WILDE LAB.

[Surface Dynamics of Hydrogen Absorbing Materials]

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Hydrogen Transport and Reactions at Surfaces

Atomic Scale Mechanisms of Hydrogen Penetration, Diffusion, and Catalysis

Hydrogen (H) absorption in and desorption from metals and oxide nanoparticles is crucially important for the storage and purification of H_2 in clean energy technology (fuel cells) and for industrial hydrogenation catalysis. Our research reveals the microscopic pathways along which gas phase H_2 dissociates at the surface and penetrates as H atoms into the interior of metals. Absorption/desorption experiments at pure and modified palladium (Pd) surfaces demonstrate that the H transport is sensitive to the surface structure and can therefore be controlled at the atomic level. We recently succeeded in clarifying the long-debated action mechanism of Pd-absorbed H in Pd-catalyzed olefin (C=C) hydrogenation. This fundamental insight supports the rational design of novel efficient hydrogenation catalysts and hydrogen storage materials.

◆ Experimental Techniques & Key Information

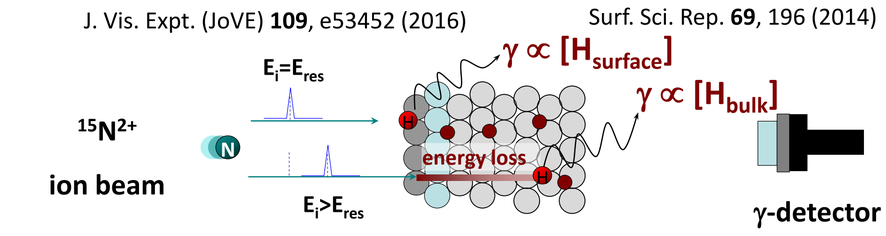
- ✓ *Nuclear Reaction Analysis (NRA)*: Quantitative ▪ Non-destructive ▪ High-resolution - Hydrogen Depth Profiling ▪ Visualization of H-breathing by nanostructures ▪ Depth-resolved H stability analysis (diffusion, desorption, reaction)
- ✓ *Thermal Desorption Spectroscopy (TDS)*: Bonding stability of H species ▪ Hydrogen absorption kinetics ▪ Isotope (D) labeling ▪ Gas/surface/subsurface-H exchange mechanisms ▪ 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
- ✓ Surface and Bulk Interactions of Hydrogen with Ceria (CeO_{2-x})

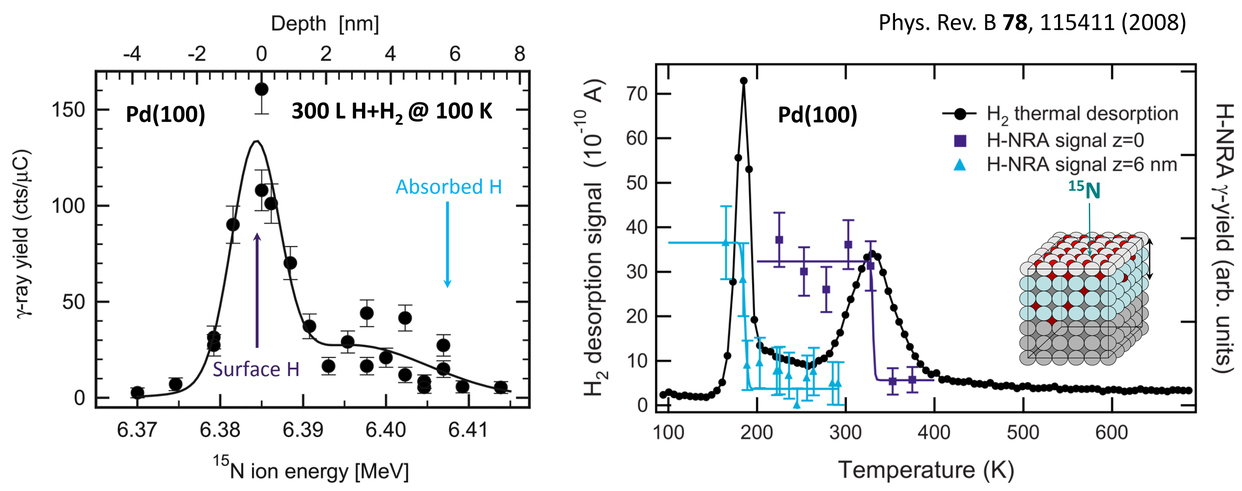
Principle of NRA $^{15}N(6.385\ MeV) + {}^{1}H \rightarrow {}^{12}C + a + \gamma(4.43\ MeV)$

