

C and S induces changes in the electronic and geometric structure of Pd(533) and Pd(320)

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We have performed *ab initio* electronic structure calculations of C and S adsorption on two vicinal surfaces of Pd with different terrace geometry and width. We find both adsorbates to induce a significant perturbation of the surface electronic and geometric structure of Pd(533) and Pd(320). In particular C adsorbed at the bridge site at the edge of a Pd chain in Pd(320) is found to penetrate the surface to form a sub-surface structure. The adsorption energies show almost linear dependence on the number of adsorbate-metal bonds, and lie in the ranges of 5.31eV to 8.58eV for C and 2.89eV to 5.40eV for S. A strong hybridization between adsorbate and surface electronic states causes a large splitting of the bands leading to a drastic decrease in the local densities of electronic states at the Fermi-level for Pd surface atoms neighboring the adsorbate which may poison catalytic activity of the surface. Comparison of the results for Pd(533) with those obtained earlier for Pd(211) suggests the local character of the impact of the adsorbate on the geometric and electronic structures of Pd surfaces.

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I. INTRODUCTION

The elementary processes in heterogeneous catalysis, such as adsorption of reactants, and their diffusion and reaction, are caused by the formation, modification, or breaking of chemical bonds between the molecules and a catalyst. Since the nature of the chemical bonds is determined by the interplay of the electronic and geometric structures of the catalyst surface, these characteristics are the focus of numerous studies.

Real catalysts usually have a complex geometric structure, because they are highly dis-

persed as small particles on substrates. The surface of these particles may have microfacets with high Miller index planes consisting of steps and kinks which may influence significantly the reactivity of catalyst surfaces [1, 2, 3, 4, 5, 6, 7, 8]. For instance, the N_2 association reaction is extremely sensitive to the presence of steps. For $\text{Ru}(0001)$, its rate at the step edges is found experimentally to be at least 9 orders of magnitude higher than that on its terrace, at 500 K [3]. The sticking coefficient of O_2 on the stepped surface $\text{Ag}(410)$ is also found to be higher than that on $\text{Ag}(100)$ as measured in a recent High Resolution Electron Energy Loss (HREEL) spectroscopy experiments [9].

The specific role of step atoms in a chemical reaction may, however, be more complex and may not always lead to enhanced reactivity. Experimental observations do not show any effect of steps on the rate of CO oxidation on $\text{Pt}(335)$ [10] or other metal surfaces [11]. Results of first principles calculation for the reaction on $\text{Pd}(211)$, $\text{Pd}(311)$ [6] and $\text{Ir}(211)$ [11] also indicate that CO oxidation barriers are insensitive to the local surface geometry. It has also been pointed out [12] that dissociation reactions are always structure-sensitive (surface steps are favored for the reactions), while association reactions may not always be so. Furthermore, the reactions with high valence reactant are usually more structure-sensitive.

Apart from steps and kinks, there are other imperfections that may affect surface reactivity. In real catalytic processes some sub-products of reactions or other gases present in the reaction environment may atomically adsorb on the catalyst surface and change its reactivity. For instance, sulfur containing molecules are common impurities in gasoline. During CO catalytic oxidation in car exhaust refinement system, sulfur, known as inhibitor for many catalytic reactions, adsorbs atomically on the catalyst surface and poisons surface reactivity. In one of the earlier studies [13], it was suggested that the depletion of the local density of states at the Fermi-level $[N_a(E_F)]$ (a denotes the atom contributing to LDOS) upon S adsorption can cause poisoning of surface reactivity. Computational studies of S adsorption on some Pd surfaces [14, 15, 16] also show a reduction of $N_a(E_F)$ due to a strong hybridization of the p states of S with the d states of Pd. Several experimental studies also focus on the poisoning effect of S on metal surfaces [17, 18, 19]. Although the rate of CO dissociation during catalytic oxidation is low, small amount of C can atomically adsorb on the catalyst surface. Our recent results [14, 15] show that C atoms adsorbed on Pd stepped surfaces suppress substantially $N_a(E_F)$ of the neighboring surface atoms which may be taken as indication of poisoning. Atomic carbon adsorption on Pd surface and its poisoning effect

were also reported for the case of catalytic vinyl acetate synthesis [20]. Moreover, since step sites are generally more reactive than others on the terrace, they are also prone to attract more impurities. The combination of steps and atomically adsorbed impurities may thus have a significant impact on the reactivity of catalysts.

