GRRM 法による Si(001)表面上の酸素吸着構造の解析

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In the present study, we apply the GRRM method to examine the surface reaction process of oxygen on Si(001)-(2 × 1), focusing on the reaction pathway of one O atom on Si_9H_{12} as a model system. This cluster model (Si_9H_{12}) has been used as the minimum structure representing a Si(001)-(2×1) surface for studies on O, N, OH, NH, BH, H_2O,CHOH,and CHNH.

Methods

Methods for GRRM on PES can be divided into uphill walking and downhill walking along reaction pathways. Although downhill walking from TS to EQor DC along the minimum energy path or IRC_{20} can be made by conventional methods such as the steepest decent method, uphill walking along a reaction route from EQ toward TS or DC has long been a major obstacle to obtain reaction route map on PES.

Results

Structural, energetic, and mechanistic features of the initial steps of the reaction of an O atom with Si(001)-(2×1) were modeled by the use of a Si_9H_{12} + O system. Transition states (TSs) and equilibrium structures (EQs) as well as dissociation channels (DCs) were systematically searched using a global reaction route mapping (GRRM) technique on the potential energy surface (PES) based on the scaled hypersphere search (SHS) algorithm. The first six low-energy structures were consistent with known structure models for oxygen adsorption on the dimer of Si(001)-(2×1). Other structures with higher energies could be well interpreted as intermediates leading toward reaction paths for migration/dissociation occurring at high temperatures.

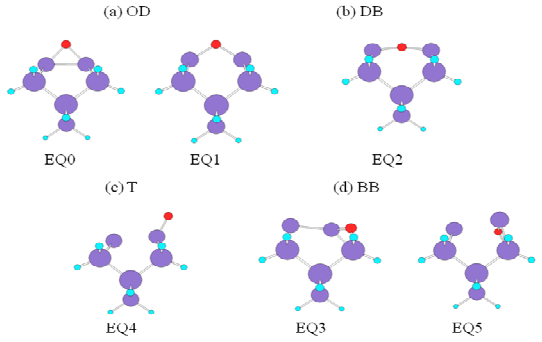

Figure 1. Atomic structures of oxygen-adsorbed surface: (a) on-dimer (OD), (b) dimer bond (DB), (c) on-top (T), (d) backbond (BB).

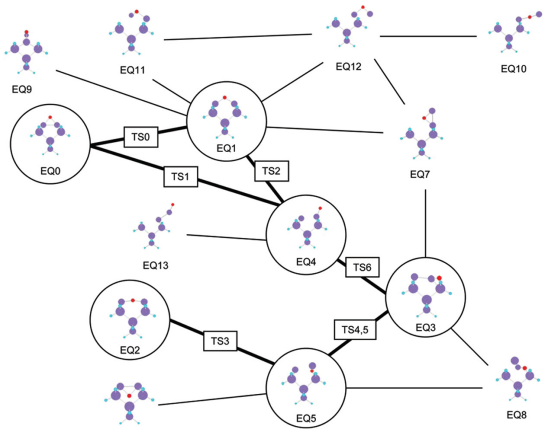

Figure 2. Connections between obtained EQ on the PES for Si-O-Si species in the Si_9H_{12} cluster model.

Conclusion

The first six low-energy EQs(EQ0-EQ5) were consistent with reported structures in the literature, corresponding to structures realized in the solid phase. The structures with the energy higher than 4.14 eV, compared with that of EQ0, should represent intermediate structures leading toward migration of SiO species on the surface, desorption in the form of SiO or migration of O into the substrate, corresponding to dynamical structures occuring at high temperatures. To obtain adequate energy levels, it is found that incorporation of lattice relaxation is indispensable. The present results suggest that the GRRM method is an effective means to assess surface dynamical processes, which would be important in catalytic reactions under realistic conditions