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Chemistry of Alanine on Pd(1 1 1): Temperature-programmed desorption and X-ray photoelectron spectroscopic study

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Abstract

The adsorption of alanine is studied on a Pd(1 1 1) surface using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). It is found that alanine adsorbs into the second and subsequent layers prior to completion of the first monolayer for adsorption at ~250 K, while at ~300 K, alanine adsorbs almost exclusively into the first monolayer with almost no second-layer adsorption. Alanine adsorbs onto the Pd(1 1 1) surface in its zwitterionic form, while the multilayer contains about 30–35% neutral alanine, depending on coverage. Alanine is thermally stable on the Pd(1 1 1) surface to slightly above room temperature, and decomposes almost exclusively by scission of the C—COO bond to desorb CO_2 and CO from the —COO moiety, and the remaining fragment yields ethylamine and HCN.

Keywords: X-ray photoelectron spectroscopy; Temperature-programmed desorption; Chemisorption; Pd(1 1 1); Alanine

1. Introduction

It has been demonstrated that enantioselective chemisorption is found on Pd(1 1 1) in ultrahigh vacuum (UHV) when the surface is chirally modified by *R*- or *S*-2-butanol, where enhanced chemisorption of propylene oxide of the same chirality as the modifier is found over a narrow 2-butanol coverage range [1]. More recently, similar behavior was found on Pt(1 1 1) [2]. This effect was also observed on a surface modified by chiral 2-amino butanoic acid, while no enantioselectivity was detected when using 2-methyl butanoate. It was suggested that the freer azimuthal rotation of the chiral center in 2-methyl butanoate results in a loss of enantioselectivity, while an amino group anchors the chiral center to the surface, thus restoring enantioselectivity [3]. In order to better understand the adsorption of α-amino acids on Pd(1 1 1) and probe their chemical stability, this paper addresses the surface chemistry of the simplest chiral amino acid, alanine, on Pd(1 1 1). The adsorption of amino acids, especially glycine (CH_2NH_2COOH) and alanine ($CHCH_3$-NH_2COOH), has been studied on a number of metal single crystal surfaces including Cu [4–15], Au [16–18], Ag [19,20], Pt [21,22], and binary metal surfaces Ni/Al(1 1 1) [23], Ag/Cu(0 0 1) and Ag/Cu(1 1 1) [24], and Cu/Au(1 1 1) [25]. The simplest amino acid, glycine has been studied recently on Pd(1 1 1) [26]. It was found that glycine adsorbs predominantly in its zwitterionic form on the surface and is stable to just above room temperature, where the major decomposition pathway was via cleavage of the C—C bond. The COO moiety further decomposed to desorb carbon monoxide and carbon dioxide, while the nitrogen-containing fragment yielded methylamine and HCN. The following presents results on the adsorption, desorption and thermal dissociation of alanine using temperature-programmed

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desorption (TPD) and X-ray photoelectron spectroscopy (XPS). D-alanine was used for this study. Since the surface chemistry on achiral Pd(1 1 1) should not depend on chirality, L-alanine will, in principle, yield identical results.

2. Experimental

Temperature-programmed desorption (TPD) data were collected in an ultrahigh vacuum chamber operating at a base pressure of 8×10^{-11} Torr that has been described in detail elsewhere [27] where desorbing species were detected using a Dycor quadrupole mass spectrometer placed in line of sight of the sample. The temperature ramp and data collection were controlled using LabView software.

X-ray photoelectron spectra (XPS) were collected in another chamber operating at a base pressure of 2×10^{-10} Torr. Spectra were typically collected with a Mg Kα X-ray power of 250 W and a cylindrical mirror analyzer pass energy of 50 eV. The binding energies were calibrated using the Pd $3d_{5/2}$ feature of clean Pd(1 1 1) at 334.8 eV as a standard. Temperature-dependent XP spectra were collected by heating the sample to the indicated temperature for 5 s, then allowing the sample to cool to ~100 K, following which the spectrum was recorded.

The Pd(1 1 1) substrate (1 cm diameter, 0.5 mm thick) was cleaned using a standard procedure, which consisted of cycles of argon ion bombardment (2 kV, 1 μA/cm^2) and annealing in 4×10^{-8} Torr of O_2 at 1000 K [1]. Following each TPD or XPS experiment, the surface is briefly annealed once again in O_2 to regain the cleanliness.

Alanine was adsorbed on the Pd(1 1 1) surface using a home-built Knudsen source described previously [26]. D-alanine powder (Aldrich, 99% purity) was stored in a stainless steel vial and was typically outgassed for at least two hours at 400 K before adsorption. The alanine was periodically replenished to ensure that the alanine flux remained constant. Alanine was dosed onto Pd(1 1 1) using a glass tube that was placed ~1 cm from the sample to avoid contaminating other parts of the chamber. ^{13}CO (ISOTEC, ⩾99% ^{13}C) was used as received.

3. Results

3.1. Alanine coverage measurements

It has been shown previously that glycine adsorbs at ~100 K into second and subsequent layers prior to completion of the first layer [26]. In this case, the bare surface coverage Θ_0 is given by $\Phi_0 = \exp(-FSt)$ where the incident flux is given by F and the sticking probability S, and t is the dosing time. The total glycine coverage Θ_{tot} is then given by $\Phi_{tot} = FSt$. The data shown below suggests that alanine films grow in an identical manner. In this case, the coverage of the bare surface was calibrated by titrating it using CO, where isotopically labeled ^{13}CO was used to distinguish it from the small amount of ^{12}CO formed by glycine decomposition. The results of a similar series of experiments for various exposures of alanine onto initially clean Pd(1 1 1), using a source temperature of ~400 K, are displayed in Fig. 1a, which shows a series of 29 amu (^{13}CO) TPD traces collected after various alanine dosing times, where the dosing times are displayed adjacent to

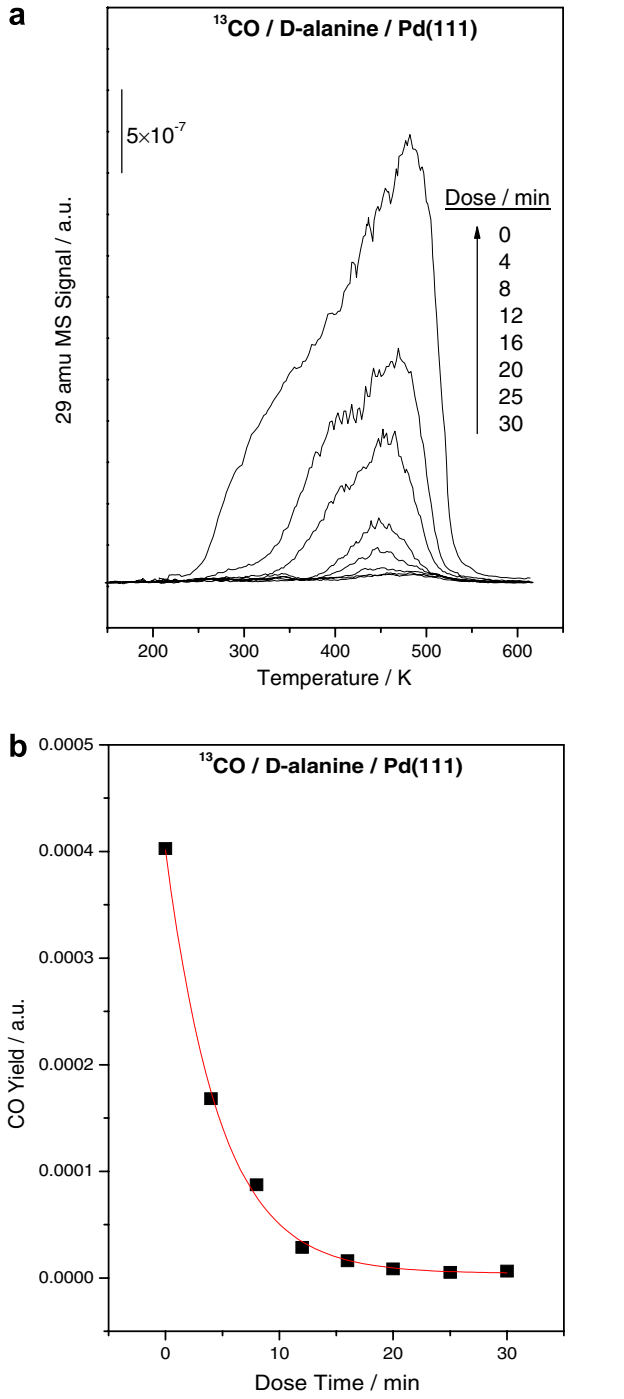


Fig. 1. (a) ^{13}CO (29 amu) temperature-programmed desorption profiles collected following exposure of Pd(1 1 1) surfaces dosed with alanine to 10 L (1 L = 1×10^{-6} Torr s) of ^{13}CO as a function of alanine dose in minutes for a source temperature of ~400 K, (b) plot of the integrated 29 amu (^{13}CO) signal yield versus alanine dose. The solid lines are fits to the data (see text).

the corresponding spectrum. The resulting peak areas are plotted versus alanine dosing time in Fig. 1b and fit to an exponential decay. The solid line displays the resulting fit and yields a value of $FS = 0.15 \pm 0.01$ ML/min. This enables the dosing time to be converted directly into alanine coverage using the equation above, and all subsequent data are labeled with the alanine coverage determined in this way.