Motivated by the above, we have investigated the effect of C and S adsorption on the geometric and electronic structures of Pd(533), a vicinal of Pd(111), and compared them with that on Pd(320), a vicinal of Pd(110), for several reasons. First a comparative study of the effect of C and S on a stepped transition metal surface would provide a measure of the strength of the impurity substrate bond and its impact on the surface electronic structure. Second, as the atoms along the steps of Pd(533) and Pd(320) have local coordination of 7 and 6, respectively, a systematic study of C and S adsorption on these two surfaces is a step towards understanding the role of undercoordinated sites in chemical reactivity. Third, comparison of the results on Pd(533) with those already available for Pd(211), a smaller terrace but of similar geometry, will provide insights on role of terrace width on the chemisorption process. Finally, examination of the relative effect of C and S on Pd(320) will provide the basis for comparison of results on stepped surfaces with fcc(110) terrace geometry to those with fcc(111) terraces [14]. Since the nonequivalent atoms on a vicinal surface, in the presence of an adsorbate, account for a complex and inhomogeneous system, these studies are expected to have implications also for the characteristics of nanoparticles which contain a range of undercoordinated sites in complex environments. Note that in an earlier study, Makkonen *et al.* [15] have already presented some results for the energetics of S adsorption on Pd(320). We have repeated these calculations and included the results here only for completeness.

II. DETAILS OF COMPUTATIONAL METHOD

The present first principles calculations are based on density functional theory (DFT) [21] with the generalized gradient approximation (GGA) [22] for the exchange-correlation potential. Optimized surface structures and the adsorption energies (E_{ad}) have been calculated using the plane wave pseudopotential method (PWPP) [23] with ultrasoft pseudopotentials [24], while the full potential linearized augmented plane wave (FLAPW) method [25] as embodied in the WIEN2K code [26] has been used to calculate the detailed electronic structure

including the local density of electronic states (LDOS) and valence charge densities for the most interesting systems.

The fcc(533) surface consists of four-atom wide (111) terrace and a monatomic (100) micro-facetted step edge. A perspective view of such a surface is shown in Fig. ??a. Throughout this article we have used the following nomenclature to describe the chains of atoms on this surface: SC (step chain) consisting of the step edge atoms, TC1 (terrace chain 1) for the chain passing through terrace atoms next to the step edge, TC2 (terrace chain 2) for the chain through the terrace atoms adjacent to the corner atoms, CC (corner chain) for the chain located between TC2 and SC, and BNN (bulk nearest neighbor) for the ones located just underneath SC. The Pd(533) surface was modelled by a supercell comprised of a 22 layer slab and 12 Å of vacuum.

The Pd(320) is a stepped surface with 3 atoms wide (110) terraces and a monatomic (100)-micro-facetted step edge. Because the fcc(110) geometry is more open than the close-packed fcc(111), a kinked structure is formed along the step edge in Pd(320) (see Fig. ??b). For this surface, we have used notations Pd1, Pd2, Pd3, and so on, to describe corresponding atoms in different layers of the surface. The Pd(320) supercell included a 19 layer slab and 11 Å of vacuum. The surfaces adsorbed with S or C contained one adsorbate atom per primitive two dimensional unit cells, shown in Fig. ??. This corresponds to the adsorbate coverage of 1/4 monolayer (ML) for Pd(533) and 1/3 ML for Pd(320).

