

Density Functional Theory studies of dehydrogenated and zwitterionic glycine and alanine on Pd and Cu surfaces

Joanna N. James, David S. Sholl*

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

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Abstract

Chiral modification of achiral metal catalysts with chiral auxiliary molecules is a promising method of creating chiral surfaces for heterogeneous catalysis. The ability of a chiral template overlayer to affect the adsorption enantioselectivity of a probe molecule depends on the local adsorption geometry of the template molecule. One potential class of chiral modifiers are the amino acids. Previous experimental studies demonstrated that glycine is adsorbed on the Cu(100) and Cu(110) surfaces in its dehydrogenated form, $\text{NH}_2\text{CH}_2\text{COO}$, at room temperature. In contrast, recent X-ray photoelectron spectroscopy experiments indicate zwitterionic adsorption of glycine to Pd(111). Using Density Functional Theory, we have studied the adsorption of glycine on Pd(111), Cu(100) and Cu(110) to examine this apparent difference in chemical states on these surfaces. We conclude that at equilibrium, glycine is adsorbed preferentially to these surfaces in its dehydrogenated form, implying that observation of zwitterions is likely a kinetic effect due to the conditions of the experiment.

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1. Introduction

Amino acids on metal surfaces are interesting prototypes for understanding chiral modification of metals. Amino acids can form well-ordered overlayers [1–13] or disordered overlayers [14,15]. In some cases, amino acids can lead to reconstruction of flat metal surfaces into stepped surfaces that are intrinsically chiral [11,12,16–21]. A starting point for a detailed understanding of the properties of amino acids on metal surfaces is the chemical and geometric structure of the adsorbed molecules. Experiments have shown that when amino acids, $\text{H}_2\text{NCHRCOOH}$, are adsorbed on Cu surfaces and the surfaces are annealed, the molecules dehydrogenate to form $\text{H}_2\text{NCHRCOO}$ on the surface [1,3,4,8,10,22–26]. Here, R is the functional group that varies among different amino acids. For glycine (Gly), $\text{R} = \text{H}$, and for alanine (Ala) $\text{R} = \text{CH}_3$. This state is frequently referred to as an anionic state, but we prefer to describe it simply as a dehydrogenated molecule because this does not imply a particular charge state on the $-\text{COO}$ group. In their molecular crystals, amino acids have a zwitterionic form, $\text{H}_3\text{NCHRCOO}$ [27,28]. Recent exper-

iments with glycine on Pd(111) indicated that these adsorbed molecules are dominated by a zwitterionic form [29]. Experimental observations of zwitterionic amino acids have also been reported on Pt(111) and Ag(110) [1,21,24,30].

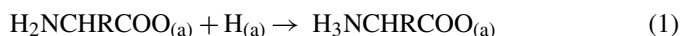
The experimental observations outlined above raise the question of why the chemical characters of adsorbed amino acids on Pd and Cu surfaces are different. One simple hypothesis that can explain the observed results is that the dehydrogenated molecules are energetically preferred to the zwitterionic states on Cu surfaces but that the reverse is true on Pd(111). If this hypothesis is correct and the experiments probe an ensemble of adsorbed molecules at equilibrium, dehydrogenated molecules would be observed on Cu surfaces and zwitterionic molecules would be observed on Pd(111). We have used Density Functional Theory (DFT) calculations to directly assess the relative stability of dehydrogenated and zwitterionic glycine and alanine adsorbed on Pd(111), Cu(110), and Cu(100). These two Cu surfaces were chosen because previous DFT calculations for these surfaces have shown excellent agreement between the structural properties of ordered amino acid overlayers predicted using DFT and those seen experimentally [3,8,9,19,31,32]. Our calculations show unequivocally that the hypothesis above is false; in fact, the dehydrogenated molecules are energetically favored on all three surfaces we have examined. This conclu-

* Corresponding author. Tel.: +1 412 268 4207; fax: +1 412 268 7139.
E-mail address: sholl@andrew.cmu.edu (D.S. Sholl).

sion suggests that the existence of zwitterionic amino acids on Pd(1 1 1) is influenced by kinetic limitations.

2. Computational methods

We used plane wave DFT calculations to compute the energy change, ΔE , associated with surface reactions of the form



where the subscript (a) indicates an adsorbed species. Details of the surfaces and surface unit cells used are defined in the next sections. Calculations for the reactants in this reaction were performed with both adsorbates coadsorbed on the surface. Calculations for the product of this reaction used the same surface unit cell as the calculations for the reactants. ΔE was defined so that positive values of this quantity indicate that the reactants are energetically preferred relative to the reaction product.