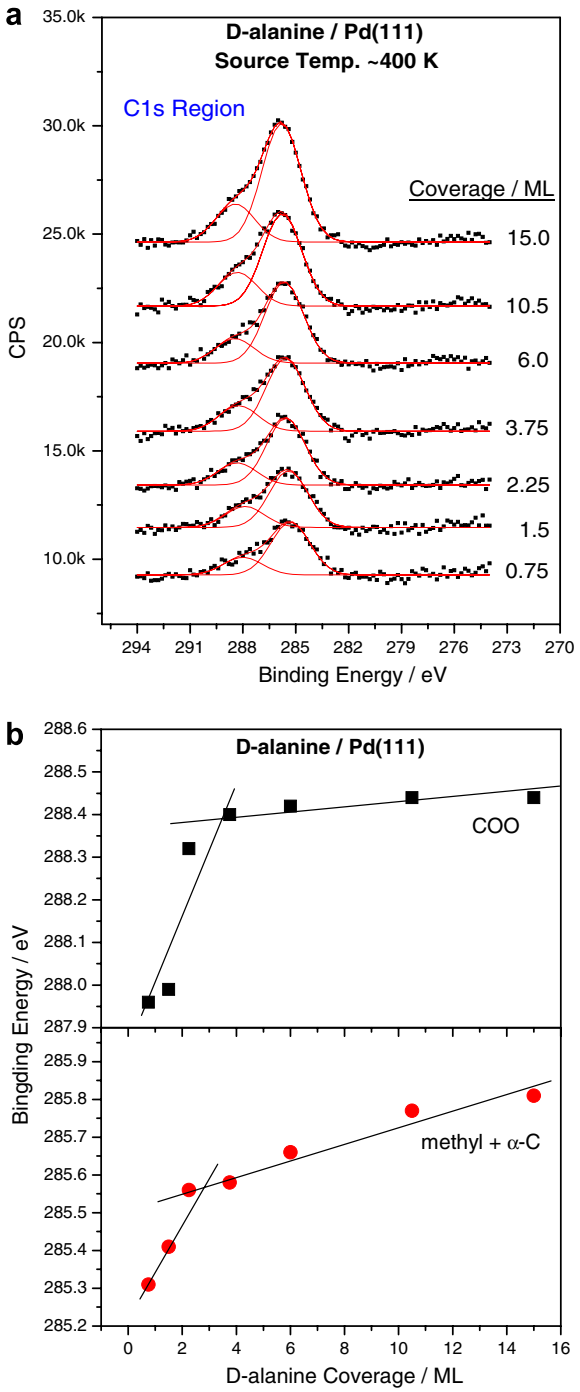


Fig. 2. (a) C 1s photoelectron spectra as a function of alanine coverage and (b) a plot of the binding energy of the C 1s feature assigned to COO and α-C + CH_3 versus alanine coverage.

3.2. Low-temperature adsorption of alanine: XPS measurements

XPS spectra were collected for alanine adsorbed onto Pd(1 1 1) at a sample temperature of ~100 K, using a source temperature of ~400 K. Fig. 2a displays the C 1s region of the spectrum, showing a continual growth in intensity with coverage, in accord with the assumptions made above that alanine adsorbs strongly into second and subsequent layers. The spectra display two features at ~288.0–288.5 eV assigned to the COO carbon, and a more intense feature at 285.3–285.8 eV due to both the α-carbon and the methyl group. Lorentzian profiles are shown fitted to each of these features. It is possible to fit two slightly separated profiles to the α-C + CH_3 feature, but since these are not well resolved, it is difficult to derive any useful information from such a fit, so that the profile is fit to a single Lorentzian. The measured integrated intensity ratio of the α-C + CH_3 to the COO feature is ~3:1, while the stoichiometry suggests that it should be 2:1. Similar lower COO C1s intensities have been observed previously for glycine on Pd(1 1 1) [26] and will be discussed in greater detail below. The binding energies of the two features are plotted versus alanine coverage in Fig. 2b. Both peaks show a rapid change in binding energy with coverage below ~3 ML, and a much slower shift for higher coverages, where lines have been included on the figures as a guide to the eye. Similar behavior has been observed previously for glycine on Pd(1 1 1) [26] and Pt(1 1 1) [22]. The slow shift in binding energy for coverages greater than ~3 ML is due to charging of the relatively thick film. It has been demonstrated previously that the first monolayer saturates after a total of ~3 ML of glycine was deposited onto Pd(1 1 1), so that the shift for coverages less that a total coverage of 3 ML is due to the combination of alanine on the surface and in second and subsequent layers having different binding energies.

The corresponding spectra of the N 1s region are displayed in Fig. 3a. These also display two features, one between 401.3 and 401.6 eV binding energy, which is assigned to $-NH_3^+$ species due to the presence of zwitterionic alanine, and the second between 398.8 and 399.4 eV assigned to NH_2 groups, and is close to the binding energy of amines on Pd(1 1 1). Measurement of the peak areas suggests that ~65% of the alanine is present in the zwitterionic form at low coverages, increasing slightly to ~70% at the highest coverages. The variation in binding energies of the N 1s features is plotted in Fig. 3b. These exhibit similar behavior in terms of binding energy shift with coverage as the C 1s features (Fig. 2), with the slow variation in binding energy above ~3 ML being assigned to charging shifts, while the more rapid shift below ~3 ML is ascribed to the presence of different species on the first and subsequent layers.

3.3. Spectroscopy of alanine decomposition and desorption

The C 1s spectra of 3 ML of alanine adsorbed on Pd(1 1 1) at ~100 K and annealed to various temperatures

