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Electronic structure studies of a clock-reconstructed Al/Pd(1 0 0) surface alloy

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Abstract

We have employed solid-state Fenske–Hall band structure calculations to examine the electronic structure of Al/Pd(1 0 0), a surface alloy that undergoes a reconstruction, or rearrangement, of the atoms in the top few surface layers. Surface alloys are materials that consist primarily of a single elemental metal, but which have a bimetallic surface composition that is only a few atomic layers in thickness. The results of this study indicate that reconstruction into a clock configuration simultaneously optimizes the intralayer bonding within the surface plane and the bonding between the first and second atomic layers. These results also allow us to examine the fundamental relationship between the electronic and physical structures of this reconstructed surface alloy.

Keywords: Aluminum; Alloys; Palladium; Surface relaxation and reconstruction; Surface electronic phenomena; Approximate methods and calculations

1. Introduction

The fields of surface chemistry and catalysis are deeply intertwined, as many important industrial catalytic processes rely on the specific chemical properties of different surfaces. One family of materials that displays a particularly strong potential for catalytic, magnetic, and/or electrochemical applications are surface alloys [1]. These bimetallic systems are formed when varying coverages of an adsorbate occupy substitutional sites on a clean metallic surface, thereby generating an alloyed structure that is only a few atomic layers in depth [2]. Because of the differences in composition between bulk and surface atoms, surface alloys often exhibit catalytic properties (i.e., reactivities and selectivities) [3] that differ from their pure metal surface counterparts [4].

Although the behaviors of different catalysts have been well documented, the inherent complexities of analyzing heterogeneous processes make the specific mechanistic details of surface reactions difficult to characterize. Analyses of catalytic processes are complicated further when the geometry of the active surface in question differs from the bulk structure, owing to a reconstruction, or rearrangement, of the surface atoms. These surface reconstructions compensate for decreased surface atom coordination and for the electronic structure differences between surface and bulk atoms [5,6]. Despite thorough experimental studies of reconstructions, however, the surface electronic structure and bonding, as well as the chemical driving forces for many different reconstructions, are still not well understood [6,7].

The goals of this study were to determine the electronic structure factors that cause a reconstruction in a Pd(1 0 0) surface alloyed with aluminum atoms. This particular surface alloy was chosen for two primary reasons: first, palladium has numerous applications in practical catalytic processes [8] that have been shown to be dependent on the physical structure of the surface [9], and second, the Al/Pd(1 0 0) surface undergoes the surface atom rearrangement known as the “clock” reconstruction. A schematic of this reconstruction is shown in Fig. 1. The clock model, which was first used to describe the geometry of the Ni(1 0 0) surface upon adsorption of a half-monolayer of

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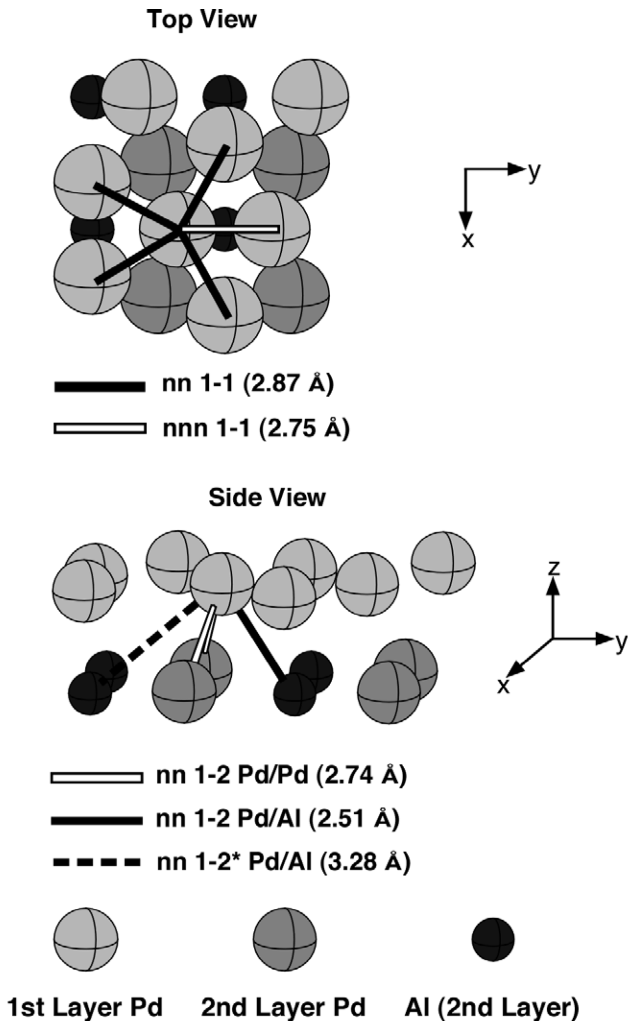