For all PWPP calculations we used an energy cut-off of 290 eV, which was found to be sufficient. A Monkhorst-Pack k -point mesh [27] of $(10 \times 10 \times 10)$, $(10 \times 3 \times 1)$ and $(10 \times 4 \times 1)$ was used to model bulk Pd, Pd(533) and Pd(320), respectively. The bulk lattice constant was calculated to be 3.96 Å which is almost 2% higher than the experimental value [28] and is typical of results obtained from DFT/GGA. During the lattice relaxations, all atoms were allowed to fully relax in all directions until forces on each atom were less than 0.02 eV/Å.

For the most interesting structures, the relaxed geometries obtained from PWPP calculations were used as input for the WIEN2K code which further refined the geometries in a few ionic iterations. In the FLAPW method, the LDOS and local charges are calculated through integration over muffin-tin (MT) spheres of radius R_{MT} . To analyze the effect of the adsorbate on these specific quantities the set of R_{MT} for Pd atoms should be chosen to be the same for both the clean and the adsorbate covered surface. Ideally R_{MT} should be as large as possible without causing the MT spheres to overlap. For bulk Pd atoms, a choice of

$R_{MT} = 1.38 \text{ \AA}$ was found to be optimal. However, for the Pd atoms with direct bonds to C and S, $R_{MT} = 1.08 \text{ \AA}$ (for C) and $R_{MT} = 1.22 \text{ \AA}$ (for S) provided more compatibility with the shorter C – Pd and S – Pd bond lengths. For C atoms, $R_{MT} = 0.926 \text{ \AA}$ and for S atoms $R_{MT} = 1.08 \text{ \AA}$ was found to be appropriate. In order to include a reasonably large number of plane waves ($RK_{max} = 7$) with the reduced R_{MT} 's for the surface atoms, we used basis sets of 1678, 3039 and 4795 LAPWs for Pd(533), S/Pd(533) and C/Pd(533), respectively. The calculations were performed for the $(10 \times 3 \times 1)$ and $(6 \times 3 \times 1)$ k -point mesh in the Brillouin zone for Pd(533) and Pd(320), respectively.

III. RESULTS AND DISCUSSION

A. Surface Relaxations

Optimized geometric structures of Pd(533) and Pd(320) with adsorbed S and C were obtained for 10 possible adsorption sites on the former and 6 sites on the latter, as shown in Fig. ???. We find the adsorbate to perturb substantially the structures of both surfaces regardless of the site it takes. For Pd(533) the effect is found to be most dramatic if S or C adsorb on site # 1, as labeled in Fig. ??. Surface lattice relaxation is usually characterized by changes in the interlayer separations $\delta \mathbf{d}_{i,i+1}$, which are defined as the distances between neighboring surface planes. In Table I, we show deviations of $\delta \mathbf{d}_{i,i+1}$ from those obtained for the bulk terminated surface. In the case of clean Pd(533), these deviations characterize the relaxation introduced upon creation of the surface from bulk material, while for Pd(533) with adsorbed S or C, the presence of the adsorbate also affects the nature of the surface relaxation. As seen from Table I, S and C perturb the surface relaxation pattern of Pd(533) in very different manners. This is caused by differences in the adsorption geometries of S and C illustrated in Fig. ??. During the relaxation, the smaller size of the C atom allows it to penetrate the surface and form chemical bonds with the CC, SC and BNN atoms. To keep the optimal C-Pd bond lengths, the separation between SC (layer 1) and BNN (layer 5) atoms is expanded causing an increase in $\delta \mathbf{d}_{1,2}$ and $\delta \mathbf{d}_{4,5}$. In contrast, the relatively larger size of the S atoms keeps them outside the step corner. They form bonds with SC and CC atoms and build extra S - TC2 bonds which induce upward displacement of the TC2 atoms (layer 3) and hence an increase in $\delta \mathbf{d}_{3,4}$. Interestingly, our recent calculations performed for Pd(211)