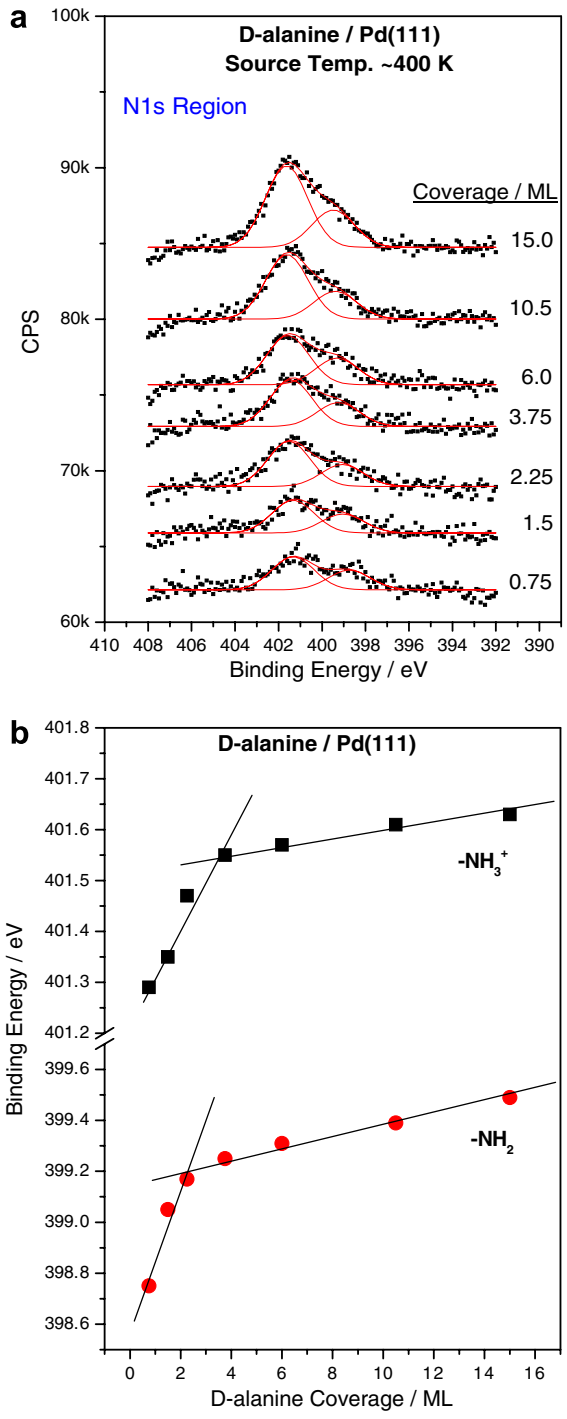


Fig. 3. (a) N 1s photoelectron spectra as a function of alanine coverage and (b) a plot of the binding energy of the N 1s feature assigned to $-NH_3^+$ and $-NH_2$ versus alanine coverage.

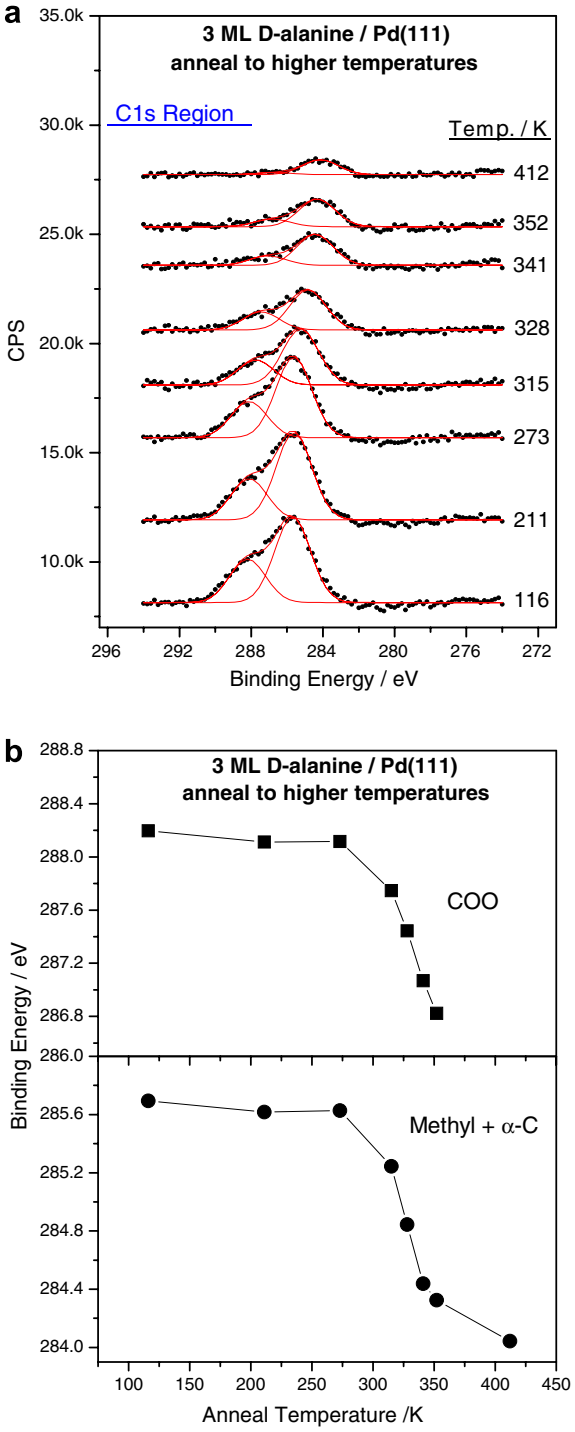


Fig. 4. (a) C 1s photoelectron spectra of 3 ML of alanine on Pd(111) as a function of annealing temperature, where the annealing temperatures are displayed adjacent to the corresponding spectrum and (b) a plot of the binding energies of the C 1s feature assigned to COO and α-C + CH_3 versus temperature.

are displayed in Fig. 4a. These experiments were performed by heating the sample to the indicated temperature for a period of 5s and allowing the sample to cool to ~100 K once again, following which the XP spectrum was recorded. The intensity of the C 1s features remains relatively constant up to an annealing temperature of ~273 K. The features then decrease significantly in intensity at ~315 K and above, and are accompanied by significant chemical shifts. The resulting COO and α-C + CH_3 binding energies are plotted in Fig. 4b. This confirms that alanine is stable on the surface up to ~300 K, but desorbs and/or decomposes at higher temperatures. While alanine does desorb in this temperature range (see below), the slightly different

shifts in the COO and α-C + CH_3 binding energies with annealing temperature indicate that alanine also decomposes on the surface, since the shift in COO C 1s signal occurs at slightly lower temperatures than for the α-C + CH_3 C 1s signal. This implies that alanine decomposes by cleavage of the OOC—C bond and this is confirmed by TPD results (see below). The C 1s features coalesce into a single peak at ~284.2 eV BE when the sample is heated above ~350 K.

The corresponding N 1s spectral region is displayed in Fig. 5a and the shift in N 1s binding energy as a function of annealing temperature is displayed in Fig. 5b. Again, the N 1s spectra are relatively unchanged on heating to ~273 K, indicating that alanine is stable on the surface to at least this temperature in accord with the C 1s results. The shift in —NH_3^+ N 1s binding energy strongly resembles that of the COO C 1s data (Fig. 4) and is due to alanine decomposition and/or desorption. However, the NH_2 N 1*s* data show an additional abrupt binding energy shift at ~325 K, which will be discussed in greater detail below.

In order to spectroscopically probe alanine desorption, the Pd 3d XPS spectra were collected for a thick (60 ML) alanine film annealed to various temperatures. These spectra are displayed in Fig. 6a, where the substrate signal is initially almost completely obscured by the thick alanine film. As the sample is heated, the 3d features become evident and this is emphasized by the plot in Fig. 6b, which displays the integrated Pd 3d peak area as a function of annealing temperature. This shows a rapid increase in signal intensity from ~325 to 350 K, indicating that alanine multilayers sublime at this temperature.

Finally, XPS measurements were made as a function of sample temperature. In this case, alanine was dosed for 40 min at various substrate temperatures and the results are shown in Fig. 7a, which displays the C 1s region. This reveals that, at ~250 K and lower, identical spectra are obtained in terms of signal intensity and binding energies. Based on the adsorption rate measured above, in each case, ~6 ML of alanine is deposited during this time. However, for a sample temperature of 300 K, drastic differences are found where marked decreases in both signal intensity and binding energy are found. For a sample temperature of 350 K, a further signal intensity decrease is observed. Apparently, at 300 K and above, the sticking probability of alanine decreases substantially. While this is not unexpected, increasing the alanine exposure (data not shown) does not result in any further increase in C 1s signal. Therefore it is concluded that adsorption is restricted to the formation of a monolayer at room-temperature. As will be shown below, this notion is further confirmed using TPD. Note also for adsorption at 250 K and below, the resulting signal intensity ratio of COO carbon (at 288.4 eV) and α-C + CH_3 carbon (at 285.8 eV) is ~1:3. However, for adsorption at 300 and 250 K, this ratio becomes ~1:2. This difference immediately suggests adsorption geometry differences at these two temperatures. Fig. 7b plots the corresponding N 1s spectral region. At adsorption temperatures of 250 K and below, the N 1s feature at 401.6 eV is assigned to zwitterionic alanine, and the feature at 399.1 eV to neutral alanine. As was found for the C 1s spectra, no signal intensity variation is found for sample temperatures of 250 K and below. However, a decrease in the proportion of neutral alanine is noticed at higher

