Self-catalyzed water reactions with silica

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Introduction

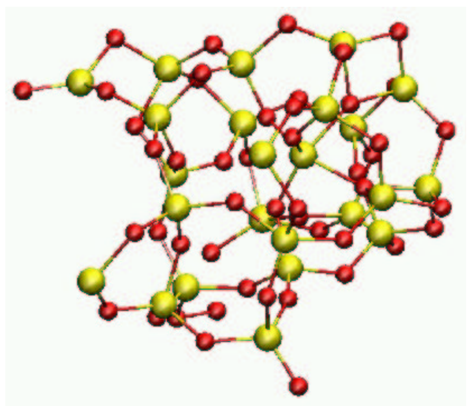
Silica (SiO_2) is one of the most abundant minerals on the Earth's surface, and is an important technological material. In its applications, the role of water and how it changes the properties of silica is very important. Here first principle molecular dynamics simulations are used to study the reaction process between silica and water.

Simulation Methods

SIESTA code [1]:

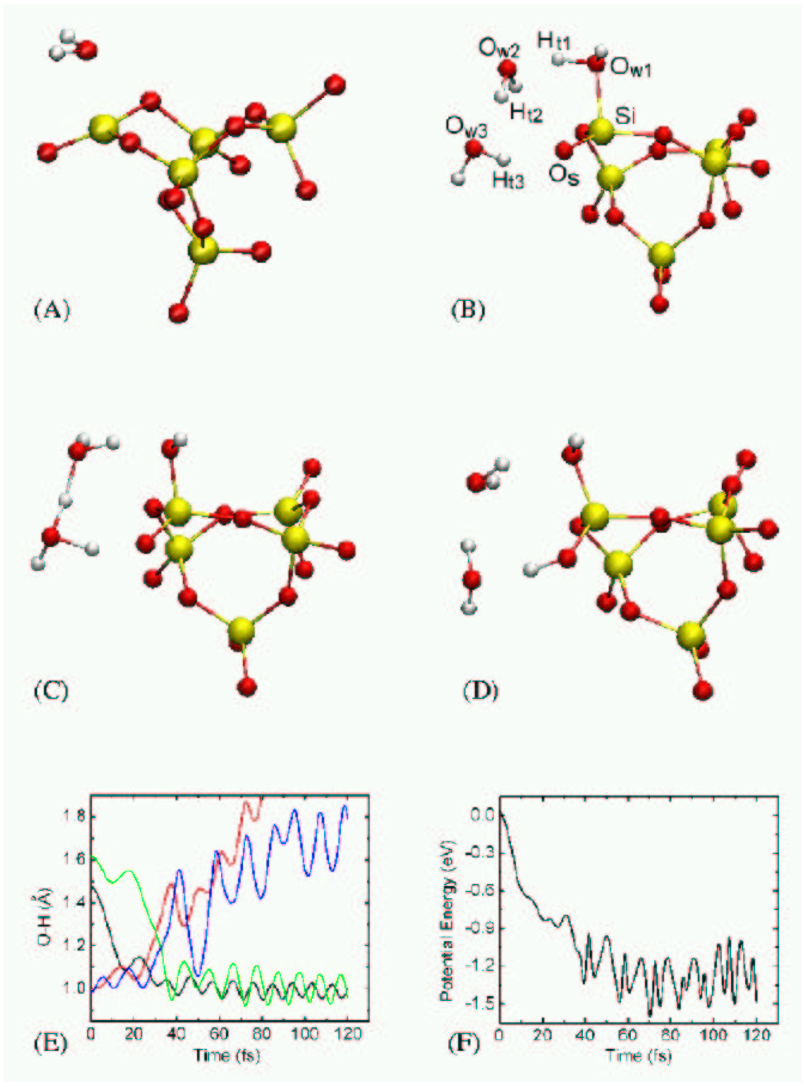
- using the Linear Combination of Atomic Orbitals basis
- implementing the Density Functional Theory in the Generalized Gradient Approximation

Silica Model



- Obtained by high-temperature simulated annealing of a $(SiO_2)_{24}$ cluster which are cut from a perfect α-quartz bulk system.
- Defects sites on the suface: two-coordinated silicon atoms, three-coordinated silicon atoms and singly-coordinated oxygen atoms.

