Hydrogen Transportation across Palladium Surfaces: Mechanism, Structure Sensitivity, and Control

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The hydrogen (H) transportation mechanism across H_2 -exposed metal surfaces is crucial for H storage and purification in hydrogen energy technology, as well as for industrial hydrogenation catalysis [1]. To elucidate the atomic-level reaction coordinate that links H₂ gas and H in the metal interior at a structurally well-defined model system, we studied the H₂ ingress into the (110) surface of an initially clean palladium (Pd) single crystal, using a unique combination of H depth profiling via ${}^{1}H({}^{15}N,\alpha\gamma){}^{12}C$ nuclear reaction analysis (NRA) [2] and thermal desorption spectroscopy (TDS) with isotope-labeled (H, D) surface hydrogen. These experiments show that the Pd(110) surface exhibits two H₂ absorption pathways, which below 145 K precipitate Pd hydride with distinctly different depth distributions and associated TDS features, i.e., a nearsurface hydride (α_1 , T_{des} = 160 K) populated through surface defects, and a bulk-dispersed phase $(\alpha_3, T_{des} > 190 \text{ K})$ formed by relatively slower H penetration at regular terrace sites [3]. The very small activation energy of H₂ absorption found at Pd(110) (< 0.1 eV) lets us exclude the common assumption that monoatomic H diffusion from chemisorption into subsurface sites (requiring at least 0.3 eV) is the rate-limiting step in the H₂ absorption process. We instead discuss either H₂ dissociation on the H-saturated Pd surface [4] or a concerted penetration mechanism (involving stabilization of weakly bound excess surface H atoms into chemisorption sites and simultaneous motion of chemisorbed H into the subsurface [5]) as possible rate determining events [3].

The H₂ absorption channel at regular Pd(110) terraces [3] stands in remarkable contrast to Pd(100) [6] and Pd(111) [7], where only defects contribute measurably to absorption. This result thus suggests that H₂ absorption kinetics are surface structure-sensitive and that Pd(110) may promote H₂ absorption due to its relative openness and atomic corrugation [3]. Experiments at even more open Pd(210), showing yet higher H₂ absorption rates, corroborate this hypothesis. Exploiting this apparent structure-sensitivity by the fact that the Pd(110) surface is susceptible to several well-defined CO-induced (de-)reconstructions, we further demonstrate the possibility to control the desorption dynamics of Pd-dissolved H (H_{abs}) through deliberate surface structural modification [8] and discuss potential implications for H storage and hydrogenation catalysis.

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