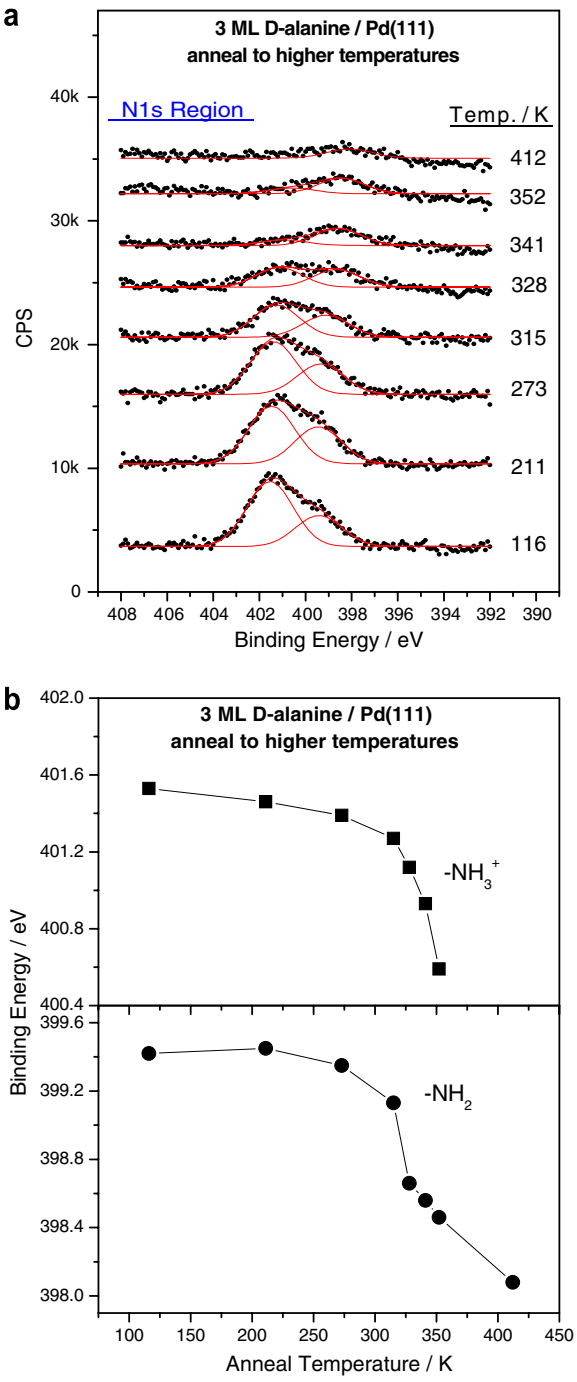


Fig. 5. (a) N 1s photoelectron spectra of 3 ML of alanine as a function of annealing temperature, where the annealing temperatures are displayed adjacent to the corresponding spectrum and (b) a plot of the binding energies of the N 1s feature assigned to —NH_3^+ and —NH_2 versus annealing temperature.

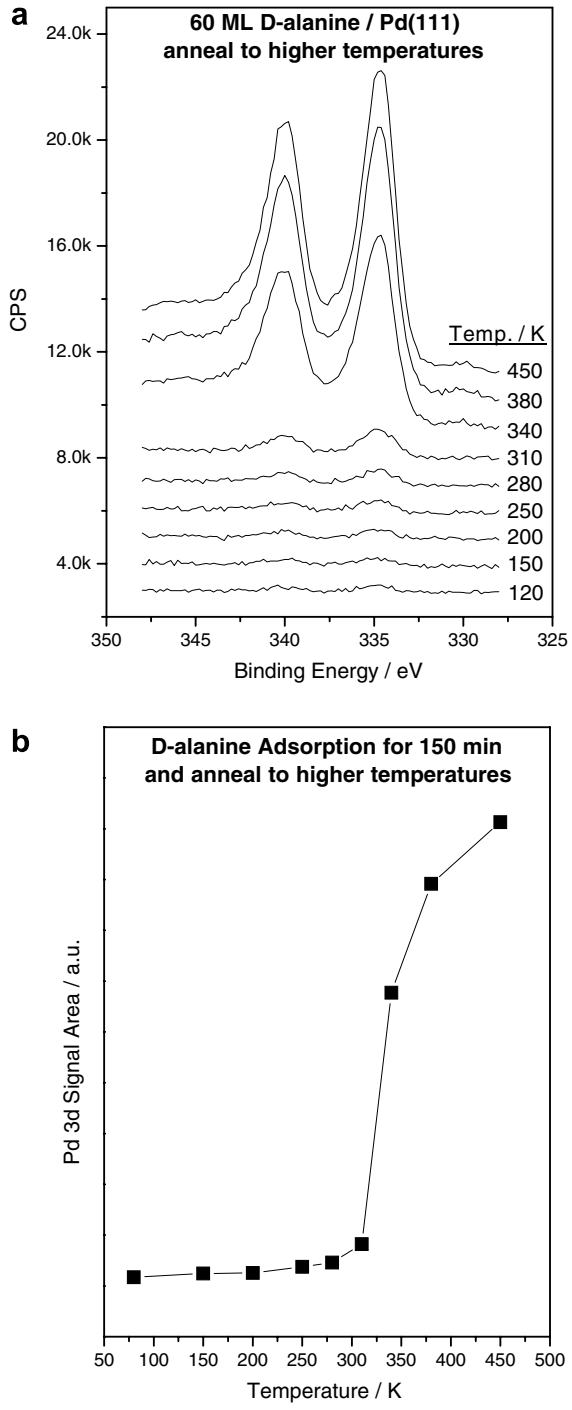


Fig. 6. (a) Pd 3d photoelectron spectra of 60 ML of alanine on Pd(1 1 1) as a function of annealing temperature, where the annealing temperatures are displayed adjacent to the corresponding spectrum and (b) a plot of the Pd 3d signal intensity versus annealing temperature.

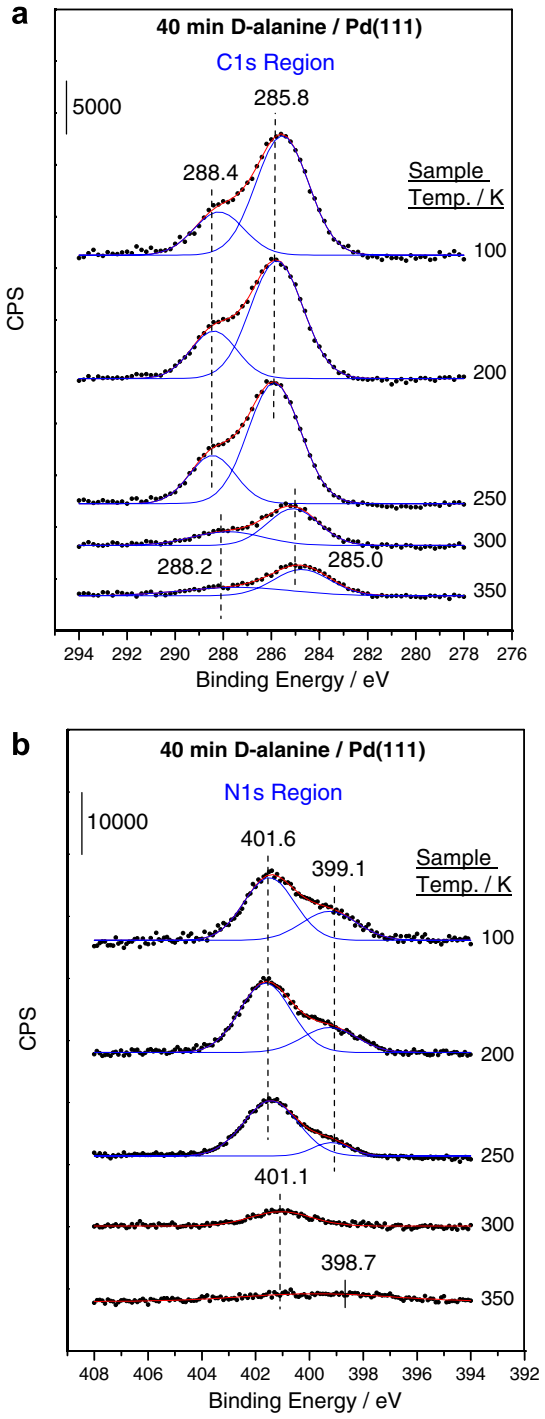


Fig. 7. (a) C 1s and (b) N 1s photoelectron spectra collected following a 40 min exposure of Pd(1 1 1) to alanine as a function of sample temperature, where the sample temperatures are displayed adjacent to the corresponding spectrum.

temperatures. In contrast, adsorption at 300 K reveals only one N 1s feature centered at 401.1 eV with substantially attenuated intensity. This indicates that, in accord with the C 1s spectrum collected at this temperature, only monolayer adsorption occurs. The N 1s binding energy suggests that, in this case, alanine is present exclusively in its zwitterionic form. For adsorption at a sample temperature of 350 K, the N 1s signal intensity at 401.1 eV decreases substantially as compared with adsorption at 300 K and a new feature appears at 398.7 eV. In contrast, the C 1s signal intensity decrease is not as profound, indicating a new species forms at this temperature, which is assigned to alaninate. A more detailed analysis will be given further below.