J. Vis. Expt. (JoVE) **109**, e53452 (2016) Surf. Sci. Rep. **69**, 196 (2014)



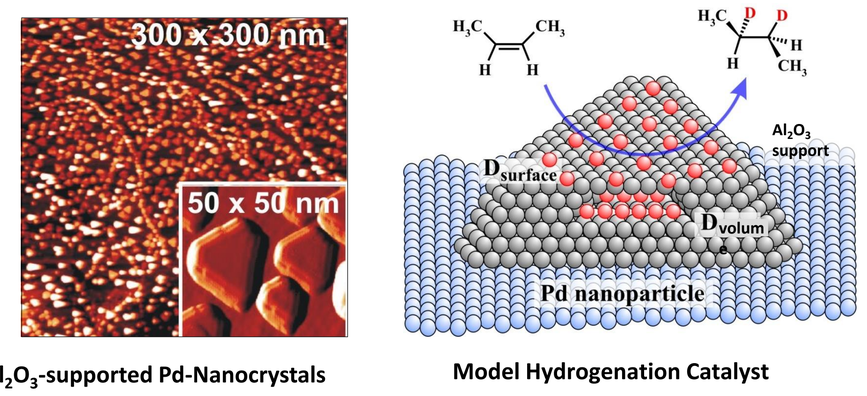
Identification of *surface-adsorbed* and a*bsorbed* hydrogen states (NRA+TDS)

Phys. Rev. B **78**, 115411 (2008)



The role of Pd nanocrystal-absorbed hydrogen in catalysis

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

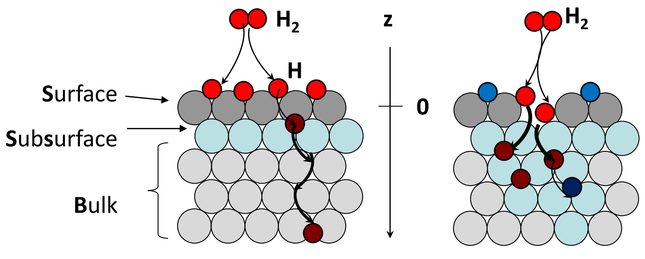


Al_2O_3-supported Pd-Nanocrystals — Model Hydrogenation Catalyst

=> Olefin (C=C) hydrogenation catalysis *requires* Pd-absorbed H !

Structure-sensitive H_2 absorption and H_2 desorption temperature control at Pd(110)

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

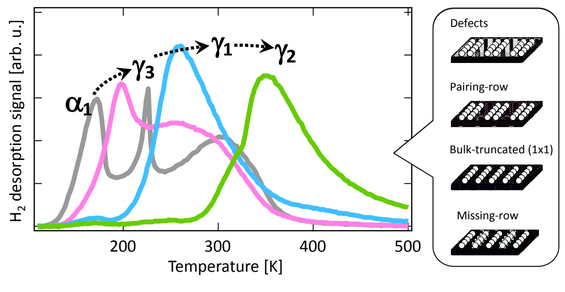


H-Penetration occurs *slowly* at **regular terrace sites**: ⟶ Bulk-dissolved H.

H-Penetration is *fast* at **defects**: ⟶ Localized near-surface hydride nucleation.

J. Phys. Chem. C **119**, 11732 (2015)

H_2 TDS after CO-induced surface restructuring



Resurfacing of Pd-absorbed H triggers hydrogenation catalysis

J. Phys. Chem. C **120**, 11481 (2016)

Mechanism of olefin hydrogenation catalysis driven by Pd-dissolved hydrogen

$C_4H_8 + H_2 \longrightarrow C_4H_{10}$