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A density functional theory study of H_2S decomposition on the (1 1 1) surfaces of model Pd-alloys

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Abstract

In this work, we report density functional theory calculations exploring H_2S dissociation on the (1 1 1) surfaces of Pd, Cu, Ag, Au, and various bimetallic surfaces consisting of those metals. To understand the contributions of lattice strain and electronic ligand effects, the thermodynamics of each elementary dissociation step were explored on model bimetallic surfaces, including PdMPd sandwiches and Pd pseudomorphic overlayers, as well as strained Pd(1 1 1) surfaces and homogeneous Pd_3M alloys. Sulfuric (H_2S, SH, and S) adsorption energies were found to correlate very well with lattice constant, which can be explained by the strong correlation of the lattice constant with d-band center, Fermi energy, and density of states at the Fermi level for strained Pd(1 1 1) surfaces. Compressing the Pd lattice shifts the d-band center away from the Fermi level, lowers the Fermi energy, and reduces the density of d-states at the Fermi level. All three effects likely contribute to the destabilization of sulfuric adsorption on Pd alloys. Introducing ligand effects was found to alter the distribution of the d-states and shift the Fermi level, which eliminates the correlation of the d-band center with the density of states at the Fermi level and the Fermi energy. As a result, the d-band center by itself is a poor metric of the H_2S reaction energetics for bimetallic surfaces. Furthermore, combining strain with ligand effects was found to lead to unpredictable alterations of the d-band. Therefore, adsorption of H_2S, SH, and S on PdMPd surfaces do not accurately predict adsorption on Pd_3M surfaces.

Keywords: Density functional calculations; Bimetallic alloy; Sulfur; Palladium

1. Introduction

The availability of high purity hydrogen is a requisite for the hydrogen economy. For most hydrogen production technologies, hydrogen must be separated from other gases to assure high purity for use as a fuel or for industrial processes [1]. Palladium membranes have been demonstrated to effectively separate hydrogen from feed streams [2]. Unlike membranes that separate molecules based on pore dimensions, Pd membranes dissociate hydrogen and allow atomic hydrogen to permeate through the lattice. However, Pd membranes exhibit mechanical problems during thermal cycling due to expansion of the lattice in the presence of hydrogen [3,4]. Additionally, Pd membranes are susceptible to poisoning by carbonaceous and sulfurous species. H_2S, at concentrations above 100 ppm, was found to totally inhibit H_2 permeation in pure Pd membranes [5]. Investigations on model surfaces have revealed that H_2S dissociates on Pd, forming H and S adatoms [6]. The strong sulfur adsorption on Pd inhibits H_2 dissociation on those sites blocked by sulfur [7–9], as well as neighboring sites [10,11]. The total inhibition of H_2 dissociation on Pd surface sites by adsorbed sulfur is thought to occur at sulfur coverages between 0.3 and 0.5 ML [9,10,12].

In addition to the superior H_2 permeation in sulfur-free environments observed for certain PdCu and PdAg membranes [2], some Pd alloy membranes exhibit improved sulfur tolerance [13]. Although the reason for this tolerance is not entirely known, sulfur adsorbs on Cu, Ag, and Au

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surfaces much more weakly than on Pd [14]. Alfonso et al. studied the adsorption energy of sulfur on Pd and Pd alloys, determining that the adsorption energy of sulfur is correlated to the d-band center of the surface site at which it is adsorbed [14]. Ag, with the most negative d-band center of the elements studied, was found to adsorb sulfur the weakest. Pd, having the least negative d-band center, was determined to adsorb S most strongly. Adsorption on the alloy surfaces was found to be more complex, but the general trend between d-band center and sulfur adsorption strength was observed [14].

More recently, Alfonso et al. studied the H_2S decomposition pathway on Pd(1 1 1) [15]. At low coverage ($\theta = 0.06$ ML), the H_2S binding energy on Pd(1 1 1) was found to be −0.71 eV. After overcoming an activation barrier of 0.37 eV, H_2S dissociates to SH and H, with a reaction energy of −0.88 eV. Following hydrogen diffusion, SH dissociates with a reaction energy of −0.73 eV and an activation barrier of 0.04 eV. Due to repulsion of neighboring adsorbates, sulfur adsorption weakens by 0.25 eV when the surface coverage is increased from 0.06 ML to 0.33 ML. However, the precursor states, adsorbed H_2S and SH, showed less coverage dependence, weakening by 0.09 eV and 0.05 eV, respectively.