3.4. Decomposition of adsorbed alanine: temperature-programmed desorption

The decomposition and desorption of alanine was explored in greater detail using TPD. The desorption of intact alanine can be followed by monitoring the parent mass (at 89 amu). However, this has a rather low mass spectrometer ionizer cross section so that desorption at lower coverages is also probed by other fragments that have higher mass spectrometer ionizer cross sections, bearing in mind that they may also be due to decomposition products. In order to obtain a general overview of the surface chemistry, TPD spectra were collected at 89 (alanine), 44 (CO_2 and alanine) and 2 (hydrogen) amu. These spectra were collected at a relatively high heating rate of ~10 K/s to enhance the intensity of the molecular desorption state and the results are displayed in Fig. 8. Molecular alanine desorption is only detected at a coverage of ~6 ML at a temperature of ~360 K, and the feature grows and shifts to higher temperatures with increasing alanine coverage, suggestive of attractive interactions between alanine in the multilayer. However, these features also have relatively common leading edges, particularly at higher coverages, suggesting zero-order desorption kinetics. This will lead to an increase in peak desorption temperature without any change in desorption activation energy. Similar behavior is observed at 44 amu, where multilayer desorption is now detected at ~1.6 ML with a desorption temperature of ~340 K. An additional feature is detected at ~390 K at low alanine coverages assigned to CO_2 formation. Hydrogen desorbs in a broad feature between ~360 and ~600 K due to complete molecular decomposition of the alanine. Since molecular hydrogen desorbs from Pd(1 1 1) at ~320 K [28], this confirms that the hydrogen arises from alanine decomposition and corroborates the XPS data suggesting that alanine is stable on the surface at slightly above room temperature.

In order to explore alanine decomposition in greater detail, experiments were carried out at lower alanine coverages and with a lower heating rate (~6.5 K/s, except for the data shown in Fig. 9) to enable features to be more easily resolved. Spectra were collected at 24, 25, 26, 27 and 28 amu and are shown in Fig. 9. The 25, 26, 27 and 28 amu spectra all display a sharp feature at ~350 K, ascribed to the desorption of molecular alanine since these are all mass spectrometer ionizer fragments of alanine. The intense feature between ~490 and 470 K at 28 amu is due to carbon monoxide desorption, and is desorption-rate limited since CO desorbs from clean Pd(1 1 1) at this temperature [29]. The 24 and 25 amu spectra are similar to each other displaying a feature that shifts from ~380 K at low alanine coverages to ~400 K at high coverages implying that they are fragments of the same decomposition product. Similarly, the 26 and 27 amu profiles are essentially identical having peaks at 460, 520 and ~740 K, also implying that they are due to the same reaction product.

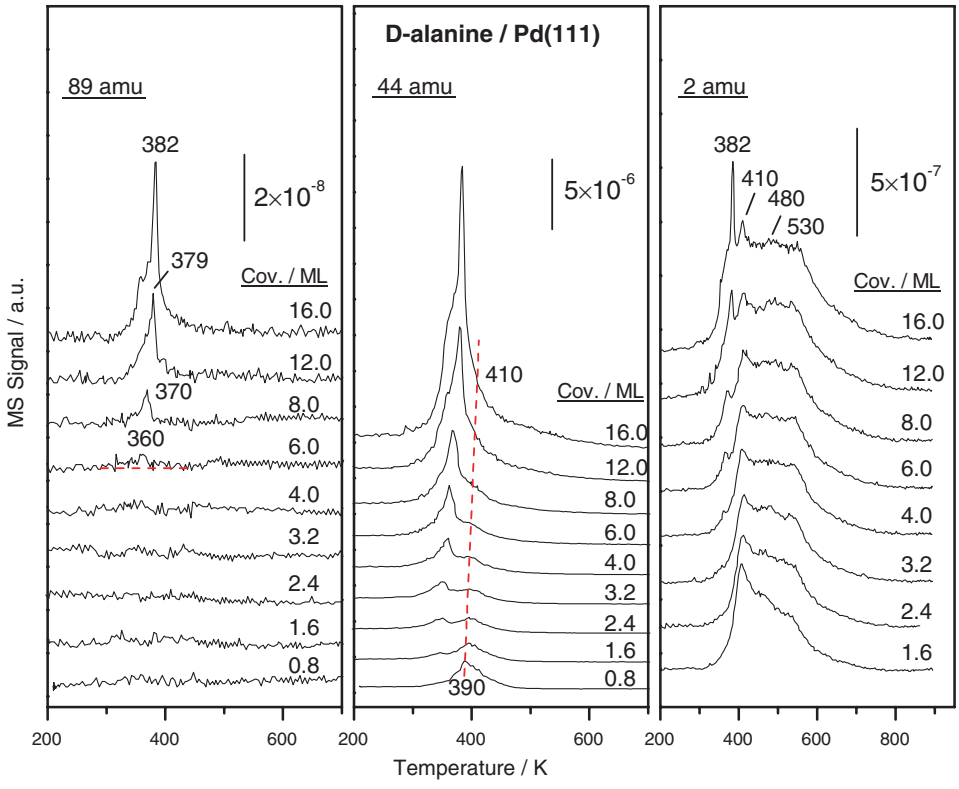


Fig. 8. 89 (alanine), 44 (CO_2 and alanine), and 2 (hydrogen) amu temperature-programmed desorption profiles for various coverages of alanine on Pd(1 1 1) collected using a heating rate of 10 K/s, where the alanine coverages are displayed adjacent to the corresponding spectrum.

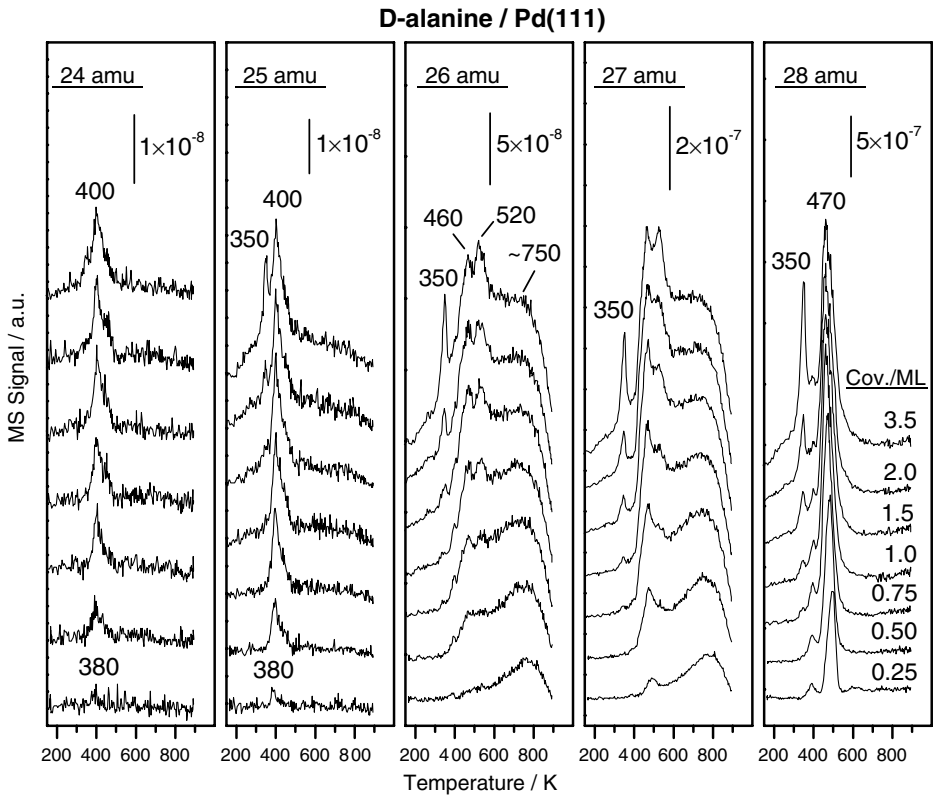


Fig. 9. 24, 25, 26, 27 and 28 amu temperature-programmed desorption profiles for various coverages of alanine on Pd(1 1 1) collected using a heating rate of 10 K/s, where the alanine coverages are displayed adjacent to the corresponding spectrum.