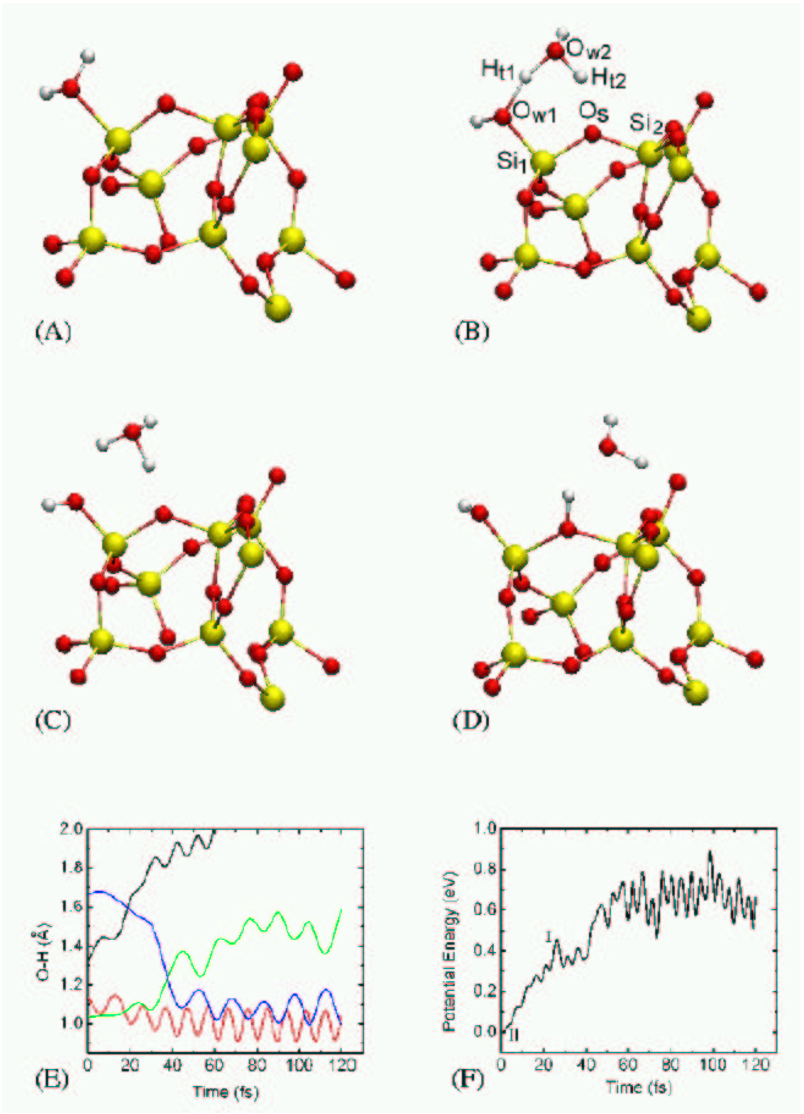
Reaction 1



Hydrolysis process of a three-coordinated silicon atom connected with a one-coordinated oxygen atom by water trimer.

- (A) A single water molecule is physisorbed on the silicon atom.
- (B) The initial configuration of the system before reaction.
- (C) and (D) are the structures at 33 fs and 130 fs, respectively.
- (E) The time evolution of the length of bonds O_{w2}-H_{t1} (black), O_{w2}-H_{t2} (red), O_{w3}-H_{t2} (green) and O_{w3}-H_{t3} (blue).
- (F) The time evolution of the potential energy of the system.

