

## 審査の結果の要旨

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Mr. Satoshi Ohno submitted the doctoral thesis entitled 'Investigation of hydrogen transport phenomena and catalytic olefin hydrogenation reactions at palladium surfaces'. As the main objective of this doctoral thesis, Mr. Ohno declared clarifying the hitherto unexplained role of Pd-absorbed hydrogen (H) in industrially important olefin hydrogenation reactions, for which palladium (Pd) is a widely employed catalyst. To achieve this larger goal, he first elucidated the microscopic mechanism of the hydrogen transport between the H<sub>2</sub> gas phase, the Pd surface, and the interior of the Pd metal during low-temperature (<160 K) H<sub>2</sub>-absorption and subsequent thermal desorption at Pd(110) single crystals, which represent a structurally well-defined model system. Utilizing temperature programmed desorption (TPD), nuclear reaction analysis (NRA), low-energy electron diffraction (LEED), and self-prepared Pd(110) samples, he unambiguously identified three of the five desorption features in the H<sub>2</sub> TPD spectrum of H/Pd(110) as surface-adsorbed (H<sub>s</sub>) and two others as Pd-absorbed (H<sub>abs</sub>) states. He characterized the latter as *near-surface* and *bulk-dispersed* Pd hydride phases that may coexist at T<145 K with distinctly different depth distributions below the Pd surface.

Through absorption experiments with isotope (H, D) labeled H<sub>s</sub>, Mr. Ohno then revealed that the H<sub>abs</sub> states form on separate absorption pathways, i.e., by nucleation of the near-surface hydride at surface defects (steps) at T<145 K and by formation of bulk hydride (T<160 K) through H<sub>2</sub> absorption in the regular terrace area. This latter absorption pathway is peculiar to Pd(110), i.e., neither observed on Pd(111) nor on Pd(100) surfaces, and described for the first time in this dissertation. Mr. Ohno further demonstrated quantitatively that H<sub>2</sub> absorption along both (defect- and regular terrace-related) routes requires very little (<0.1 eV) activation energy and transfers pre-chemisorbed hydrogen below the surface with high (>50%) probability. On the basis of these results, Mr. Ohno developed a novel model for the H<sub>2</sub> absorption mechanism, in which either H<sub>2</sub> dissociation at mono-vacancies in the H chemisorption layer on the H<sub>2</sub>-exposed (i.e., H-saturated) Pd surface or the concerted penetration of chemisorbed H into the subsurface accompanied by simultaneous reoccupation of the vacated chemisorption sites by excess H atoms (produced in the dissociation events) represent the rate-determining step.

The proposed mechanism may provide explanations for the peculiar H<sub>2</sub> absorption at (1×2) reconstructed Pd(110) terraces as well as for the strongly enhanced absorption rate at surface defects and suggests that the decisive structural factors to accelerate H<sub>2</sub> absorption at metal surfaces are coordinative 'openness' and corrugation. Low-coordinated sites provide wider and hence less strongly activated interstitial channels for the penetration of

chemisorbed H into the subsurface and may thereby increase the formation rate of H mono-vacancies as a prerequisite for H<sub>2</sub> dissociation, while corrugated structures such as the atomic step-edge like ridges of the (1×2)-reconstructed Pd(110) surface are known to enhance dissociation by stabilizing H<sub>2</sub> precursor states. Consistent with his hypothesis, Mr. Ohno proved further that a small amount (0.3 ML) of CO, which binds preferentially to defects and lifts the H-induced (1×2) reconstruction of Pd(110), suppresses H<sub>2</sub> absorption. His work highlights the need to understand the hitherto largely unexplored H<sub>2</sub> dissociation process on H-saturated Pd surfaces and thereby indicates an important direction for future research.

To address the role of H<sub>abs</sub> in catalytic olefin hydrogenations, Mr. Ohno investigated the model reaction of cis-2-butene (C<sub>4</sub>H<sub>8</sub>) to butane (C<sub>4</sub>H<sub>10</sub>) at H<sub>2</sub>-preexposed Pd(110) with reaction-TPD. He revealed that H<sub>s</sub> steers the thermal activation behavior of butene from decomposition on clean Pd(110) towards desorption from H/Pd(110), presumably due to an equilibrium shift of the C<sub>4</sub>H<sub>8</sub> dehydrogenation to C<sub>4</sub>H<sub>6</sub> (butadiene), which is the first step of its decomposition. Mr. Ohno then demonstrated that in addition to H<sub>s</sub>, C<sub>4</sub>H<sub>8</sub> hydrogenation requires H<sub>abs</sub> (a first-time success at Pd single crystals, which hitherto have been considered unreactive). The C<sub>4</sub>H<sub>10</sub> reaction yield is shown to depend nearly linearly on the quantity of H<sub>abs</sub> but not on its in-depth distribution. Mr. Ohno explained this convincingly with the aid of NRA H profiles, which indicate that the ‘memory’ of the initially prepared (at 115 or 160 K) H<sub>abs</sub> distribution is wiped out by H diffusion into the Pd bulk at the reaction temperature (~200 K). Unlike clean Pd(110), the C<sub>4</sub>H<sub>8</sub>-co-adsorbed Pd surface preserves H<sub>abs</sub> at this temperature, since H<sub>2</sub> desorption from the H<sub>abs</sub> states is retarded so that its maximum rate shifts towards a 100 K higher temperature. Mr. Ohno’s results thus invite the interpretation that H<sub>abs</sub> provides a reservoir of reactive H species that complete the second half-hydrogenation step of an adsorbed butyl-intermediate. The re-emergence of H<sub>abs</sub> on the surface as excess H atoms in a microscopic reversal of the absorption process may provide a tentative explanation for its special reactivity, but would need further verification.

In summary, Mr. Ohno’s doctoral research has brought to light unprecedented details of the H<sub>2</sub> absorption mechanism at Pd surfaces and contributed significantly to clarifying the role of Pd-absorbed H in the Pd-catalyzed hydrogenation of olefins. Through this dissertation, Mr. Ohno has presented a substantial body of novel and scientifically highly relevant findings as a result of his rigorous execution of skillfully arranged experiments, detailed data analysis, keen observation of trends and sound physical interpretation. All examiners decided unanimously that Mr. Ohno has clearly demonstrated sufficient academic knowledge, self-motivation, inquisitiveness and perseverance, as well as presentation and discussion skills to conduct independent scientific research. Therefore, Mr. Ohno’s dissertation is deemed fully acceptable as a qualification to obtain his doctorate degree (in engineering).

よって本論文は博士（工学）の学位請求論文として合格と認められる。