reveal a similar response of the surface lattice to S and C adsorption [14]: the separation between SC and BNN is substantially increased upon C adsorption and TC is displaced upwards upon S adsorption. Note that Pd(211) has one less chain of atoms on its terrace as compared to that of Pd(533). This similarity reflects the predominantly local character of the perturbation induced by the adsorbate. The surface atoms are displaced to form chemical bonds with the adsorbate affecting mostly the nearest neighbors. However, some difference in magnitudes of atomic displacements found for Pd(533) and Pd(211) may be traced to long range interactions. It should be mentioned that the surfaces under consideration are high Miller index surfaces with small interlayer separations (for Pd(533) it is only 0.604 Å). Therefore the large percentage of interlayer separation shown in Table I corresponds to less dramatic absolute shifts. Nevertheless, $\delta \mathbf{d}_{3,4} = +44.7\%$ obtained for S/Pd(533) is 0.27 Å or 9% of the Pd-Pd bond length which is a significant factor and reflective of strong perturbation induced by the adsorbate.

Lattice relaxation upon S and C adsorption has also been studied for the kinked Pd(320) surface. The results for $\delta \mathbf{d}_{i,i+1}$ for S and C adsorbed at the site 1, (Fig. ??) are shown in Table II. In general, the calculated relaxation pattern (— — + — +) for clean Pd(320) matches well with LEED results [29]. As in the case of Pd(533), the size and chemical composition of the adsorbate atom have a remarkable effect on the relaxation patterns for S/Pd(320) and C/Pd(320) which are strikingly different. C atoms penetrate the kink site and form bonds with five neighboring surface atoms including Pd1, two Pd3, Pd5 and Pd6. Optimization of bond length causes the displacements of all these atoms giving rise to a significant multilayer relaxation. The S atoms, on the other hand, stay above the kink site and cause a substantial displacement only for Pd1 and Pd5 atoms. Also for the case of S on Pd(320), the surface relaxations reported here are in agreement with those obtained earlier by Makkonen *et al.* [15].

An unexpected result has also been revealed for carbon adsorption at the bridge site (C5) between Pd1 and Pd2 on Pd(320). The adsorbed C atom is found to penetrate the surface spontaneously by pushing the Pd1 atom away from Pd2 and diffusing between Pd1 and Pd2 followed by backward displacement of Pd1 to restore the Pd1 - Pd2 bond. As a result, C forms a sub-surface structure in which it has chemical bonds with 6 neighboring Pd atoms. The initial and final (equilibrium) geometries of this adsorption are shown in Fig. ?. This also induces a large outward displacement of Pd1 resulting in a significant (38.1%) increase

in $\delta\mathbf{d}_{1,2}$ (see Table II).

B. Adsorption Energies

For each adsorption site shown in Fig. ??, we have calculated the adsorption energy E_{ad} for both S and C on Pd(533) C on Pd(320) and listed them in Table III. We find that for all sites under consideration carbon has higher adsorption energy than sulfur. This reflects the difference in the nature of the chemical bonding for S and C to be discussed in the next subsection. The E_{ad} values spread over the range of 4.13 eV to 5.40 eV for S and 5.31 to 8.44 eV for C atoms. Similar is the range of E_{ad} for adsorption on Pd(320) (Table III) for C and Ref. [15] for S. As found in earlier work on vicinal surfaces [14, 15], E_{ad} scales roughly linearly with the number of bonds, N_b , that the adsorbate makes with the substrate, as illustrated in Fig. ?. For Pd(533), the highest E_{ad} is obtained for S or C adsorption at a 4 fold hollow site (the site # 1). Then, in the order of decreasing E_{ad} values we have four 3 fold hollow sites (# 2, 3, 4 and 5), three 2 fold bridge sites (# 6, 7, and 8) and two on-top sites (# 9 and 10). The physics behind this trend can be understood in terms of the tight binding approximation in which the $pC-dPd$ band width is proportional to the number of nearest neighbors. Broadening the band leads to depopulation of the anti-bonding $pC-dPd$ states and this way makes the bonds stronger. Some scattering of the results seen in Fig. ?? can be attributed to the fact that the notion of interatomic bond is not well-defined, especially for such complex geometries as considered in the present work. For instance, formally carbon adsorbed at the site #6 has two neighboring Pd: SC and CC, but, in fact, it also experiences some weak chemical bonding with two BNN atoms. These extra bonds increase the adsorption energy and produce a deviation from the linear dependence. Similarly, C adsorbed at the site #1, has 5 bonds: four bonds to the SC and CC Pd atoms which are almost equal, and a fifth bond to BNN which is longer and causes a downward shift of E_{ad} . Nevertheless, the obtained proportionality of E_{ad} to N_b can be used for rough estimation of adsorption energies of C or S on stepped or kinked Pd surfaces, while deeper insight into the nature of these phenomena can be gained from analysis of the electronic structure.