Fig. 1. A schematic of the top and side views of the unit cell used in the clock-reconstructed Al/Pd(1 0 0) surface alloy calculations. Coordinates for this model are taken from Ref. [12]. The third and fourth atomic layers have been omitted for clarity.

carbon atoms [10], is so named because the four surface atoms that surround each adsorbed C atom are slightly rotated in either clockwise or counterclockwise directions.

Structural analyses of the Al/Pd(1 0 0) surface alloy using low-energy electron diffraction (LEED) have shown that at the equivalent of a half-monolayer of Al atoms, every other Pd in the second atomic layer is replaced by an Al atom [1,11–15]. Pd atoms in the top layer undergo a rotational displacement that simultaneously lengthens the distance between Pd–Pd “nearest neighbors” (indicated by the solid line in Fig. 1) from a bulk length of 2.75 Å [16] to 2.87 Å [13] and shortens one of the Pd–Pd “next-nearest neighbor” distances (the dashed line in Fig. 1) from 3.89 Å to 2.76 Å. The substituted Al adsorbates occupy positions in the second atomic layer directly beneath the shortened next-nearest neighbor Pd–Pd interactions.

Because of the strong correlation between the structure of a catalyst and its properties, the ability to explain (and ultimately, to predict) the atomic displacements that occur during a surface reconstruction would be invaluable to the targeted syntheses of catalysts with greater activity and/or selectivity. Currently, the driving forces behind surface reconstructions are most often explained in terms of a surface stress model, which is based on the classical idea that atoms can be modeled by rigid, charged spheres [17]. The adsorption or alloying of additional atoms onto a surface increases the density of the rigid spheres and can lead to a quantifiable compressive stress within the system. Surface reconstructions can subsequently alleviate some of this stress by moving the atoms into more optimal positions.

Although there is considerable evidence to support the surface stress model for certain systems [18,19], it does not appear to explain the driving force for the reconstruction of Al/Pd(1 0 0). The formation of this particular surface alloy involves substituting Al atoms, which have smaller atomic radii, for Pd atoms in the second layer of the Pd(1 0 0) surface. This substitution should result in an overall decrease in the atomic density within the alloyed layers. The observation that Al/Pd(1 0 0) does reconstruct illustrates one of the drawbacks of the surface stress model: it neglects both the existence of bonds between atoms in the surface and the effects of those bonds on the overall surface structure. Similar observations of other adsorbate-induced surface reconstructions [20] have led to the recent suggestion that simple stress reduction is not always sufficient in determining the driving forces for surface reconstructions, and that a thorough analysis of surface reconstructions must also take the electronic structure into account.

It has been shown that the results of Fenske–Hall (FH) [21] band structure [22] calculations can be used to correlate experimentally-observed reconstructions into an optimization of the metal–adatom and metal–metal bonding in the first few layers of the clock-reconstructed C/Ni(1 0 0) surface [23,24]. The FH method is an approximate, nonempirical Hartree–Fock method that replaces the computationally demanding electron repulsion term in the Fock operator with evaluations of point charges. Because of these approximations, the evaluation of total energies is not possible with the FH approach; however, the results of FH band structure calculations can provide reliable and detailed information about the electronic structure of any atom in the unit cell [22,25]. The geometrical similarities between the surface structures of reconstructed C/Ni(1 0 0) and Al/Pd(1 0 0) suggested that the FH band structure method is capable of providing us with an explanation of the electronic structure factors responsible for the reconstruction of the Al/Pd(1 0 0) surface alloy.

We begin our discussion with brief analyses of the bonding in bulk Pd and on a clean Pd(1 0 0) surface. The results of these calculations allow us to identify the electronic structure effects that are solely the result of cleaving a (1 0 0) surface from the bulk metal. This discussion is followed by an analysis of two different Al/Pd(1 0 0) surface alloys: a hypothetical unreconstructed surface, where the Pd atoms occupy identical sites to their counterparts in clean Pd(1 0 0) and the Al atoms are substituted for half the Pd atoms in the second atomic layer, and a recon-