博士論文(要約)

論文題目

Investigation of hydrogen transport phenomena and catalytic olefin hydrogenation reactions at palladium surfaces

（パラジウム表面における水素輸送現象および炭化水素の触媒的水素化反応に関する研究）

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This doctoral thesis investigates 1) the microscopic mechanism of H atom transitions across metal surfaces and related hydride nucleation upon H_2 absorption, and 2) the processes that control the activity and selectivity of olefin hydrogenation reactions on metal catalysts. A Pd(110) single crystal is chosen as a structurally well-defined model system that offers facile H incorporation ability and high catalytic activity. The examined reaction is the catalytic hydrogenation of *cis*-2-butene (C_4H_8) to butane (C_4H_{10}). Providing well-controlled conditions, the H sorption and catalytic properties of the Pd(110) surface are characterized by a combination of ultra-high vacuum techniques such as Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), Temperature Programmed Desorption (TPD), Resonant Nuclear Reaction Analysis (RNRA), and Resonance-Enhanced Multiphoton Ionization (REMPI).

1. Hydrogen absorption mechanism and hydride formation at Pd(110)

As a first step, the total of five features in the complex H_2/Pd(110) TPD spectrum that sequentially develop with increasing H_2 exposure at 130 K (0.3 − 2000 L, Fig. 1) are ascribed to surface-adsorbed H states (β_1, β_2, and α_2), a near-surface hydride state (α_1), and a bulk hydride state (α_3). LEED observations and NRA H depth profiles (Fig. 2) recorded after characteristic H_2 exposures that populate the respective

TPD features enabled these unambiguous assignments.

The population rates into the absorbed H states exhibit pronounced *normal* isotope effects. This contrasts with the well-known *inverse* isotope effect of hydrogen diffusion in bulk Pd, indicating that H_2 absorption is kinetically controlled at the surface. The absorption rate-limiting step is shown to have an activation energy of <0.1 eV. This is notably smaller than the energy barrier of monatomic surface to subsurface diffusion of H atoms at Pd surfaces as which H absorption has often been imagined. This leads to the important conclusion that the actual H_2 absorption process is not a spontaneous in-diffusion of chemisorbed H species.