The results reported here are from plane wave DFT calculations implemented in the Vienna *ab initio* Simulation Package (VASP) [33–35]. These calculations were performed within the generalized gradient approximation (GGA) using the Perdew–Wang 91 functional [36]. A plane wave expansion energy cut-off of 396 eV was used with a $3 \times 3 \times 1$ Monkhorst–Pack [37] *k*-point sampling of the Brillouin zone. Total energy calculations used the residual minimization method for electronic relaxation and geometries were relaxed using a Conjugate Gradient algorithm until the forces on all unconstrained atoms were less than 0.03 eV/Å. We defined the periodicity of the material in the plane of each surface using the DFT-optimized lattice parameter. Our calculations on Pd(1 1 1) and Cu(1 0 0) were performed using slabs of four layers with the bottom two layers constrained in their bulk positions. Cu(1 1 0) was represented as a slab seven layers thick with the bottom three layers constrained. A vacuum spacing of 14 Å was used in the direction of the surface normal for all calculations. All calculations include dipole corrections [36,38] in the direction normal to the surface. Because the charge distributions of the reactants and products in the reaction we are considering can be quite different, dipole corrections are important in obtaining accurate results.

The zero point energies associated with H on metal surfaces and in molecules can be appreciable [39–41]. To assess the role of zero point energies in Eq. (1), we calculated the normal modes and vibrational frequencies of the adsorbed molecules within the harmonic approximation. Specifically, we estimated the mass-weighted Hessian matrix for each system using displacements of individual atoms of 0.1 Å about energy minima and computed normal mode frequencies from the resulting matrix. Test calculations using displacements of 0.03 Å gave very similar results. All degrees of freedom in the adsorbed molecule(s) were included in these calculations but the positions of all metal atoms were fixed. Once the normal mode frequencies, ν_i , were computed, the zero point energy is given by $\sum_i h\nu_i/2$.

3. Results

3.1. Glycine/Pd(1 1 1)

We first consider the adsorption of Gly on Pd(1 1 1) at coverages where the adsorbed molecules are well separated. Specifically, we examined surfaces with one adsorbed amino acid in a (3×3) surface unit cell. From the results of our previous studies of formate and acetate on Pd(1 1 1) [42,43] and work done on other surfaces [3,4,10,19,20,24,31,32,44], we expected the OCO group to prefer an atop–bridge–atop configuration. We therefore performed calculations with Gly in a variety of initial states with the O atoms in the OCO group in atop sites. These initial states examined a number of possible positions for the N atom in the adsorbed molecule. For the zwitterionic structure, we also examined multiple initial states that placed the N atom at various heights above the surface.

The preferred geometries of dehydrogenated and zwitterionic Gly on Pd(1 1 1) are illustrated in Fig. 1, and structural information for these molecules is summarized in Table 1. These results for the dehydrogenated molecule do not include the presence of coadsorbed H, but including coadsorbed H in the surface unit cell does not significantly perturb the dehydrogenated molecule. The dehydrogenated molecule exhibits tridentate bonding with the surface, with bonding through the N atom and both O atoms. Each of these bonds can be roughly characterized as being in on-top sites on the surface. This structure was the only stable state

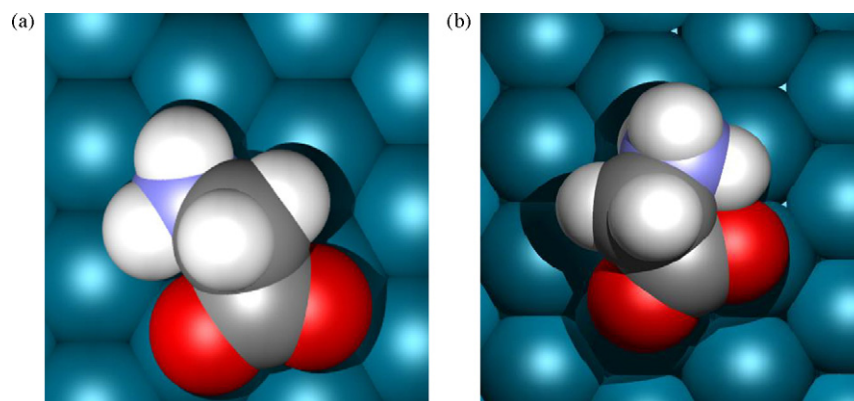


Fig. 1. Top-down views of the DFT-optimized geometries of (a) dehydrogenated Gly/Pd(1 1 1) and (b) zwitterionic Gly/Pd(1 1 1) in a (3×3) surface unit cell.

