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Hydrogen adsorption energies on bimetallic overlayer systems at the solid–vacuum and the solid–liquid interface

Ata Roudgar [1], Axel Groß *

Physik-Department T30, Technische Universität München, James-Franck-Str. 1, D-85747 Garching, Germany

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Abstract

Atomic hydrogen adsorption energies on bimetallic overlayer systems have been determined by periodic density functional theory calculations within the generalized gradient approximation. On the pseudomorphic Pd/Cu(1 1 1) surface, both the substrate interaction and the lattice compression of the Pd overlayer lead to smaller hydrogen binding energies. For pseudomorphic Cu/Pd(1 1 1), on the other hand, the strong Cu–Pd interaction results in larger binding energies. Hence, both Pd/Cu(1 1 1) and Cu/Pd(1 1 1) exhibit an intermediate behavior between pure Cu(1 1 1) and pure Pd(1 1 1). In addition, we have determined the atomic hydrogen adsorption on Pd/Au(1 1 1) in the presence of a water overlayer. The hydrogen adsorption energies are changed by less than 60 meV by the most stable H_2O bilayer compared to the clean surface. This indicates that theoretical adsorption studies at the solid–vacuum interface might also be relevant for the solid–liquid interface.

Keywords: Ab initio quantum chemical methods and calculations; Metallic films; Chemisorption; Solid–gas interfaces; Solid–liquid interfaces; Hydrogen atom; Palladium; Water

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1. Introduction

The study of bimetallic surfaces has recently been of strong interest [1–4]. Bimetallic systems offer the possibility to prepare specific surface compositions and structures. This might be used to influence catalytic and other properties of the surface in a well-defined way [4]. Hence, an understanding of the electronic factors determining the reactivity of bimetallic surfaces could lead to the rational design of better catalysts. Bimetallic systems are also of particular interest in electrochemistry [5] since the catalytically active material has to be placed on a conductive electrode.

In the case of pseudomorphic overlayers, two effects influence the reactivity of the bimetallic

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* Corresponding author. Present address: Department of Theoretical Chemistry, University of Ulm, D-89069 Ulm, Germany. Tel.: +49 731 50 22810; fax: +49 731 50 22819.

E-mail address: axel.gross@uni-ulm.de (A. Groß).

[1] Present address: Chemistry Department, Simon Fraser University, Burnaby, BC, Canada V5A 1S6.

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surfaces: the direct electronic interaction between substrate and overlayer, and geometric strain effects due to the lattice mismatch of substrate and overlayer. Both effects can be disentangled experimentally only if the pseudomorphic structure of the overlayers is preserved for a film thickness of several layers as for example in the system Pt/Ru(0001) [1].

However, often the strain of thick overlayers is relieved by the formation of dislocations making an analysis of the microscopic origins of a modified reactivity of the bimetallic system rather cumbersome. Therefore, electronic structure calculations are rather helpful since they allow to separate strain from substrate interaction effects by addressing model systems that cannot be realized experimentally.

In electrochemistry, Pd overlayers deposited on Au single crystal surfaces have served as a model system of a transition metal deposited on an inert noble metal electrode [6–10]. The electrocatalytic activity of the Pd/Au overlayers with respect to hydrogen adsorption/desorption [9,11] and to the electro-oxidation of small organic molecules such as formaldehyde [9] and formic acid [12] are very sensitive to the layer thickness of the deposited Pd films. Furthermore, significantly enhanced hydrogen evolution rates have been found on small Pd islands deposited on Au(111) in an electrochemical STM set-up [6].

We have recently studied atomic hydrogen and CO adsorption on Pd/Au bimetallic surfaces by performing density functional theory (DFT) calculations [13,14]. We have found that both the expansion of the Pd overlayer by 5% and the relatively weak coupling between the d-bands of Pd and Au cause an upshift of the d-band which in agreement with the predictions of the d-band model [15,16] leads to a stronger adsorbate bonding. Furthermore, we have determined H and CO adsorption energies on Pd_n clusters with $n \leqslant 10$ deposited on Au(111) [17]. Interestingly enough, we find that the adsorption energies on these supported clusters are smaller than on the corresponding overlayer although the cluster atoms are less coordinated than the overlayer atoms. This is caused by the compression of the supported cluster together with the relatively strong cluster-substrate interaction.

We have now extended these studies into two directions. In order to establish chemical trends, we have replaced the Au(111) substrate by another noble metal substrate, Cu(111). Pd/Cu bimetallic surfaces are also interesting from a catalytic point of view as far as the CO oxidation and hydrogenation are concerned [18]. Besides, both H/Cu and H/Pd have served as model systems for the study of dissociative adsorption in surface science [19–22]. Usually the bimetallic PdCu system forms surface alloys [23,24]. Still we have studied the pseudomorphic overlayer systems in order to establish chemical trends. Cu has a much smaller lattice constant than Au; thus, pseudomorphic Pd overlayers on Cu(111) are compressed by 8%. We find that this compression does in fact lead to smaller adsorption energies. However, also the Pd/Cu interaction results in weaker binding in contrast to the Pd/Au system. As far as the hydrogen adsorption on the overlayer system with the opposite stacking sequence, a pseudomorphic Cu overlayer on Pd(111), is concerned, we find that the lattice expansion of Cu(111) has a negligible influence on the hydrogen adsorption energy, in agreement with a previous study [25]. However, for this stacking order the Cu–Pd interaction leads to a larger binding of hydrogen.

In all these calculations, the adsorption energies are determined at the solid–vacuum interface. The question arises whether these calculations are of relevance for the electrochemical situation of the solid–liquid interface. In order to address this question, we have calculated hydrogen adsorption energies in the presence of a water layer on Pd/Au(111). We find that the hydrogen adsorption energies are only slightly modified by the presence of water. Thus, calculated adsorption energies at the solid–vacuum interface can indeed be meaningful for an understanding of the binding at an electrochemical electrode.

This paper is structured as follows. First, we give an overview about the computational methods used. We will then briefly summarize the results for the Pd/Au overlayer system before we discuss in detail the hydrogen adsorption on bimetallic PdCu surfaces. Finally we address the hydrogen adsorption on Pd/Au(111) in the presence of a