It is interesting to compare the adsorption energy for C on Pd(533) with those on Pd(211)–two vicinal surfaces with same terrace geometry but different terrace width. We find from

Table III here and Table I in Ref. [14] that the respective adsorption energies are very similar, indicating that the step-step separation on Pd(211) itself is large enough so as to not affect the C binding energy to the Pd atoms.

C. Electronic Structure

Using the FLAPW method, we have calculated the valence charge densities and local densities of electronic states for Pd(533) and Pd(320) with S and C adsorbed on the site labeled # 1 in Fig. ???. To understand the character of chemical bonding between C, S and metal surface atoms, we have plotted the valence charge densities along the planes including the most important C-Pd or S-Pd bonds. Projections of these planes on the (533) surface are schematically shown in Fig. ??. Note that as a result of the complex adsorption geometry, centers of some atoms appear to be slightly out of the planes in the figure. Contour plots of valence charge densities along these planes are shown in Fig. ??. We cut off high densities around the atomic cores to show in detail the most important low density charge distribution in interstitial regions. Although in Figs. ??a and ??c the centers of the C and S atoms are not in the plane of interest here, the charge density "bridges" indicating covalent bonds are clearly seen between the adsorbates and the SC and CC atoms. The densities shown in Figs. ??b and ??d reflect the above mentioned differences in the location of C and S on Pd(533): the C atom is linked to BNN, while the S atom is located far from it, but close to the TC2 atom. Further, the intense charge density bridge connecting C and BNN in Fig. ??b suggests a strong covalent bonding between these atoms, while for the same token the S-TC2 bond appears to be weaker, as seen from Fig. ??d.

More details about chemical bonding can be obtained from plots showing the difference $\delta\rho(r)$ between the self-consistent charge density of the system and the sum of densities of free atoms placed at the corresponding sites. Such plots reflect the charge redistribution caused by chemical bonding. Figs. ??a and ??b show the $\delta\rho(r)$ calculated for C/Pd(533) and S/Pd(533) plotted along the planes (b) and (d) as defined in Fig. ??. It is seen from the figures that bulk-like Pd atoms (located comparatively far from the surface) donate some electronic density to interstitial region to build comparatively weak Pd – Pd covalent bonds. Both C and S accept a significant amount of electronic charge from neighboring Pd atoms, making the C – Pd and S – Pd bonds essentially ionic. However, the distinctive large

electronic density bridge between C and BNN atoms (see Fig. ??a) reflects strong C – Pd covalent bonding. In contrast, no significant electronic charge density is seen between S and TC2 atom in Fig. ??b. Thus, the S – Pd bonding in the S/Pd(533) case is mostly ionic with a small covalent contribution, whereas C and the BNN atom form a mixed ionic-covalent bond.

