

Reaction Profiles of Phosphate Nucleation on Silica Glass

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The nucleation of calcium phosphate on silica glass surfaces has been elaborated with density functional calculations combined with molecular dynamics simulations on model systems. The two reactions examined comprise the formation of Si–O–P bridges, i.e. covalent linkages between the silica surface and the phosphate ions. Protons seem to catalyse the formation of the linkages in the sense that reaction barriers are decreased significantly and reactions energies become negative.

We attempt to determine potential reaction pathways for the nucleation of CaHPO₄ on silica (SiO₂) glass surfaces [1]. Our contributions are density functional calculations combined with classical molecular dynamics simulations (DFT MD) performed on model systems which consist of a silica surface, CaHPO₄ and water molecules (Fig 1). The molecular dynamics approach employed [2] allows to calculate profiles of the Helmholtz free energy, ΔA , along a defined reaction coordinate, ϕ via thermodynamic integration. Note, the atoms move on the Born-Oppenheimer energy surface. The SiO₂ glass surface is represented by a periodically extended, i.e. crystalline surface. The SiO₂ scaffold consists of linked trisiloxane rings. The latter are common defect site in silica glasses and are apparently the preferred adsorption sites of calcium ions.

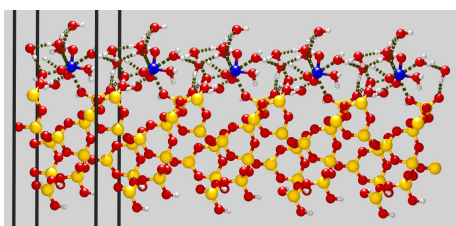


Figure 1: Slab model to describe a silica glass surface which interacts with CaHPO₄ and water molecules. The solid lines represent the slab unit cell. Color code: yellow – Si, red – O, blue – P, green – Ca, white – H.

The two reactions examined and the corresponding free energy profiles obtained are depicted in Fig. 2. In both reactions one Si atom of a trisiloxane ring is attached by an oxygen atom of the nucleophile HPO₄²⁻. The result is the formation of a covalent Si–O–P linkage and the opening of the trisiloxane ring. The difference between the two reactions is that in the second scheme (Fig. 2b) the oxygen atom of the trisiloxane ring, O_R is attached by a proton.

For every point of the free energy profiles an DFT MD simulation is performed where the reaction coordinate, ϕ , is constrained to the appropriate value. In each MD simulations the model system is propagated for 2–5 ps with a time step of 0.5 fs at T=300 K.

The two energy profiles have the same topology: three energy minima separated by two energy barriers. Hence, the reactions proposed have a two-step mechanism. The metastable states enclosed by the two barriers (5C) are assigned to structures with penta-oxo-coordinated Si atoms (not shown). The proton attached to O_R has a catalytic effect on the ring opening. On one hand the proton reduces both

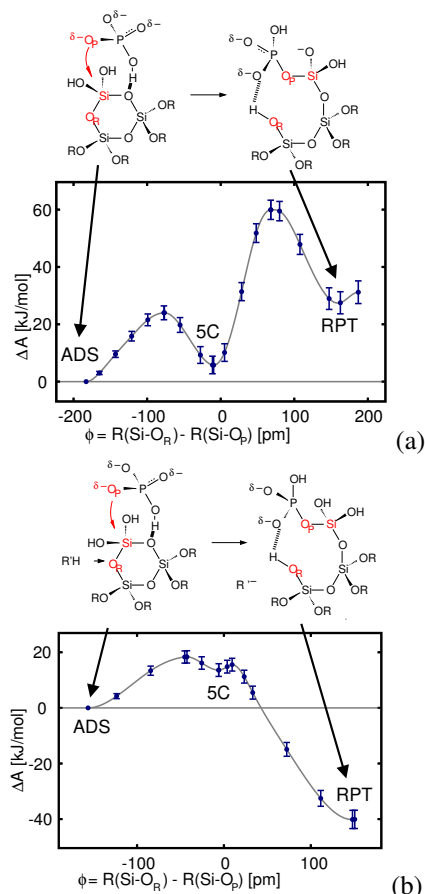


Figure 2: Reactions schemes examined and the corresponding calculated profiles of the Helmholtz free energy ΔA along the reaction coordinate ϕ . The symbols R and R' represent the remaining part of the SiO₂ scaffold and the anion of a soft acid.

energy barriers significantly. On the other hand it turns the reaction from an endothermic, $\Delta A > 0$ into an exothermic one, $\Delta A < 0$.

- [1] R. Windiks and B. Delley, *Calcium Phosphate Nucleation on Silica Glass Surfaces: Molecular Dynamics Simulations*, PSI NuM Annual Report (2003).
- [2] R. Windiks and B. Delley, *J. Chem. Phys.* **119**, 2481 (2003).