281g Density Functional Theory Investigation of the Hydrolysis and Condensation of Polysilicic Acid: a Mechanistic and Energetic Analysis

Charles L. Schaffer and Kendall T. Thomson

The discovery of new materials is often a heuristic pursuit. Today, many nano-porous materials with functionality beyond their traditional roles of catalysis, ion exchange, and separations are discovered quite serendipitously. The need for a systematic synthesis approach has kept this subject an area of active research. With the advent of modern computational and experimental techniques and the increasing speed of computers, research has focused on obtaining a detailed understanding of the synthesis mechanism. To this end, we conducted a reaction path analysis of the hydrolysis and condensation reaction of various polysilicic acid species using density functional theory (DFT). We considered clusters containing up to eight silicons: the dimer Q_2^1, the linear trimer $Q_2^1Q_1^2$, the cyclic-trimer Q_3^2, the branched cyclic-trimer $Q_2^2Q_1^3Q_1^1$, the cyclic-tetramer Q_4^2, the six silicon prism Q_6^3, and the octamer cage Q_8^3. In particular, we elucidate the reaction mechanism as well as report the energies and configurations of the reactive intermediates and transition states along the reaction pathway for each cluster under neutral, acidic, and basic conditions – both in vacuo and incorporating hydration effects.

Previous studies of these systems have lead to a variety of proposed mechanism with two being accepted as most probable: the first involving an S_N2-type attack and the second occurring through a ‘flank' or lateral attack. Our results show the S_N2-type or ‘backside' attack with inversion of the molecular geometry to be the lowest energy reaction pathway for every species studied. In addition, we found that in all cases the reaction proceeds through the formation of a stable pentacoordinated intermediate. The results obtained from thermochemical analysis of each reaction under varying ionic conditions provide valuable insight into the chemical behavior of these clusters, such as the preferential formation of linear trimer species prior to trimer rings and the marked absence of stable hydrolysis products for neutral clusters larger then six silicons. With the ultimate goal of modeling these clusters in solution, we present first the results of our calculations on clusters in vacuo followed by a discussion of our techniques and a comparison of conformational and energetic changes that occur when hydration effects are incorporated into the model. In particular, we are interested in the effects the presence of excess water has on the hydrolysis and condensation rate-limiting activation barriers.