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パラジウム(110)表面における水素吸収の機構  
Mechanism of Hydrogen Absorption at the Palladium (110) Surface

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Despite its enormous technological relevance for hydrogen purification, storage, and hydrogenation catalysis, the exact atomic-level transportation mechanism of hydrogen (H) from the gas phase across the surface into the metal interior during H<sub>2</sub> absorption at palladium (Pd) surfaces has still not been clarified. The actual penetration mechanism and the role of surface-adsorbed hydrogen in the absorption process remain disputed.

The decisive elementary step in the H<sub>2</sub> absorption mechanism has often been envisioned as monatomic diffusion of chemisorbed H atoms into interstitial sites just underneath the Pd surface. *Ab-initio* (DFT) calculations, however, indicate that the activation barrier for this monatomic diffusion is much (>0.3 eV) larger than the activation energy of H<sub>2</sub> absorption (<0.1 eV), ruling out monatomic in-diffusion of chemisorbed H as the rate-limiting step. A second issue is that chemisorbed D on Pd(100) and (111) surfaces appears to be ‘bypassed’ during H<sub>2</sub> absorption and subsequent desorption of absorbed H, which has been attributed to exclusive absorption at defect sites. A microscopic explanation for the small activation energy has yet been lacking. We therefore investigated the H<sub>2</sub> absorption mechanism at a structurally well-characterized Pd(110) surface with H depth profiling via <sup>15</sup>N nuclear reaction analysis and thermal desorption spectroscopy with isotope (H,D) labeled surface hydrogen.

We thus discovered that on Pd(110) two distinct H absorption pathways exist that at low temperatures (<145 K) populate two hydride states of distinctly different depth distributions: Near-surface hydride nucleates after localized H<sub>2</sub> absorption at minority sites (defects), whereas nucleation of bulk Pd hydride results from absorption in the *regular* Pd(110) terrace area. The latter is observed for the first time at a Pd single crystal and suggests that the absorption process is strongly structure-sensitive. Unlike the previously suggested ‘bypassing’ scenario, both absorption pathways effectively transfer chemisorbed H below the surface and replace it by the gas phase isotope in a process that requires only very little (< 100 meV) activation energy.

We discuss these findings in the framework of a novel absorption mechanism, in which H<sub>2</sub> dissociates at vacancies in the H chemisorption layer and thereby generates ‘excess’ H atoms, which exist in a state of high potential energy on the H-saturated Pd surface. Such excess H atoms may elicit penetration of pre-adsorbed H into the subsurface while simultaneously reoccupying the chemisorption sites that the latter vacate. Theoretical calculations suggest that either this *concerted* penetration or the H<sub>2</sub> dissociation on the H-saturated Pd surface may be the rate-limiting step of the H<sub>2</sub> absorption process [1].

[1] S. Ohno, M. Wilde, K. Fukutani, *J. Chem. Phys.*, *submitted*.