Note that these have no fragments at lower masses. Very similarly shaped desorption features, with peaks at ~430, 535 and 749 K were found for glycine on Pd(1 1 1) and assigned to HCN formation, where parent mass of HCN is 27 amu and 26 amu is due to the CN fragment. This assignment is in accord with the lack of intensity at 24 and 25 amu.

Additional spectra were collected at 29, 30 and 31 amu and are displayed in Fig. 10. These show no intensity at ~400 K, but all have similar profiles to each other with a sharp peak at 340 K, with a low-temperature shoulder at ~260 K. All of these masses, in particular those at 29 and 30 amu, are fragments of molecular alanine and the desorption temperature of ~340 K is close to that found for molecular alanine desorption (89 amu, Fig. 8). Thus, 30 amu in particular, is very sensitive to the desorption of molecular alanine. This demonstrates the onset of molecular alanine desorption at 1.0 ML, and no molecular desorption occurs at 0.5 ML. A small amount of alanine also appears to desorb at lower temperatures (~260 K). This desorption state is also found at other masses (see below) and may be due to desorption of weakly adsorbed alanine molecules from the Pd surface.

To further investigate the nature of the ~400 K state observed in Fig. 8, spectra were collected at 38, 39, 40, 41 and 42 amu (Fig. 11). These all display a ~340 K feature due to alanine desorption, and a 390 K feature with fragments at 38, 39, 40 and 41 amu, but not at 42 amu. Comparison with the fragmentation patterns of possible reaction products reveals that this is due to the formation of ethylamine. In particular, the absence of a 42 amu signal is strongly supportive of this conclusion. Fig. 12 displays desorption at 43 and 44 amu. For both masses, two desorption states are found. Desorption at 340 K is again assigned to fragmentation of alanine. Since both 43 and 44 amu are fragments of ethylamine, the 390-K desorption state must include contributions from ethylamine. However, the signal intensity at 44 amu is far too large to be an ethylamine fragment. Therefore it is concluded that this is due predominately to the formation of CO_2. The lineshape similarity between the 43 and 44 amu profiles indicates that the 43 amu signal contains some level of cross talk at this mass from the intense 44 amu signal. Final confirmation of ethylamine formation comes from the TPD profiles in Fig. 13, where 45, 46, 55, 56 and 57 amu are monitored. Again, the features at ~260 and 340 amu are due to alanine desorption, while the 390 K feature only appears at 45 amu (parent mass of ethylamine) and 46 ($C_2H_5NH_3^+$) amu (formed in the mass spectrometer ioniozer), providing final proof that the ~390 K state is due to ethylamine. Formic acid also has fragments at 45 and 46 amu. However, it also has an intense 29 amu fragment, not detected at 390 K (Fig. 10).

Finally, in order to confirm the notion that room-temperature adsorption leads to only monolayer growth, TPD experiments were performed following adsorption at

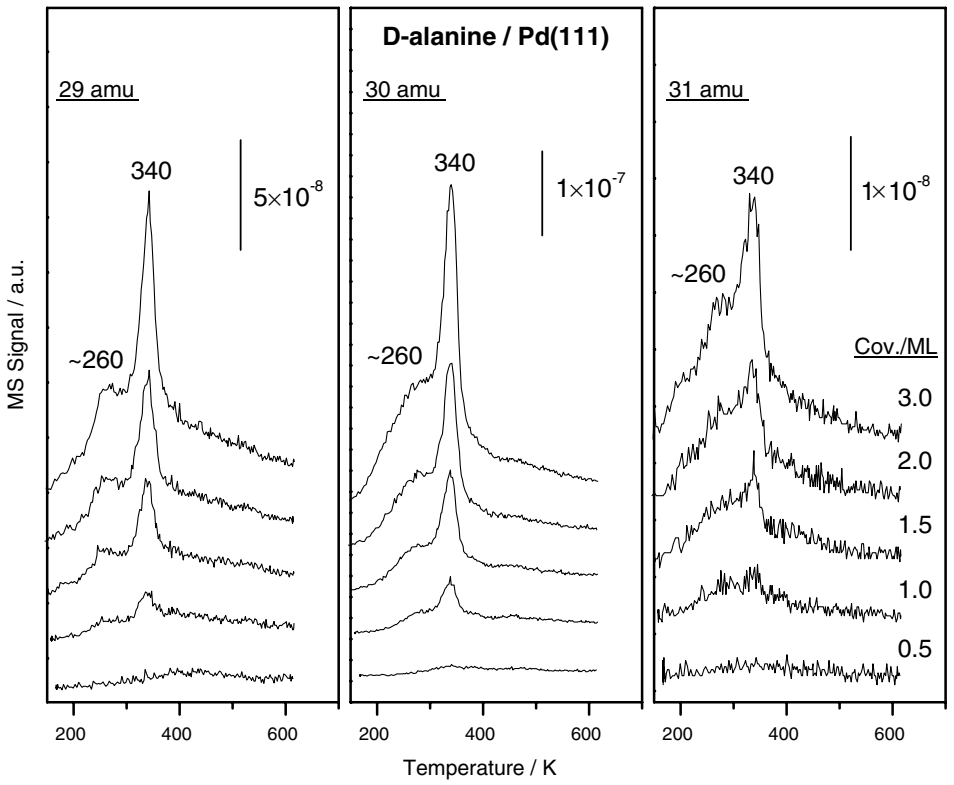


Fig. 10. 29, 30 and 31 amu temperature-programmed desorption profiles for various coverages of alanine on Pd(1 1 1) collected using a heating rate of 6.5 K/s, where the alanine coverages are displayed adjacent to the corresponding spectrum.

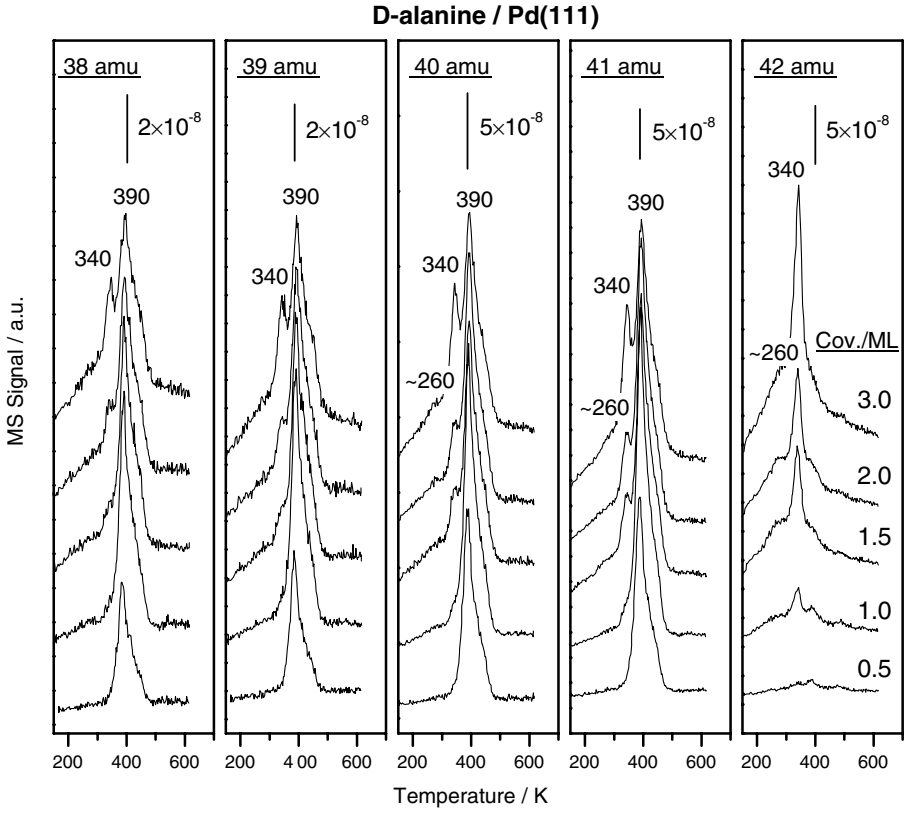


Fig. 11. 38, 39, 40, 41 and 42 amu temperature-programmed desorption profiles for various coverages of alanine on Pd(1 1 1) collected using a heating rate of 6.5 K/s, where the alanine coverages are displayed adjacent to the corresponding spectrum.

