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QCMD study to investigate the Influence of the surface hydrogen vacancy for the dissociative adsorption of hydrogen on Pd (111) surface

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【Introduction】

How molecules adsorb and dissociate under dynamics conditions is often poorly understood. Recently, Mitsui et al. showed by scanning tunneling microscope analysis, which is contrary to conventional thinking [1], that two-vacancy sites seems inactive, and that aggregates of three or more hydrogen vacancies, are required for efficient H_2 dissociation. Our UA-QCMD results successfully demonstrate the dynamics of dissociative adsorption of hydrogen on Pd (111) surface which clearly supports the STM study of Mitsui et al. Furthermore, theoretical methods based on quantum chemistry can give us some electronic and atomic level information that cannot easily be obtained by experimental methods.

【Method】

The program, *New-Colors* was used for quantum chemical calculation for energy, charge and atom populations. Another program, *New-Ryudo* was used for dynamics calculation using potential parameters optimized by using *New-Colors*. Ultra accelerated quantum chemical molecular dynamics under the periodic boundary condition was performed based on the combination of those two programs.

【Result and discussion】

The dissociative adsorption of H_2 was simulated applying the UA-QCMD to a target model of Pd (111) surface. In this model, Pd (111) surface consists of 96 Pd atoms, which was prepared with pre-adsorbed hydrogen. Here five different models were prepared on the basis of surface hydrogen vacancy. Five different models were like, saturated surface, which was fully covered with fcc site adsorbed hydrogen, next four models were prepared by removing 2, 3, 4, 5 adsorbed hydrogen atoms. In Figure 1(a) Pd (111) surface was fully saturated with hydrogen where molecular dynamics calculation showed that H_2 molecule without adsorbing departs from the surface at 280 fs. In Figure 1(b) in case of two H vacancy, UA-QCMD calculation shows that no dissociation occurs but hydrogen molecule adsorbed on the surface in molecular form at 165 fs. In case of three H vacancy, Figure 1(c) UA-QCMD calculation shows that dissociative adsorption of hydrogen molecule occurs after at 562 fs. Two more similar calculations were performed for 4 and 5 hydrogen vacancy surfaces, which also confirm the dissociative adsorption of hydrogen on Pd (111) surface. Comparison of different electronic properties PDOS, atomic charges, repulsion energies further confirm the dissociative adsorption of hydrogen required at least three or more hydrogen vacancy. Our UA-QCMD results successfully demonstrate that two-vacancy sites seem inactive, and that aggregates of three or more hydrogen vacancies, are required for efficient H_2 dissociation.

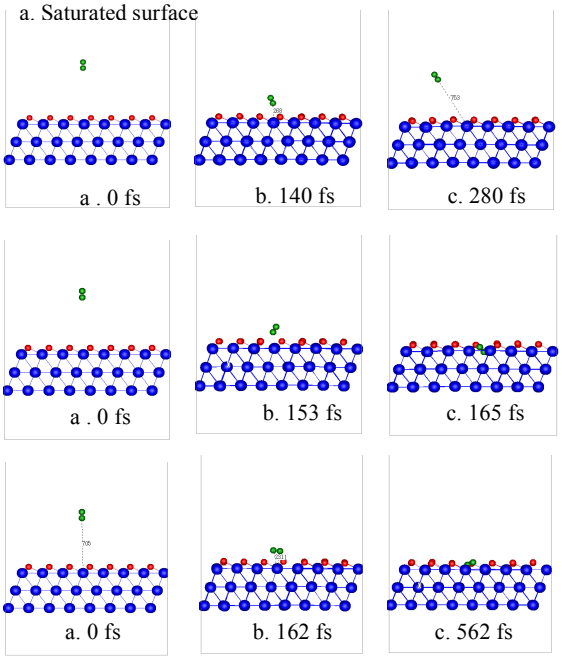

Fig.1 Dissociative adsorption of hydrogen and influence of surface hydrogen vacancy

【Reference】

[1] Mitsui, T.; Rose, M. K.; Fomin, E.; Ogletree, D. F.; Salmeron, M. *Nature*, **422** (2003), 705.