Next we turn to the analysis of the local densities of electronic states (LDOS), which provide additional information about the character of chemical bonding between adsorbates and metal atoms and some insights about properties related to catalytic activity of the surfaces. In Fig. ?? we show LDOS calculated for S/Pd(533) and C/Pd(533). We find a large splitting of p states of C and S with two main structures (A and B in the figure) separated by (7 – 8 eV). Since similar (but less intense) structures are found in the LDOS of Pd atoms at the same energies, we conclude that there is a strong hybridization of adsorbate p states with the local states of surface Pd atoms. The B and A structures thus represent bonding and anti-bonding states, respectively. As seen from the figure, the SC, CC and BNN surface atoms are involved in the hybridization. The B and A structures in the LDOS of carbon are quite distinct (low density between them) and the anti-bonding states are empty. These are indications of strong covalent C – Pd bonding, in agreement with the obtained valence charge densities. In contrast, only part of p states of sulfur is involved in the hybridization (the rest are distributed between B and A structures). Furthermore, the S anti-bonding states are partially occupied. This explains why the S – Pd covalent bonds are weak, as inferred also from the plots of the valence charge densities in Fig. ??.

Similar results are obtained for the adsorbates on Pd(320) (see Fig. ??): there is a strong hybridization between the electronic states of the adsorbate and neighboring Pd atoms, and because of larger B – A splitting and fewer occupation of the anti-bonding states, carbon forms stronger covalent bonds with Pd than done by sulfur.

Such significant modification of the electronic structure as we have documented above for the Pd surfaces upon C and S adsorption should affect their properties. Since Pd is a widely used catalyst, the property of interest is its catalytic activity (reactivity). Recalling the model that links the surface reactivity to the local densities of electronic states at the Fermi level [$N_a(E_F)$] [13], we examine the change of this quantity upon C and S adsorption on the Pd surfaces. As seen from the Figs. ?? and ??, the splitting caused by hybridization reduces dramatically the LDOS around the Fermi-level for Pd atoms, which have direct

covalent bonds with the adsorbate. In Tables IV and V we list $N_{Pd}(E_F)$ calculated for clean Pd(533) and Pd(320), as well as for those adsorbed with C and S. All atoms of the clean Pd surfaces are found to have high $N_{Pd}(E_F)$, which are not much affected by the presence of the step or kink. This is consistent with the fact that Pd is an efficient catalyst. For both Pd(533) and Pd(320), the presence of C and S leads to drastic decrease in $N_{Pd}(E_F)$ for neighboring Pd atoms, while the next neighbors are only slightly affected. We thus can expect that both S and C poison surface reactivity of Pd(533) and Pd(320). Interestingly, for the case of S/Pd(533) the $N_{Pd}(E_F)$ are suppressed for SC, TC2 and CC, which are all exposed to the surface. On the other hand, for C/Pd(533), three Pd sites (SC, CC and BNN) are strongly affected, but only two of them (SC and CC) are exposed to the surface. Since only actual surface atoms are involved in catalytic reactions, decrease in $N_a(E_F)$ of BNN should not affect surface reactivity. Nevertheless, the effect of C on $N_{Pd}(E_F)$ of Pd(533) is remarkable. Again, the effect of the S and C adsorbates on $N_{Pd}(E_F)$ of metal atoms in Pd(533) appears to be similar to that obtained earlier [14] for Pd(211). However, in the case of Pd(211) this results in suppression of $N_{Pd}(E_F)$ for all surface atoms, while in Pd(533), which has wider terrace, some surface atoms continue to retain high values of $N_{Pd}(E_F)$.

