica substrate which was used in the deposition studies. Simulations of dry silica surfaces gave structures which coincided with the averages observed in experimental data of dehydroxylated silicas. Bonding defects and strained ring structures were observed in the surfaces and were expected to be highly reactive with water molecules.

In order to bring water molecules into the simulations, reasonable interatomic potentials had to be developed to describe the O-H, H-H, and Si-H interactions. These potentials also had to be consistent with our already developed Si-O, Si-Si, and O-O potentials (silica potentials). We simulated the interactions between silicic acid molecules (H_4SiO_4) and H_2O molecules and compared our results to the available quantum chemical calculations of these interactions. Our results gave structures and energies similar to the quantum calculations and therefore enabled us to study larger systems and surfaces.

Using these combined potentials, we simulated the formation of the silica

surface in the presence of a water vapor. Results showed the anticipated rupture of the most strained Si-O-Si siloxane bonds to form silanols (Si-O-Si + HOH ---> Si-OH + Si-OH), removal of the most reactive defect sites in the silica surface, the formation of the correct number of silanol sites, and even the correct number of geminal silanols. Those water molecules which did not react with the surface were hydrogen bonded to it via the surface silanols. These results are consistent with our current knowledge of this system, indicating the applicability of using these simulations in molecular studies of silica surfaces.

We also saw a heretofore unrecognized reaction in which the rupture of a siloxane bond by a water molecule created the expected two silanols, but one silanol was 10-15Å away from the initial reaction site (site of adsorption of the water molecule). This reaction was caused by a migration of the bond rupture process away from the initial reaction site. This migrating bond rupture process was caused by the presence of a second, non-reacting water molecule in the vicinity of the tetrahedra adjacent to the initial reaction site. The importance of this result is that our common view of the rupture of a siloxane bond by a water molecule is incomplete; the migrating bond rupture process gives the correct two silanols for every siloxane bond broken by the water molecule, but indicated that those silanols need not be adjacent to each other as had previously been assumed. It also indicates that any feature which distorts the neighboring tetrahedra may cause a bond rupture process to migrate away from the initial rupture site, regardless of the cause of the rupture. These ideas may have implications in the oxidation of silicon in the presence of water vapor or in current Raman/ESR studies of defects in silica fibers.

In addition, because of our ablility to simulate the molecules mentioned above, we were also able to evaluate polymerization of silicic acid molecules in a simulation of condensation in a sol-gel process. Results were again consistent with expectations based on experimental or quantum chemical results.

The details of the above-mentioned work can be found in the publications listed below.

PUBLICATIONS IN REFEREED JOURNALS RESULTING FROM THIS SUPPORT:

"Water Induced Relaxation of the Vitreous Silica Surface" B. P. Feuston and S. H. Garofalini, J. Applied Physics 68 (1990) 4830-4836.

"Molecular Dynamics Simulations of Silica Surface Structure and Adsorption of Water Molecules", S. H. Garofalini, J. Non-Cryst. Sol. 120 (1990) 1-12.

"Onset of Polymerization in Silica Sols, B. P. Feuston and S. H. Garofalini, Chem. Phys. Lett. 170 (1990) 264-270.

"Oligomerization of Silica Sols" B. P. Feuston and S. H. Garofalini, J. Physical Chemistry 94 (1990) 5352-5356.

"Topological and Bonding Defects in Vitreous Silica Surfaces", B. P. Feuston and S. H. Garofalini, J. Chem. Phys. 91(1989) 564.

"The Structure of Sodium Trisilicate Glass Via a Molecular Dynamics Simulation Employing Multibody Potentials", R. G. Newell, B. P. Feuston, and S. H. Garofalini, J. Materials Research, 4 (1989) 434.

"Empirical Three-Body Potential for Vitreous Silica", B. P. Feuston and S. H. Garofalini, J. Chem. Phys., 89 (1988) 5818.

PRESENTATIONS:

Presentations were made during each year of the support period and were documented in the progress reports. A summary is given below.

American Ceramic Society Annual Meetings and Division Meetings
Materials Research Society Spring and Fall Meetings

Seventh Roermond/Third European Conference on Catalysis (invited)

Gordon Conference on Water Interactions with Solids Surfaces (invited)

Gordon Conference on Glass (invited)

Goldschmidt Conference on Geochemistry (invited)

10th International Conference on Glass Science (invited)

SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT:

Post-Doctorate Researcher:

Bradley Feuston

Graduate student (partial support):

Heidi Melman

Undergraduate students:

Gene Bohensky

Alfred Kaulius

Senta Fowler

Richard Newell