In the current work, we extend the above work of Alfonso et al. [15] by using DFT to examine the effects of alloying the Pd surface on the H_2S decomposition reaction. Real Pd alloy surfaces are highly complex. PdCu alloys, for example, exhibit random distributions of the alloying metal [16]. Large concentrations of Cu, e.g., those present in the much studied $Pd_{60}Cu_{40}$ system, result in a transition from an fcc to a bcc bulk lattice structure [17]. Furthermore, segregation of one of the metal components to the surface is observed, though whether the surface becomes Pd- or Cu-enriched depends on the chemical environment [17]. Rather than attempting to simulate surface chemistry on such complex alloy surfaces, this manuscript instead focuses on understanding the role of specific *mechanisms* in the alteration of H_2S decomposition on Pd alloy surfaces. DFT calculations are well-suited to such mechanistic investigations, because they allow for the “construction” of model bimetallic surfaces that are not easily prepared experimentally but permit isolation of certain factors influencing adsorption strength.

Alloying a pure surface has several potential impacts. Incorporating a second metal into the lattice alters the lattice spacing, inducing strain. This strain alters the electronic structure of the surface [18,19]. Recent theoretical work shows that by compressing or expanding the lattice of a metal, reaction energetics can change significantly [19–21]. Alloying metals can also interact chemically with Pd, further changing the electronic structure of the surface, known as the ligand effect [22]. Because alloys break up the homogeneity of the surface, modeling surface reactions on alloys is more complex than on pure metals. One approach to simplify modeling alloys is to use homogenous surfaces that incorporate strain and ligand effects. Straining the surface without ligand effects can be accomplished by artificially compressing or expanding the Pd lattice. Ligand effects can be introduced by substituting the first subsurface layer with an alloying metal. In these PdMPd sandwiches, the Pd layers are not strained, unlike in pseudomorphic overlayers. Pseudomorphic overlayers consist of a single layer of Pd on top of a substrate metal. Because the Pd layer adopts the lattice spacing of the substrate, it becomes strained. The current work explores the use of homogeneous alloys, pseudomorphic Pd overlayers, strained Pd lattices, and PdMPd sandwich models to understand how alloying metals alter the sulfur tolerance of Pd surfaces.

2. Methods

Adsorption of H_2S and its decomposition products was studied using density functional theory calculations performed with Vienna Ab-initio Simulation Package [23,24]. Basis sets consisted of plane waves generated using the projector augmented wave (PAW) method [25], with a 400 eV cutoff energy. To determine lattice constants, bulk metal calculations were performed with an $11 \times 11 \times 11$ Monkhorst–Pack *k*-point mesh to obtain the lowest energy lattice constant. The optimized lattice constants are reported in Table 1. Surface calculations were performed on metal slabs with a thickness of four atomic layers using 2×2 unit cells with the equivalent of six substrate layers in the vacuum space. Adsorption and decomposition of 0.25 ML H_2S was examined on the (1 1 1) planes of pure metals, alloys, sandwich structures, and pseudomorphic overlayers. Unless stated otherwise, the top two surface layers were allowed to relax, while the bottom two layers

Table 1
Lattice constants and electronic properties of surfaces

Surface	Lattice constant (Å)	Weighted d-band center (eV)	Fermi energy (eV)	DOS at Fermi level[a]
Cu(1 1 1)	3.64	−2.54	−4.71	0.11
Pd/Cu(1 1 1)	3.64	−2.29	−5.38	0.41
$Pd_{3.64}$	3.64	−2.14	−5.39	0.65
Pd/Rh(1 1 1)	3.85	−2.12	−5.18	0.69
$Pd_{3.85}$	3.85	−1.83	−5.35	0.80
Pd_3Cu	3.89	−1.86	−5.11	0.65
Pd(1 1 1)	3.97	−1.73	−5.31	1
PdCoPd	3.97	−2.23	−4.98	0.69
PdNiPd	3.97	−2.05	−5.12	0.77
PdCuPd	3.97	−1.78	−5.22	0.39
PdRhPd	3.97	−2.05	−5.09	0.74
PdAgPd	3.97	−1.46	−5.34	0.32
PdIrPd	3.97	−2.20	−5.01	0.68
PdPtPd	3.97	−1.80	−5.23	0.90
PdAuPd	3.97	−1.48	−5.33	0.54
Pd_3Au	4.01	−1.59	−5.31	0.84
Pd/Ag(1 1 1)	4.16	−1.25	−5.28	0.68
Ag(1 1 1)	4.16	−4.09	−4.41	0.03
Pd/Au(1 1 1)	4.17	−1.24	−5.28	0.88
Au(1 1 1)	4.17	−3.32	−5.21	0.12
$Pd_{4.17}$	4.17	−1.56	−5.17	1.06

[a] Values normalized to that of Pd(1 1 1).