IV. CONCLUSIONS

In the present work we have studied from first principles the effect of adsorption of carbon and sulfur on the geometric and electronic structures of the stepped surfaces Pd(533) and Pd(320). We find the surface lattice to be perturbed dramatically in response to the adsorption. Our calculations show that C adsorbed at the bridge site at the edge of the Pd chain in Pd(320) penetrates the surface to form a sub-surface structure. The adsorption energies are found to be site dependent and ranging from 5.31 to 8.58 eV for C and from 2.89 to 5.40 for S. The S – Pd and C – Pd bonding have mixed ionic-covalent character with prevailing covalency for the C – Pd bonds and dominating ionicity for the S – Pd bonds. The strong hybridization between adsorbate and metal electronic states results in large splitting of the bands, which causes a dramatic suppression of the local densities of states at Fermi-level for Pd surface atoms neighboring the adsorbate. This effect is expected to poison catalytic activity of these surfaces. We have compared the results obtained for C and S chemisorption on Pd(533) with those obtained earlier for Pd(211) [14]. These two

stepped surfaces have similar structures, but Pd(533) has one atomic chain wider terrace. The adsorption energies, surface relaxation patterns and the effects of adsorbates on the local densities of electronic states and valence charge densities obtained for both surfaces are found to be quite similar suggesting the local character of the adsorbate impact on geometric and electronic structures of Pd surfaces.

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- [1] B. Hammer and J. K. Nørskov, Phys. Rev. Lett. **79**, 4441 (1997).
 - [2] P. Gambardella, Z. Zljivancanin, B. Hammer, M. Blanc, K. Kuhnke, and K. Kern, Phys. Rev. Lett. **87**, 056103 (2001).
 - [3] S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Törnqvist, and J. K. Nørskov, Phys. Rev. Lett. **83**, 1814 (1999).
 - [4] P. J. Feibelman, S. Esch, and T. Michely, Phys. Rev. Lett. **77**, 2257 (1996).
 - [5] B. Hammer, Phys. Rev. Lett. **83**, 3681 (1999).
 - [6] B. Hammer, J. Catal. 199, **171** (2001).
 - [7] M. Mavrikakis, P. Stoltze, and J. K. Nørskov, Catal. Lett. **64**, 101 (2000).
 - [8] D. Loffreda, D. Simon, and P. Sautet, J. Catal. **213**, 211 (2003).
 - [9] L. Savio, L. Vattuone, and M. Rocca, Phys. Rev. Lett. **87**, 276101 (2001).
 - [10] J. Xu and J. T. Yater, J. Chem. Phys. **99**, 725 (1993).
 - [11] Z.-P. Liu and P. Hu, Top. in Catal. 28, 71 (2004).
 - [12] Z.-P. Liu and P. Hu, J. Am. Chem. Soc. **125**, 1958 (2003).
 - [13] P. J. Feibelman and D. R. Hamann, Phys. Rev. Lett. **52**, 61 (1984).
 - [14] S. Stolbov, F. Mehmood, T. S. Rahman, M. Alatalo, I. Makkonen, and P. Salo, Phys. Rev. B **70**, 155410 (2004).
 - [15] I. Makkonen, P. Salo, M. Alatalo, and T. S. Rahman, Phys. Rev. B **67**, 165415 (2003).
 - [16] S. Wilke and M. Scheffler, Phys. Rev. Lett. **76**, 3380 (1996).
 - [17] M. K. Rose, A. Borg, T. Mitsui, D. F. Ogletree, and M. Salmeron, J. Chem. Phys. **115**, 10927 (2001).
 - [18] M. Rutkowski, D. Wetzig, and H. Zacharias, Phys. Rev. Lett. **87**, 246101 (2001).

- [19] K. Habermehl-C'wirzen' and J. Lahtinen, Surf. Sci. **573**, 183 (2004).
- [20] M. Bowker and C. Morgan, Catal. Lett. **98**, 67 (2004).
- [21] W. Kohn and L. Sham, Phys Rev. **140**, A1133 (1965).
- [22] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
- [23] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).
- [24] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- [25] M. Weinert, E. Wimmer, and A. J. Freeman, Phys. Rev. B **26**, 4571 (1982);
D. Singh, Planewaves, *Pseudopotentials and the LAPW Method* (Kluwer, Dordrecht, 1994).
- [26] P. Blaha, K. Schwarz, G.K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Technische Universität Wien, Austria, 2001).
- [27] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- [28] *American Institute of Physics Handbook* (McGraw-Hill, New York, 1970), Table 9a-2.
- [29] K. Pussi, M. Hirsimäki, M. Valden and M. Lindroos, Surf. Sci. **566-568**, 24 (2004).

