WILDE LAB.

[Understanding & Control of Hydrogen Absorption]

Department of Fundamental Engineering

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Nanoscale Surface Physical Chemistry

Graduate School of Engineering, Department of Applied Physics

How does hydrogen enter into metal surfaces?

Nanoscale Analysis of Hydrogen Penetration, Diffusion, and Reactions at Surfaces and Interfaces

Hydrogen absorption into bulk metals and nanoparticles plays a key role in ① industrial storage and purification of H_2 for clean energy applications (such as fuel cells) and ② in hydrogenation catalysis. Our research clarifies the microscopic reaction routes that link gas phase H_2, surface-adsorbed hydrogen, and hydrogen in the interior of H-absorbing metals such as palladium (Pd). We provide atomic level insight into the surface penetration mechanism by absorption studies with isotopic labeled (H, D) TDS at structurally well-characterized pure and modified (alloyed) Pd single crystals. This fundamental knowledge of the absorption process is required for the controlled design of novel high-efficiency hydrogen storage materials and hydrogenation catalysts.

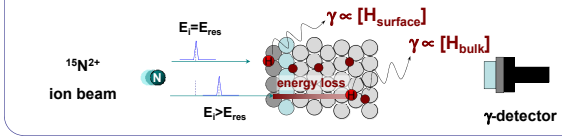
◆ Experimental Techniques & Key Information

- ✓ *Nuclear Reaction Analysis (NRA)*: Non-destructive • Quantitative • High-resolution - Hydrogen Depth Profiling • Visualization of H-breathing by metallic nanocrystals and hydride nucleation beneath surfaces
- ✓ *Thermal Desorption Spectroscopy (TDS)*: Bonding stability evaluation of hydrogen species • Hydrogen absorption kinetics • Gas/surface/subsurface-H exchange mechanism • Kinetic isotope effects

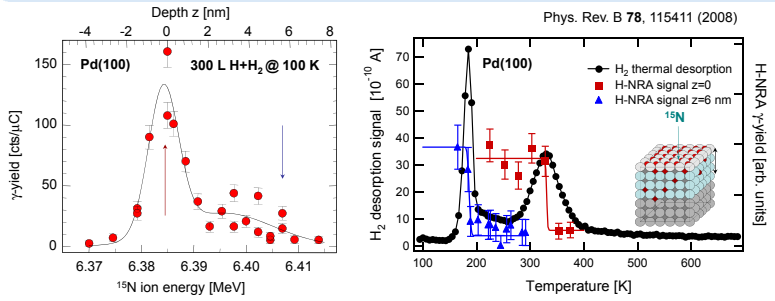
◆ Latest Research Topics

- ✓ *Hydrogen storage* → H-Absorption/Release Mechanism
- ✓ *Hydrogenation Catalysis* → Reactivity of 'Subsurface-H'
- ✓ *MOS Devices* → Relation of H-Impurities and Reliability

Principle of NRA $^{15}N(6.385\ MeV) + {}^1H \rightarrow {}^{12}C + \alpha + \gamma(4.43\ MeV)$

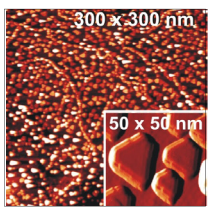


Identification of *surface-adsorbed* and *absorbed* hydrogen states (NRA+TDS)

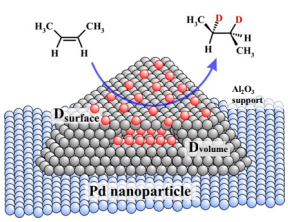


Relation of hydrogen absorption in Pd-nanocrystals and catalysis

Angew. Chem. Int. Ed. **47**, 9289 (2008); Phys. Rev. B **77**, 113412 (2008)



Oxide-supported Pd-Nanocrystals

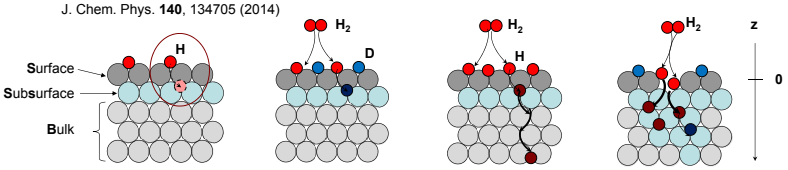


Model Hydrogenation Catalyst

NRA directly proves the necessity of **nanocrystal-absorbed hydrogen** for **catalytic olefin hydrogenation.**

Atomic-level mechanism of surface penetration and hydride nucleation at Pd surfaces

J. Chem. Phys. **140**, 134705 (2014)



The activation energy of H_2 absorption is much smaller than that for $H_s \rightarrow H_{ss}$ diffusion!

H_2 absorption transfers surface hydrogen below the surface and replaces it at the chemisorption sites.

Penetration is *slow* at regular terrace sites: → Bulk-dissolved H.

Penetration is fast at defects: → Localized near-surface hydride nucleation.