Table 1
Selected bond distances for the DFT-optimized geometries of dehydrogenated and zwitterionic Gly/Pd(1 1 1) in a (3 × 3) surface unit cell, with all distances in Å

	Dehydrogenated Gly/Pd(1 1 1)	Zwitterionic Gly/Pd(1 1 1)
$d(\text{C-N})$	1.48	1.50
$d(\text{C-O})$	1.27, 1.28	1.26, 1.28
$d(\text{C-C})$	1.53	1.54
$d(\text{C-H})$	1.09, 1.10	1.09, 1.10
$d(\text{N-H})$	1.02, 1.02	1.03, 1.04, 1.07
$d(\text{O-Pd})$	2.20, 2.23	2.26, 2.27
$d(\text{N-Pd})$	2.20	3.00

found. In the zwitterionic molecule, bidentate bonds exist with the surface through the two O atoms in the molecule. As might be expected, the distance between the N atom and the nearest Pd atom is considerably larger in the zwitterionic molecule than in the dehydrogenated molecule. As a result, there were other less stable structures for the zwitterionic molecule with varying positions of the amine group relative to the surface.

It is established in the literature [45] that H binds to both the threefold hollow sites on Pd(1 1 1) with the fcc site being more stable than the hcp site. We performed separate calculations for coadsorbed dehydrogenated Gly with a single H in each available fcc and hcp site in the (3 × 3) unit cell. As expected, we found the H to prefer an fcc site when coadsorbed with Gly. There are three available fcc sites in the (3 × 3) unit cell. Two of these sites gave equal energies in our calculations for the coadsorbed species, while the third was less favorable by 0.03 eV. Our discussion below is based on having H in one of the energetically favorable sites.

The energy difference between the coadsorbed state, $\text{H}_2\text{NCHRCOO}_{(a)} + \text{H}_{(a)}$, and the zwitterionic state, $\text{H}_3\text{NCHRCOO}_{(a)}$, for the energy minima described above was found to be $\Delta E = 0.37$ eV. That is, the coadsorbed state has a significantly lower energy than the zwitterionic state. When the zero point energy for each configuration was computed, the zero point energy for the zwitterionic state was found to be 0.13 eV larger than for the coadsorbed state. This means that when zero point energies are included, $\Delta E = 0.50$ eV for Gly/Pd(1 1 1) at this coverage. It is relatively easy to understand this zero point energy contribution. In going from the coadsorbed state to the zwitterionic state, three vibrational modes for an H atom adsorbed on the surface are replaced by three modes associated with the amine group. Two of the amine modes that appear have frequencies that are similar to the vibrational modes of H adsorbed on the surface, but the N–H stretching mode has a significantly higher frequency. It is this mode that dominates the additional zero point energy that is present in the zwitterionic state.

Similarly, we considered the adsorption of Gly on Pd(1 1 1) at a higher coverage where adsorbed molecules are more densely packed. Specifically, we examined surfaces with one adsorbed amino acid in a (2 × 3) surface unit cell. The molecules were aligned longitudinally along the elongated direction of the unit cell. This coverage gives a surface packing density of $47 \text{ \AA}^2/\text{molecule}$ as compared with $70 \text{ \AA}^2/\text{molecule}$ for our

(3 × 3) unit cell calculations. This surface density is still moderate compared to the dense adlayers that are known to exist for Gly on Cu(1 0 0) ($29 \text{ \AA}^2/\text{molecule}$ in a (4 × 2) unit cell) and Cu(1 1 0) ($26 \text{ \AA}^2/\text{molecule}$ in a (3 × 2) unit cell) [26]. As with the lower coverage, the coadsorbed state has a significantly lower energy than the zwitterionic state, with $\Delta E = 0.36$ eV. Adding a zero point correction for each configuration, the coadsorbed state was found to be 0.47 eV more stable.

Our calculations indicate that the adsorbed molecules in the (2 × 3) surface unit cell are energetically preferred compared to the molecules in the (3 × 3) unit cell by ~ 0.08 eV/molecule. This occurs because in the denser structure there is one hydrogen bond formed per molecule (as defined by geometric criteria used by Rankin and Sholl [20]) while for the larger unit cell there are none. These hydrogen bonds stabilize the molecule on the surface but do not substantially perturb the geometry of the molecule's compared to the result for the (3 × 3) unit cell. The interaction energy we calculated for the change between the (2 × 3) and (3 × 3) adlayers corresponds well to the hydrogen bond strengths quantified by Jones et al. [46] for various H-bond lengths in amino acids adsorbed on metal surfaces. It is certainly possible that Gly forms other more complicated adlayers on Pd(1 1 1) that allow additional hydrogen bonds to form. We have examined other possible orientations of the molecule in the (2 × 3) surface unit cell that create additional hydrogen bonds, but these resulted in less stable structures than the one we have discussed above because of deformation of the molecular geometries.

