

Pd (110) 表面における水素吸収の配位反応機構

Concerted reaction mechanism of hydrogen absorption at palladium (110) surfaces

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The hydrogen absorption mechanism at palladium (110) single crystals is elucidated by quantitative hydrogen depth profiling with nuclear reaction analysis and thermal desorption spectroscopy. These techniques allow for a clear experimental distinction of surface-adsorbed hydrogen species from subsurface-absorbed hydrogen that may exist in near-surface Pd hydride and hydrogen bulk solid solution phases, respectively [1,2]. Surface adsorption of H on Pd(110) saturates rapidly by small H₂ dosages below 200 K and induces a characteristic (1×2) pairing-row reconstruction on which 0.5 monolayer (ML) H is bound 0.25 eV less strongly than the low coverage chemisorption state (1 ML, 0.51 eV/H). Absorption of H proceeds more slowly, requiring larger exposures of the H-saturated surface to H₂. Below 145 K and <10⁻³ Pa H₂, hydride nucleates beneath the surface; otherwise the absorbed hydrogen is distributed into the bulk by diffusion.

By isotopic labeling (H, D) of the surface and absorbed species we discovered that the hydride and the solid solution phases are formed on two different and locally separated absorption pathways. Hydride nucleation occurs only in ~4% of the surface area (presumably at defects), where absorption is particularly rapid and no isotopic exchange by surface diffusion takes place with species adsorbed in the surrounding area.

Hydrogen absorption into the solid solution phase, on the other hand, proceeds with lower probability at regular terrace sites. Both absorption routes critically require gas phase molecular hydrogen, involve activation energies below 100 meV, and locally replace pre-adsorbed H atoms with the gas phase isotope. On the basis of these findings we propose a concerted absorption mechanism in which the gas phase supplies dissociated hydrogen atoms in a state of high potential energy that elicit penetration of pre-adsorbed hydrogen into the subsurface and simultaneously reoccupy the vacated surface sites [3]. Different local efficiencies of dissociation and/or concerted penetration may account for the site specific absorption probabilities as well as for the possible role of the weakly adsorbed H state on the (1×2) reconstruction for the absorption at terrace sites, which is particular to Pd(110) and neither observed on Pd (111) nor on Pd(100).

[1] M. Wilde, M. Matsumoto, K. Fukutani, T. Aruga, *Surf. Sci.* **482-485**, 346 (2001).

[2] M. Wilde and K. Fukutani, *Phys. Rev. B* **78**, 115411 (2008).

[3] S. Ohno, M. Wilde, K. Fukutani, in preparation for *J. Phys. Chem. C*.