TABLE I: Multilayer relaxation for Pd(533).

$\delta \mathbf{d}_{i,i+1}$	S/Pd(533)	C/Pd(533)	Pd(533)
$\delta \mathbf{d}_{1,2}$	-12.3	+29.7	-15.8
$\delta \mathbf{d}_{2,3}$	-19.7	+3.7	-11.9
$\delta \mathbf{d}_{3,4}$	+44.7	-32.0	-6.6
$\delta \mathbf{d}_{4,5}$	-4.2	+36.0	+24.3
$\delta \mathbf{d}_{5,6}$	-22.5	+3.4	-6.8
$\delta \mathbf{d}_{6,7}$	+5.9	-8.4	-10.1
$\delta \mathbf{d}_{7,8}$	+14.3	+3.6	+5.8
$\delta \mathbf{d}_{8,9}$	-4.1	+7.2	+4.1
$\delta \mathbf{d}_{9,10}$	-14.4	-5.1	-6.7
$\delta \mathbf{d}_{10,11}$	+9.4	-4.2	-0.2

TABLE II: Multilayer relaxation for Pd(320).

$\delta \mathbf{d}_{i,i+1}$	S1/Pd(320)	C1/Pd(320)	C5/Pd(320)	Pd(320)
$\delta \mathbf{d}_{1,2}$	-24.4	+26.4	+38.1	-15.4
$\delta \mathbf{d}_{2,3}$	-5.5	-55.7	+1.0	-18.7
$\delta \mathbf{d}_{3,4}$	-8.3	+45.5	-0.8	+1.4
$\delta \mathbf{d}_{4,5}$	+34.9	-8.5	+4.1	-10.1
$\delta \mathbf{d}_{5,6}$	-16.4	+23.9	-5.6	+21.3
$\delta \mathbf{d}_{6,7}$	-3.2	-9.6	+16.5	-7.0
$\delta \mathbf{d}_{7,8}$	+12.4	+9.6	-3.6	-1.7
$\delta \mathbf{d}_{8,9}$	-14.1	-4.8	+7.9	+2.4
$\delta \mathbf{d}_{9,10}$	+11.5	+0.8	-4.4	-1.4

TABLE III: C and S adsorption energies at various sites on Pd(533) and Pd(320).

Site	S/Pd(533)	C/Pd(533)	C/Pd(320)
1	5.40	8.44	8.58
2	5.31	7.52	8.29
3	5.28	7.49	8.47
4	5.28	7.49	7.30
5	5.26	7.43	8.49
6	5.09	7.10	5.53
7	4.62	6.32	
8	4.72	5.85	
9	4.25	5.58	
10	4.13	5.31	

TABLE IV: Local density of states at Fermi level (state/eV*atoms) calculated for Pd surface atoms in clean Pd(533), S/Pd(533), and C/Pd(533).

	SC	TC1	TC2	CC	BNN
clean-Pd(533)	2.01	1.95	2.00	1.78	1.93
S/Pd(533)	0.93	1.73	1.30	0.90	2.04
C/Pd(533)	0.37	1.78	1.98	0.46	0.65

TABLE V: Local density of states at Fermi level (states/eV*atoms) calculated for Pd surface atoms in clean-Pd(320), S/Pd(320), and C/Pd(320).

	Pd1	Pd2	Pd3	Pd4
clean-Pd(320)	1.59	2.26	1.81	1.88
S/Pd(320)	1.13	0.73	0.83	1.63
C/Pd(320)	0.44	1.27	0.24	1.30