Reaction 2



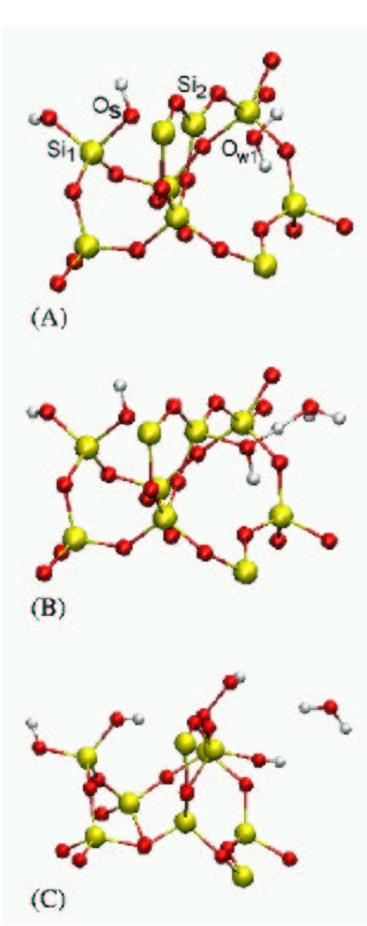
Hydrolysis process of a three-coordinated silicon atom by water dimer.

- The optimizing structures with one (A) and two (B) water molecules on the silicon defect site.
- The structures at 30 fs (C) and 254 fs (D) after heating the structure in (B) to 150 K.
- (E) The time evolution of the length of bonds O_{w1}-H_{t1} (black), O_{w2}-H_{t1} (red), O_{w2}-H_{t2} (green) and O_s-H_{t2} (blue).
- (F) The time evolution of the potential energy of the system.

References

[1] J. M. Sole, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter 14, 2745 (2002).

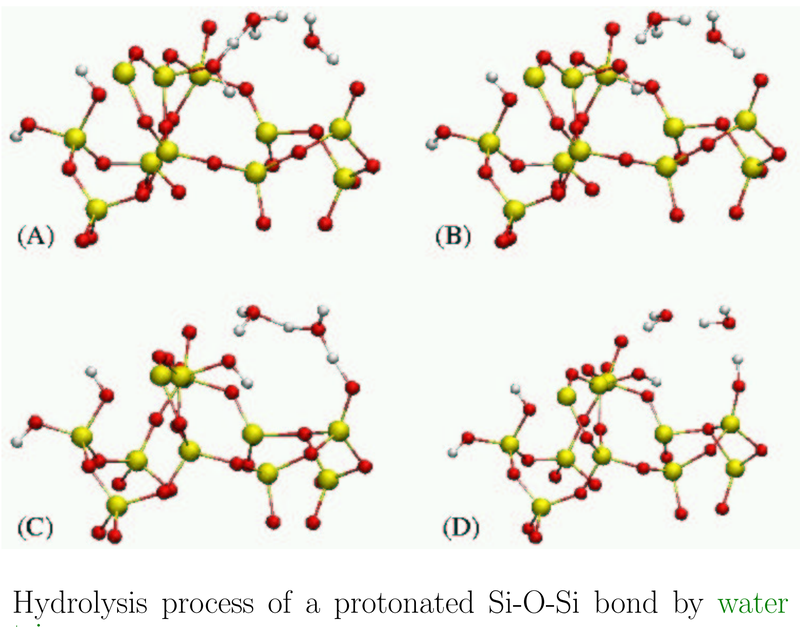
Reaction 3



Hydrolysis process of a protonated Si-O-Si bond by water dimer.

- Optimizing structures after adding one (A) and two (B) water molecules around Si_2 atom.
- (C) The structure at 350 fs after heating the system (B) to 150 K.

Reaction 4



Hydrolysis process of a protonated Si-O-Si bond by water trimer.

- (A) The initial configuration before reaction.
- The structures at 8 fs (B), 94 fs (C) and 140 fs (D). After 76 fs, the system was heated to 150 K.

Results

- Reaction between water and silica could occur through hydrogen transfer at low temperature.
- Addition of extra water molecules can reduce the activation energy of the hydrolysis reaction.
- Water stabilizes the transition states through hydrogen bonding and participates in hydrogen transfer.