The NRA and TPD data reveal that H_2 absorption below 145 K leads to formation of two Pd hydride phases that differ in their depth extension below the surface. TPD experiments with isotope-labeled surface hydrogen were performed to clarify the absorption mechanism. As shown in Fig. 3, a clear difference is observed in the isotopic composition of the near-surface and bulk hydride states during their growth, suggesting that these two states evolve through different pathways. Detailed analysis of the isotopic compositions reveals that the near-surface hydride is populated by penetration at surface defects, whereas the bulk hydride forms by absorption at regular terrace sites of Pd(110). A stochastic model is constructed to investigate the penetration mechanism at the atomic scale. This demonstrates that H_2 absorption proceeds with the transition of chemisorbed H species into
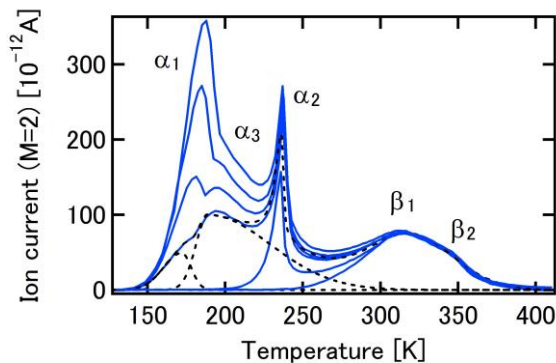
Fig. 1 Series of H_2 TPD spectra of Pd(110) exposed at 130 K to 0.3 L, 0.5 L, 500 L, 1000 L, 1500 L, and 2000 L.
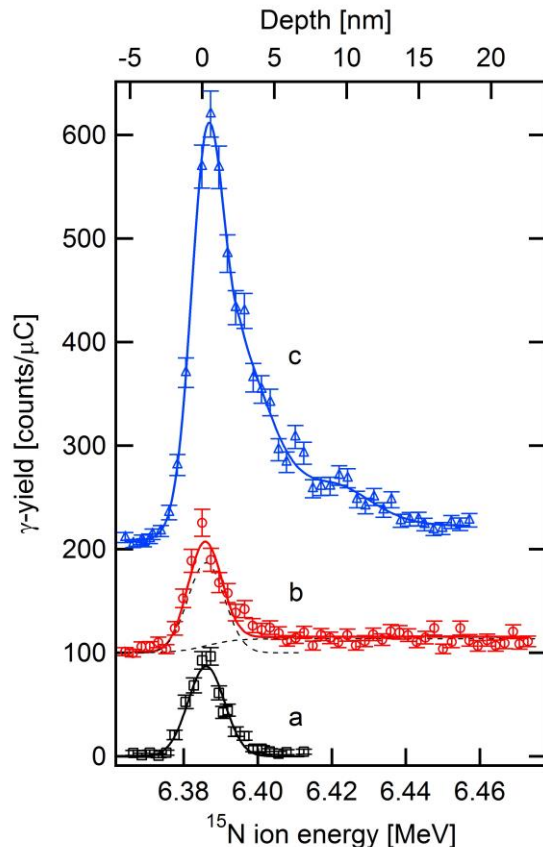
Fig. 2 NRA hydrogen depth profiles after (a) 1.3 L H_2 at 180 K, (b) 2000 L H_2 at 115 K, and (c) 2000 L H_2 at 145 K.
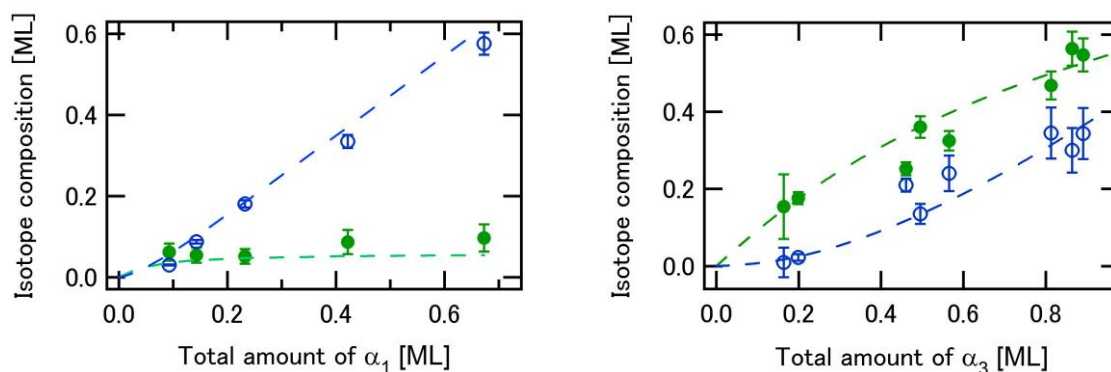
Fig. 3 Content of pre-adsorbed (filled) and post-dosed (open) isotopes in the TPD (a) α_1 and (b) α_3 state.

Pd interior while their vacated surface sites are reoccupied by dissociative adsorption of H_2 molecules. On the contrary, a mechanism in which penetrating hydrogen 'bypasses' chemisorbed H at the surface sites as proposed earlier in the literature, is incompatible with the experimental data. A novel concerted penetration mechanism is proposed, where chemisorbed H atoms penetrate the surface while excess H atoms (species weakly bound to less favorable sites (such as on-top) after H_2 dissociation on the H-saturated surface) simultaneously reoccupy the vacated surface site. The energy gain in stabilizing the excess H atom in the deep chemisorption well may partially compensate for the energy cost of transporting the pre-adsorbed H atom below the surface, which rationalizes the small (<0.1 eV) activation barrier of H_2 absorption.

To gain insight into the microscopic H_2 desorption mechanism from the Pd interior, the rovibrational state distribution of the desorbing H_2 molecules was examined by REMPI. The rotational state population in v"=0 shows non-thermal character. Higher rotational states (J>3) are more strongly populated than in thermal equilibrium with the surface whereas lower rotational states (J<3) follow a thermal distribution. These results indicate that the potential energy surface with respect to the H_2 molecular axis orientation is isotropic and that energy transfer occurs from molecular rotation to translational motion during H_2 associative desorption.

