

# Accepted Manuscript

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PII: S0039-6028(12)00010-6  
DOI: doi: [10.1016/j.susc.2012.01.005](https://doi.org/10.1016/j.susc.2012.01.005)  
Reference: SUSC 19562

To appear in: *Surface Science*

Received date: 3 January 2012  
Accepted date: 5 January 2012



Please cite this article as: Axel Groß, Hydrogen on metal surfaces: Forever young, *Surface Science* (2012), doi: [10.1016/j.susc.2012.01.005](https://doi.org/10.1016/j.susc.2012.01.005)

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## Hydrogen on metal surfaces: Forever young

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It is true that the study of hydrogen on metal surfaces has a long tradition in surface science. Experimentally, hydrogen is relatively easy to handle, which made it very popular [1] in spite of the fact that hydrogen is a bad electron scatterer rendering it invisible to many detection techniques. Because of the simplicity of their electronic structure, hydrogen atoms and molecules and their interaction with metal surfaces can be well described by electronic structure methods [2–4]. This simplicity also allows to derive fundamental concepts with respect to the surface reactivity and the principles underlying bond-making and bond-breaking processes at surfaces based on the study of hydrogen-metal systems [5]. Furthermore, because of its light mass, quantum effects in the hydrogen interaction dynamics are most prominent making their study interesting from a fundamental point of view [6–9]. At the same time, the interaction of hydrogen with metal surfaces has been of great technological relevance because of its role in hydrogenation reactions [10] and in hydrogen storage and bulk sorption [11].

These facts have made the interaction of hydrogen with metal surfaces a model and benchmark system in surface science from its early days onwards, as reflected in several contributions addressing this particular system in the collection covering the first thirty years of the journal *Surface Science* that was published in 1994 [12]. Now in a paper in this issue, Ferrin et al. [13] present a comprehensive theoretical study addressing adsorption and absorption energies and subsurface penetration barriers of hydrogen on different low-index surface terminations of seventeen transition metals from first principles based on periodic density functional theory (DFT) calculations. One might of course ask: Is there a need for yet another theoretical paper on the interaction of hydrogen with metal surfaces?

First of all, the interaction of hydrogen with metal surfaces is as relevant as ever, and has recently even become more important due to the role of hydrogen for future energy storage and conversion. Catalyzed hydrogenation reactions are among others crucial for the efficient storage of chemical energy in hydrocarbons [14]. And although elemental bulk metals are not considered as possible hydrogen storage materials because of the unfavorable mass ratio, the subsurface penetration of hydrogen in elemental metals is still of interest. For example, recently it has been shown that subsurface hydrogen might be the crucial promoter for the olefin hydrogenation in Pd nanoparticles [15].

Furthermore, recent candidate materials for hydrogen storage are typically capped by a palladium layer of nanometer thickness [16] in order to reduce the barriers for the hydrogen bulk penetration and its subsequent release.

Second, there is certainly a need for a comprehensive study addressing the hydrogen-metal interaction for a broad number of systems using the same computational approach so that chemical trends among the metals can easily be established. Periodic DFT codes have matured enough so that different codes basically give the same results within the numerical accuracy if the same functional is used. Still, previous DFT studies addressing hydrogen-metal interaction typically have focussed on few systems (for an exhaustive list, see Ref. [13]), and furthermore, they differ in technical parameters such as slab thickness, choice of the surface unit cell and coverage that influence the results.

Having assembled such a large database for the hydrogen-metal interaction within the same setup, the authors of Ref. [13] have thus been able to derive several interesting trends among the considered metals. *En passant*, they have solved a puzzle that has at least bothered me for quite some time. As far as the bonding of H atoms to metal surfaces is concerned, usually hydrogen behaves like a metal: hydrogen typically prefers high-coordinated adsorption sites [1]. This is the reason why the effective medium theory (EMT) was so successful in reproducing trends in the adsorption of hydrogen on metal surfaces [17] since the EMT scheme (and the related embedded atom method (EAM) [18]) are well-suited to describe metal bonding. Yet, there are some (100) surfaces where hydrogen prefers the lower-coordinated bridge site [1]. Are specific bonding configurations or details of the electronic structure responsible for the lower coordination? Ferrin et al. [13] find that this site preference is strongly correlated with the lattice constant of the host metal. For larger lattice constants, the hydrogen-metal distance in the four-fold hollow site to the four metal atoms of the surface layer becomes too large so that no real hydrogen-metal bond can evolve within the surface layer; instead, the hydrogen atom rather binds to adjacent metal atoms at the bridge site.

As far as the subsurface absorption is concerned, Ferrin et al. [13] confirm that it is exothermic only for few metals (Pd, Ta, V), and that the adsorption is always energetically favored compared to the subsurface absorption. However, the authors have also considered the penetration into the second subsurface layer what

has been rarely done before. In general, they find a correlation between the stability of the subsurface states and the barriers for subsurface penetration, i.e., a kind of Brønsted-Evans-Polanyi relation already known for barriers in surface reactions [19].

The present work represents the current status of theoretical studies covering the interaction of hydrogen with low-index metal surfaces, but it will definitely not be the end of the story. The interaction of hydrogen with metal surfaces will continue to be interesting and relevant. As the

general trend in theoretical surface science is to address more and more complex structures, the interaction of hydrogen with stepped [20] and precovered surfaces [21, 22] will be on the agenda, as first steps have already been successfully taken. Still, this interesting paper by Ferrin et al. In this issue [13] will certainly serve as a major reference for future studies addressing hydrogen-metal systems.

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