3.2. Glycine on Cu(1 1 0) and Cu(1 0 0)

Using structural details obtained from Rankin and Sholl for the dehydrogenated forms of Gly on Cu(1 1 0) and Cu(1 0 0) [19,32], we performed DFT calculations to compare these results with the respective zwitterionic forms. For Cu(1 1 0), we placed one adsorbed amino acid in a (3 × 2) unit cell. In the case of Cu(1 0 0), Gly was placed in a (3 × 3) unit cell. All the high symmetry sites were explored for each potential binding atom and in both cases, as expected, the dehydrogenated Gly preferentially adsorbed to the surface. It has been found that for H on Cu(1 1 0), the short bridge site and pseudo-threefold sites are energetically more favorable than the hollow site with the short bridge site being slightly lower in energy than the pseudo-threefold site [47,48]. Our calculations confirm this. We coadsorbed H with dehydrogenated Gly in each site and found the short bridge site is preferred by 0.04 eV to the pseudo-threefold site. In the case of H on Cu(1 0 0), the hollow site is energetically preferred [48,49] and thus we coadsorbed Gly with H in this stable site. For Cu(1 1 0), the coadsorbed state was 0.97 eV more stable than the zwitterionic state. For Cu(1 0 0), $\Delta E = 0.75$ eV.

3.3. Alanine/Pd(1 1 1)

Ala has been previously studied theoretically on Cu(1 0 0), Cu(1 1 0) and Cu(3 1 17) [19,20,31]. These calculations demonstrate a clear similarity between the bonding footprints of Gly and Ala on these surfaces. Because Ala differs from Gly by only

Table 2

Selected bond distances for the DFT-optimized geometries of dehydrogenated and zwitterionic Ala/Pd(1 1 1) in a (3 × 3) surface unit cell, with all distances in Å

	Anionic alanine/Pd(1 1 1)	Zwitterionic alanine/Pd(1 1 1)
<i>d</i> (C–N)	1.49	1.51
<i>d</i> (C–O)	1.27, 1.27	1.26, 1.28
<i>d</i> (C–C)	1.52, 1.54	1.52, 1.55
<i>d</i> (C–H)	1.10	1.10
<i>d</i> (N–H)	1.02, 1.03	1.03, 1.04, 1.07
<i>d</i> (O–Pd)	2.19, 2.19	2.25, 2.26
<i>d</i> (N–Pd)	2.31	3.00

an extra methyl group, we used our calculated results for Gly as starting points to optimize Ala on Pd(1 1 1). We investigated the additional degrees of freedom by exploring rotations of the methyl group relative to the surface. We only studied Ala at low coverage on this surface, with one Ala placed in a (3 × 3) unit cell. Comparing the coadsorbed state with the zwitterionic state, we found that the zwitterionic state was less stable by 0.46 eV. With zero point corrections included, $\Delta E = 0.60$ eV for Gly/Pd(1 1 1) at this coverage. The structural information for these states is summarized in Table 2.

4. Conclusion

Using Density Functional Theory (DFT), we have studied the relative stability of dehydrogenated and zwitterionic glycine and alanine adsorbed on Pd(1 1 1), Cu(1 1 0), and Cu(1 0 0). Our calculations clearly show that the dehydrogenated molecules are energetically favored relative to the zwitterionic species on all three surfaces we have examined. To relate this result to the experimental observation of zwitterionic glycine on Pd(1 1 1), it is important to consider the conditions of these experiments [29]. As we noted in our Introduction, glycine, like other amino acids, has a zwitterionic form as a molecular crystal. Experimentally, glycine is adsorbed on metal surfaces following the sublimation of molecules from their molecular crystal into a vacuum chamber. It is therefore reasonable to expect that when glycine is initially adsorbed on a metal surface in this way, it is zwitterionic. In order for the dehydrogenated species to be present on the surface, one of the N–H bonds in a zwitterionic molecule must be broken. Our results suggest that under the conditions of the experiments by Gao et al. [29], which adsorbed glycine at relatively low temperatures, the kinetics of this reaction are sufficiently slow to prevent the formation of the energetically stable dehydrogenated adsorbates on the surface. This idea is supported by the observation that when the dehydrogenated molecules are observed on Cu surfaces they are in adlayers that have been annealed at temperatures that are significantly higher than those used for the adlayers analyzed by Gao et al. on Pd(1 1 1). It is possible to directly assess the reaction kinetics for N–H bond breaking in the adsorbed zwitterionic molecules if the transition state for this process is located. We are currently performing DFT calculations with the aim of finding these transition states and assessing the kinetics of this process.

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