

論文の内容の要旨

論文題目:**First-principles Study on Hydrogen Adsorption on Platinum Surfaces**

(白金表面への水素吸着の第一原理計算)

トランティテュハン

(TRAN THI THU HANH)

In recent years, much attention has been paid on hydrogen (H) atoms and molecules on a solid surface interfaced with liquid, especially H at the platinum (Pt) - solution interface. Many properties, including adsorption, diffusion, and vibration have been intensively studied. In spite of such efforts, however, theoretical understanding is still insufficient and there is much room for theoretical advancement. In this thesis the focus is put on removing known theoretical inconsistency regarding H on the Pt(111) surfaces and, through detailed comparison with experiment, justify the thermodynamic approach based on the density functional theory (DFT). The approach is then used to explore H on the Pt(110) surfaces. The present theoretical work is motivated by the aforementioned inconsistency regarding the most stable H site on the Pt(111) surfaces. Some calculations predicted the fcc site as the most stable one while others predicted the top site. Experimentally the fcc site was conjectured most stable from the electrochemical measurements while spectroscopic signal from the top site can be detected. Detailed comparison between theory and experiment is a key to settle this problem but most theory used very small lateral cell and provided only zero temperature properties, which cannot be directly compared with the measured thermodynamic data. Karlberg et al. [1] performed a Monte Carlo simulation using a parameter determined from DFT calculations but only the fcc site was assumed to exist. Our DFT calculation for H/Pt(111) reveals that the H adsorption energy depends very sensitively on the parameters adopted for the calculation and, to obtain reliable energy, large number of k-points and many Pt layers are required, which are much larger than those adopted by many foregoing researches. Then performing converged DFT calculations, the results were used to construct a

lattice gas model with which we perform Monte Carlo simulations. The obtained isothermal adsorption properties were used to calculate the g-value, which reflects the H-H interaction, as a function of the H coverage. The obtained g-value is in good agreement with the precise measurement, with the effective H-H interaction being underestimated only by 10%. It is emphasized that the theory is most stringently tested by this comparison. From the comparison dominance of the fcc site is confirmed. The good agreement with experiment possibly suggests minor contribution of the hydration effect neglected in the present model. This theoretical approach is then applied to H on the missing row Pt(110)-(1×2). The dominant site is found to be the bridge site on the ridge, which is in agreement with the LEED experimental and DFT theoretical results found in the literature. The calculated g-value is in reasonable agreement in the lower coverage $\Theta_H < 1/3$ conditions and in fair agreement for $\Theta_H > 1/2$, while the theory predicts a distinct peak at $\Theta_H \approx 1/3$ although no such peak appears experimentally. The inconsistency with experiment will indicate that the present modeling with the missing row structure only is questionable and further calculation is then necessary to explain the experiment.

[1] G.S. Karlberg, T.F. Jaramillo, E. Skúlason, J. Rossmeisl, T. Bligaard, and J.K. Nørskov, Phys. Rev. Lett. 99 (2007) 126101.