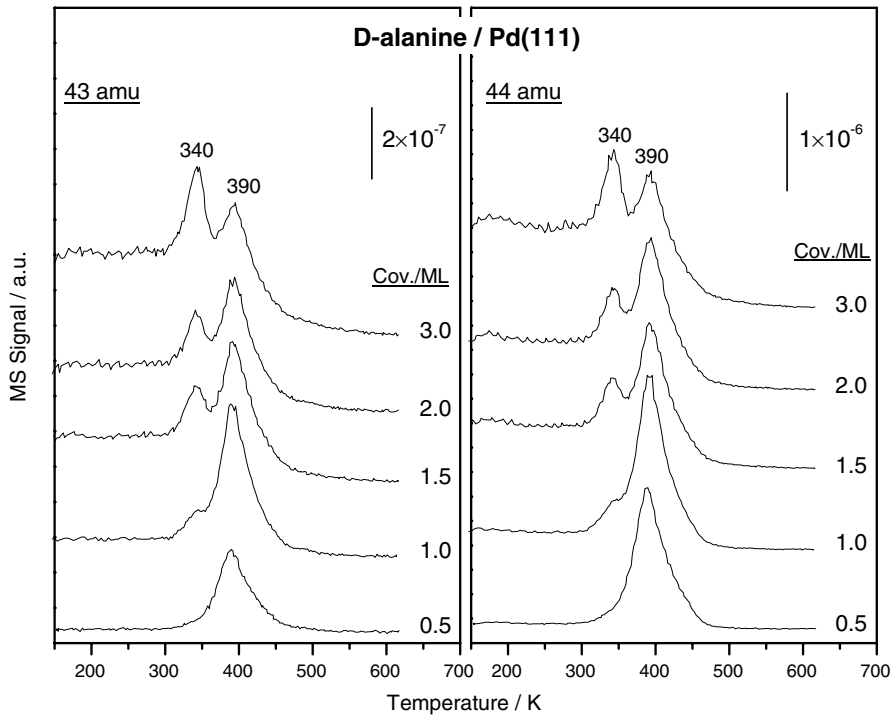


Fig. 12. 43 and 44 amu temperature-programmed desorption profiles for various coverages of alanine on Pd(1 1 1) collected using a heating rate of 6.5 K/s, where the alanine coverages are displayed adjacent to the corresponding spectrum.

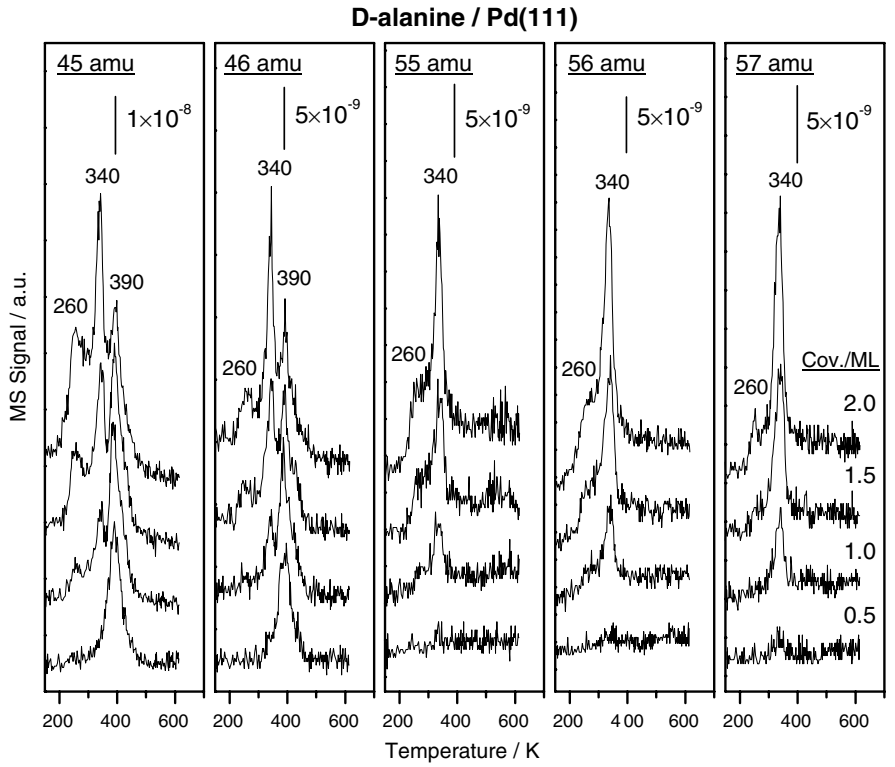


Fig. 13. 45, 46, 55, 56 and 57 amu temperature-programmed desorption profiles for various coverages of alanine on Pd(1 1 1) collected using a heating rate of 6.5 K/s, where the alanine coverages are displayed adjacent to the corresponding spectrum.

a sample temperature of ~300 K. Since the sticking probability of alanine is much lower in this case (Fig. 7), ^{13}CO titration experiments were first performed to determine the growth rate (data not shown). This reveals that

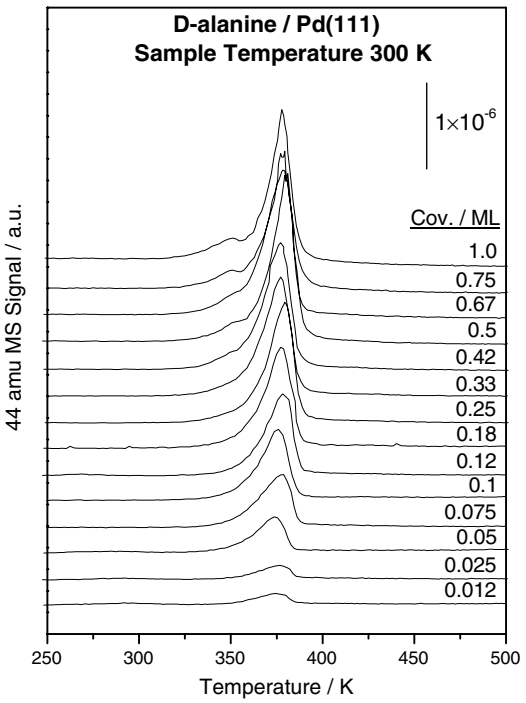


Fig. 14. 44 amu temperature-programmed desorption profiles for various coverages of alanine adsorbed on Pd(1 1 1) at room temperature collected using a heating rate of 6.5 K/s, where the alanine coverages are displayed adjacent to the corresponding spectrum.

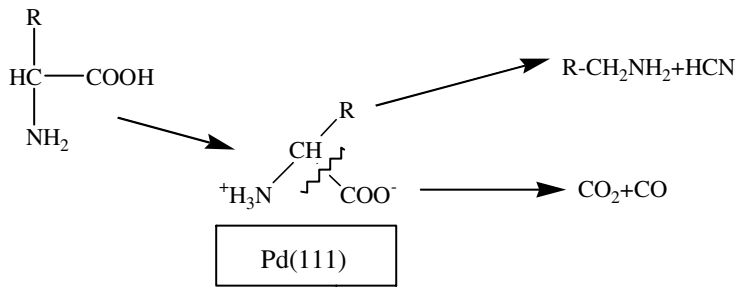
$FS = 0.025$ ML/min and this is used to determine alanine coverage following room-temperature adsorption. Fig. 14 plots desorption at 44 amu (CO_2) as a function of alanine coverage. This reveals that at alanine coverages of 0.5 ML and above, very weak desorption at ~350 K appears and is assigned to desorption from the multilayer. This immediately suggests that some multilayer adsorption still occurs even during room-temperature adsorption. Again, consistent with XPS measurements, extending the adsorption time does not increase the intensity of this multilayer feature. According to a recent study by Zhao and Rodriguez [25], this is due to re-evaporation from the multilayer during room-temperature adsorption. Apparently, since the adsorption rate of alanine at room- temperature is sufficiently low, the desorption rate becomes comparable with rate of adsorption, leading to a situation in which extensive multilayer adsorption is inhibited.