2. Reactivity of olefin hydrogenations at Pd catalysts

The catalytic hydrogenation of cis-2-butene at the Pd(110) surface was investigated by TPD and NRA measurements. As shown in Fig. 4, hydrogenation does not occur with surface-adsorbed H, but proceeds only in presence of Pd-absorbed H. Then, the butane reaction product is seen to desorb at 190 K. The butane yield dependence on the absorbed H quantity indicates that the maximum yield is limited in case that the H is distributed in the bulk, whereas the reaction yield increases proportional to the 1.1th order of the absorbed H quantity in the near-surface region.

Thus, near-surface hydride is demonstrated to provide a necessary reservoir of reactive H species. It is further remarkable that the desorption of absorbed H is shifted to almost 100 K higher temperatures in presence of co-adsorbed butene (cf. Fig. 1), so that absorbed H is enabled to participate in the reaction which takes place at ~190 K. The NRA H depth profiles in Fig. 5 show that a fraction of absorbed H still remains underneath the surface at 190 K and that this amount is larger when H_{abs} is prepared as near-surface hydride. NRA also reveals that the absorbed H completely disappears from the near-surface region at 230 K. These results allow for the conclusion that the hydrogenation reaction requires moderate heating (~190 K) to overcome the activation barrier but that excessive heating prohibits the reaction by dissipating the near-surface H into the bulk by diffusion. Consequently, only a narrow temperature window for the Pd-catalyzed hydrogenation of *cis*-2-butene exists around 190 K.

Fig. 4 shows in addition that co-adsorbed H induces a new large butene desorption feature at 186 K, which indicates that butene decomposition is suppressed. It can thus be concluded that the catalytic hydrogenation activity of the Pd(110) surface results from a synergetic effect, in which H activates the butene adsorption state and the reaction proceeds with active absorbed H specie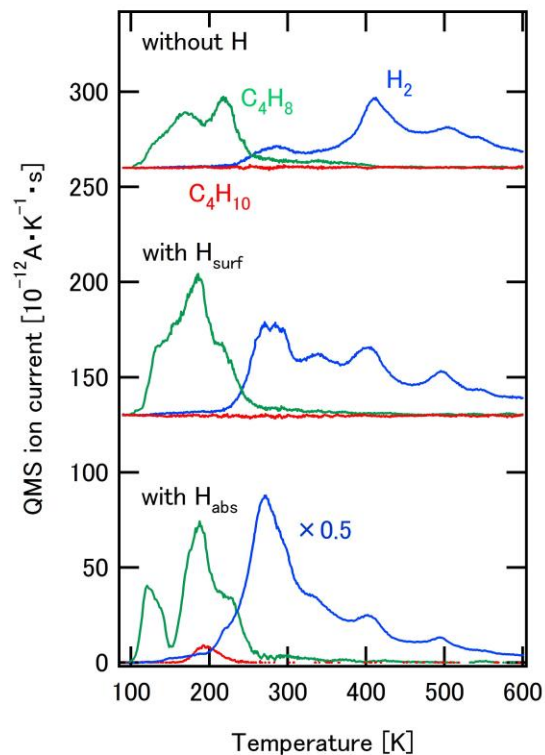s supplied from the near-surface region, which in turn are stabilized against desorption up to the reaction temperature of T_R=190 K by the presence of co-adsorbed butene.

Fig. 4 TPD spectra of butene (C_4H_8), butane (C_4H_{10}), and H_2 obtained after sequential dosage of first H_2 and then butene.
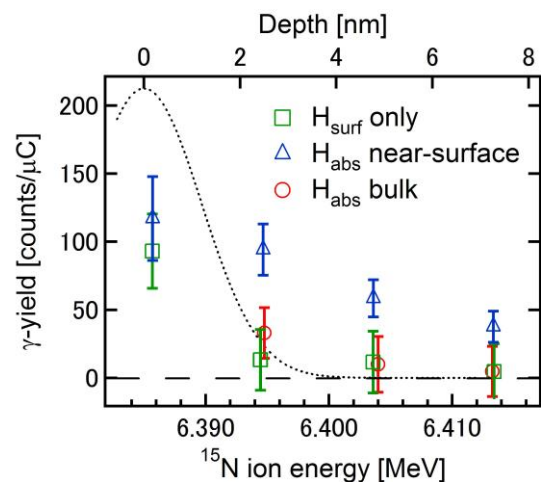

Fig. 5 NRA hydrogen depth profiles taken after sequential exposure to first H_2 and then butene and flash annealing to T_R=190 K.