

8. Summary

This work presents investigations of the interaction of hydrogen with a Pd(210) and Ni(210) surface using LEED (low energy electron diffraction), thermal desorption spectroscopy (TDS), work-function measurements ($\Delta\Phi$), vibrational loss measurements (HREELS), and isotope exchange experiments.

The interaction of hydrogen with both surfaces is very similar.

For temperatures above 100K, hydrogen chemisorbs spontaneously forming atoms in three binding states ($\beta_1, \beta_2, \beta_3$). The atomic adsorption leads to a work function increase. If the temperature is reduced to 50K, hydrogen additionally chemisorbs into two molecular states (γ_1, γ_2). In contrast to the β -adsorption, the population of γ -states induces a work-function decrease.

The molecular nature of the γ -states was confirmed by observation of the H-H vibration mode in HREELS, by the detection of the σ -H₂/Pd- and σ^* -H₂/Pd-bonding in UPS, and by H₂/D₂-exchange experiments.

The energy range of the HREELS- and UPS-signals and the relatively high desorption temperature in TD-spectra verify a real chemisorptive interaction between molecule and surface. We consider a side-on complex configuration which allows a σ/σ^* -synergism equivalent to the Blyholder backbonding mechanism for CO chemisorption or the classical Dewar-Chat-Duncanson model for the bonding situation in olefine or other organometallic complexes.

A molecular chemisorption of H₂ on a transition metal surface is unusual. In general, hydrogen adsorbs dissociatively. While on noble metals the dissociation is hindered by a sizable energy barrier, it occurs spontaneously on transition metal surfaces. If molecular adsorption states exist, they are usually very weakly bound in shallow physisorption wells; beyond, it requires surface temperatures below 20K to stabilize those states.

At Ni(510), molecular chemisorption has been observed at surface temperatures up to 125K, presumably at the steps, but only after the surface was passivated with a dense atomic layer.

We made similar observations, namely the coexistence of chemisorbed molecular and atomic hydrogen on the relatively open Pd(210) and Ni(210) surfaces although the surfaces were not fully passivated. While the atomic adsorption takes place in high coordinated sites, the molecule adsorbs *on top*.

It is very difficult to identify experimentally the exact location and nature of the hydrogen adsorption states. In order to obtain this microscopic information, A. Groß et al. performed DFT calculations. The results suggest that the hydrogen molecule is first attracted to the top Pd atoms. At the clean Pd(210) surface, no stable molecular adsorption state should exist and the hydrogen molecule dissociates into the higher coordinated sites. Due to the presence of atomic hydrogen on the surface however, this behavior changed considerably. The presence of hydrogen atoms leads to a molecular adsorption state at the top site. That the top site's reactivity is hardly influenced by the pre-adsorbed hydrogen atoms can be traced back to the induced change in the local density of states.

In the case of Pd, we observed the absorption of hydrogen atoms which reside “close to the surface”. Evidence for such a “subsurface state” is a low-temperature thermal desorption feature which cannot be saturated, combined with a vanishing work function change and negligible vibrational loss contributions of the respective H state. We discuss our observations using the stamping model developed by Okuyama.

The hydrogen absorption has already been observed on other open palladium surfaces and is considered as a specific feature of the element palladium. But in contrast to other open Pd surfaces, the Pd(210) surface need not to reconstruct for absorption. Furthermore, the absorption velocity depends on the preparation of the sample. Both observations give rise to the assumption that a certain ensemble of substrate atoms necessary for chemisorption exists on the non-reconstructed Pd(210) surface. We can identify this ensemble as the four-fold coordinated hollow site and the neighbouring three-fold coordinated site.

In addition, we examined the H/CO-coadsorption on the Pd(210) surface. If the Pd crystal was first exposed to hydrogen and then to carbon monoxid, we observed the formation of H/CO-complexes. This observation was verified by the detection of a so-called Σ desorption signal in TDS and by a O-H vibrational loss in HREELS. In contrast to other coadsorption systems the Σ -hydrogen does not desorb in the low temperature area. Rather, hydrogen desorbs simultaneously with the strongly bound carbon monoxid, indicating an unusually stable complex.