4. Discussion

The chemistry of alanine broadly resembles that found previously for glycine on Pd(1 1 1) [26]. In that case, glycine adsorbed predominantly as the zwitterion on the Pd(1 1 1) surface and was stable to slightly above room-temperature and decomposed by C—C bond scission, where the COO moiety desorbed as CO and CO_2, while the nitrogen-containing fragment desorbed as methylamine and HCN.

The binding energies of C 1s and N 1s features displayed in Figs. 2 and 3 show that alanine adsorbs molecularly at ~100 K, and remains intact until at least at 290 K (Figs. 4 and 5. The C 1s and N 1s binding energies vary with coverage, showing a rapid change with coverage up to ~3 ML, but vary more slowly at higher coverages. For coverages above 3 ML, when the multilayer is growing, the change in binding energy has been previously assigned to a charging effect [22]. The rapid change below ~3 ML is due to varying coverages of alanine on the Pd(1 1 1) surface and in second and subsequent layers with different binding energies. Thus, extrapolating the data in Figs. 2b and 3b to zero coverage should yield reasonable estimates of the binding energies for alanine on Pd(1 1 1), yielding C 1s binding energies of ~288.0 and ~285.2 eV and N 1s binding energies of ~398.6 and ~401.2 eV. Acetate species on Pd(1 1 1) exhibit C 1s features at ~288.5 eV due to the carboxylate and at 284.9 eV due to the methyl group [30]. These values are in reasonable agreement with the C 1s features of alanine assigned to the COO group (~288 eV) and the α-C + CH_3 (285.2 eV). The N 1s binding energy of ~401.2 eV is in good agreement with previous assignments to NH_3^+ species for glycine on Pd(1 1 1) (400.7 eV [26]) and on Pt(1 1 1) (401.3 eV [22]), while a N 1s binding energy of 398.6 eV is assigned to an amino group of neutral alanine. However, this feature shifts by ~0.6 eV on heating to ~325 K (Fig. 5b) and is assigned to the formation of an alaninate species.

Interestingly, substantial differences are found for room-temperature adsorption compared with adsorption at 250 K and below (Fig. 7). First of all, according to the binding energy analysis shown above, alanine is present exclusively in its zwitterionic form following room-temperature adsorption. As summarized in our recent paper [26], the adsorption of amino acids on a surface (zwitterionic, neutral and anionic forms) depends delicately on the nature of the metallic substrate and temperature. For Pd(1 1 1), below the H_2 desorption temperature (~350 K, Fig. 8), alanine should be present in either the zwitterionic or neutral form. In the monolayer regime, the conversion from neutral alanine to zwitterion may occur with the participation of the surface while in the multilayer regime, this occurs exclusively through an intermolecular interaction. The XPS data shown in Fig. 7b indicate that higher temperatures favor this conversion, but this process predominates only at 300 K. Also note that this process appears not to be extremely fast since annealing a 3 ML alanine film rapidly to slightly above room-temperature does not necessarily convert neutral alanine to zwitterions (Fig. 5). Second, room-temperature alanine adsorption leads to an intensity ratio of 1:2 between the COO and α-C + methyl carbon, while low-temperature adsorption results in an intensity ratio of 1:3. This correspondingly implies that the COO groups are partially obscured by α-C + methyl carbons during low-temperature adsorption, while this does not occur at room-temperature. In both cases, alanine is predominantly in its zwitterionic form (Fig. 7) so that the above mentioned ratio difference is unlikely due to conformational differences in these two situations, so that this reori-



Scheme 1. Reaction pathways for α-aminoacids on Pd(1 1 1).

entation must derive from the influence of multilayers at low temperatures. The data of Fig. 6, as well as the TPD spectra in Figs. 8, 10, 11 and 12 indicate that molecular alanine desorbs from the multilayer at ~340 K for total alanine coverages up to ~3 ML. The desorption temperature increases with increasing coverage and shifts to ~360 K for ~6 ML of alanine and ~380 K for ~16 ML (Fig. 8), indicating that there are relatively long-range attractive interactions between adsorbed alanine molecules in the multilayer. Such an attractive interaction is likely to be due to electrostatic attractions between negatively charged COO^- and positively charged $-NH_3^+$. Therefore it is expected that this interaction, that apparently occurs between layers, causes a change in geometry of the $-CH(NH_3^+)—CH_3$ species during low-temperature adsorption. For room-temperature adsorption, on the other hand, since the multilayer is almost absent, interactions between the layers is nonexistent and the intensity ratio of 1:2 between the COO and α-C + methyl carbon indicates that both COO and nitrogen anchor to the surface. A recent study by Held et al. [31] found very similar signal intensity ratio differences for multi- and monolayers of alanine on Cu(1 1 0), although in that case, the monolayer consists exclusively of alaninate.

Alanine is relatively stable on the surface, with no significant changes in the XPS spectra being observed until ~300 K. Two decomposition pathways are possible for alanine, either C—C bond and/or C—N bond scission. The former reaction would yield ethylamine and carbon dioxide or carbon monoxide, while the second would form a carboxylate and ammonia. Furthermore, the charge distribution of zwitterionic glycine has been suggested to weaken the C—C bond thus facilitating cleavage [21]. The TPD and XPS results demonstrate that alanine decomposes by OOC—C bond scission on Pd(1 1 1) and is confirmed by the following observations: (1) the COO C 1s signal disappears at lower temperatures than the α-C + CH_3 C 1s signal (Fig. 4), (2) substantial amount of ethylamine and CO_2 are formed.

Thus, a general picture emerges for the chemistry of α-amino acids on Pd(1 1 1). For adsorption at ~100 K, since amino acids adsorb strongly in second and subsequent layers, these layers start to form before the first layer was saturated. The amino acids are stable up to ~300 K, and then start to decompose by OOC—C bond scission. This decomposition pathway has been found for glycine [26] and now alanine on Pd(1 1 1) and it is anticipated that all α-amino acids will behave similarly. The decomposition pathways are summarized in Scheme 1, where it is proposed, based on the XPS results that the amino acid adsorbs onto the surface in its zwitterionic form. Decomposition is initiated by OOC—C bond scission, where the COO moiety desorbs as CO_2 (Fig. 12) and CO (Fig. 9). The nitrogen-containing fragment forms methylamine following glycine adsorption [26] and ethylamine from alanine. It is thus anticipated that RCH_2NH_2 will form from amino acids with a functional group R.

In addition, there is clear evidence for HCN formation over a relatively wide temperature range from alanine (Fig. 8) and glycine [26]. This arises from the hydrogenation of $CN_{(ads)}$ originated from thermal decomposition of the nitrogen-containing fragments and similar chemistry has been observed previously for methylamine on Pd(1 1 1) [32]. It should be emphasized that, while this represents a major decomposition pathway for α-amino acids on Pd(1 1 1), there are clearly other pathways that presumably involve complete thermal decomposition of the amino acid since a substantial amount of hydrogen desorbs from the surface (Fig. 8).

5. Conclusions

Alanine adsorbs strongly on the clean Pd(1 1 1) surface at ~100 K and into second and subsequent layers, where the bare surface coverage is monitored using ^{13}CO titrations, enabling alanine coverage to be calibrated as a function of dose. XPS results suggest that essentially all of the alanine adsorbs into the first layer in its zwitterionic form, while condensation into second and subsequent layers contain both zwitterionic and neutral alanine, with about 30–35% being neutral depending on the total coverage. Adsorption at ~300 K forms only a monolayer of alanine in its zwitterionic form. Molecular alanine desorbs from the multilayer between 350 and 380 K, depending on coverage. A small portion of alanine desorbs molecularly from the first layer, with the remainder undergoing thermal decomposition. This occurs almost exclusively by C—C bond scission with the fragments desorbing as CO_2 and CO from the COO^- moiety, and as ethylamine or HCN from $CH_3—CH—NH_3^+$.

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