Structure sensitivity in adsorption: CO interaction with stepped and reconstructed Pt surfaces

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The structure sensitivity of CO adsorption on different flat, stepped, kinked and reconstructed Pt surfaces is studied using large-scale density-functional calculations. We find an extremely strong structure sensitivity in the adsorption energy with variations up to 1 eV (or 100%) from one structure to the next. We propose a model to explain this behavior, and use it to discuss more generally the origin of structure sensitivity in heterogeneous catalysis.

Keywords: structure sensitivity, chemisorption, stepped surfaces, kinked surfaces, reconstructed surfaces, platinum, carbon monoxide, density-functional calculations

Many catalytic reactions are structure sensitive – the rate depends on the detailed geometrical structure of the surface atoms of the catalyst [1,2]. Structure sensitivity usually manifests itself as a dependence of the rate per surface atom on the average size of the catalyst particles. The understanding is that for particle diameters $d < 100$ Å the relative number of step and kink sites increases dramatically with decreasing d, and these very under-coordinated surface atoms could have a substantially different ability to interact with molecules from the gas phase. Structure sensitivity may reflect a variation in the intrinsic ability of the surface atoms to participate in surface chemistry (the ''electronic'' or ''ligand'' effect), or it may be related to the availability of a certain number of surface atoms in special geometrical arrangements of importance for the interaction with the reactants (the ''ensemble'' effect). In the present letter we concentrate on the intrinsic effect by studying the adsorption of a test molecule, CO, which binds to only a single atom on many metal surfaces. Structure sensitivity for CO adsorption on small Pd particles has been demonstrated by Henry et al. [3], who showed the average CO chemisorption energy to increase strongly with decreasing particle size. Similarly, several experimental investigations [4–7] of CO on stepped Pt(111) surfaces have shown clear evidence of new step-induced adsorption features with larger binding energies relative to CO on the flat terraces. In spite of the importance of structure sensitivity in catalysis and the extensive experimental interest, there is no detailed atomistic understanding of the phenomenon.

We discuss in the following the bonding of CO to steps and other defects on Pt surfaces on the basis of a series of first-principles density-functional calculations. We find that the CO adsorption energy is 0.7 eV larger at a step on a Pt(111) surface than on the flat terraces. Further, we compare CO adsorption on steps with adsorption on kinks and on the ''hex''-reconstruction on the Pt(100) surface. Here variations up to 1 eV in the adsorption energy are found. We use the calculations to identify the underlying reason for the large variation in the ability of the surface Pt atoms to bind CO. This leads to a generalization of our results to other adsorbates and provides a conceptual starting point for more complex surface reactions.

First, we consider CO adsorption on a Pt(211) surface. This surface has (111) terraces separated by steps as illustrated in figure 1. Our density-functional theory calculations are carried out in a repeated slab geometry. The valence electrons are described using a plane wave basis [8] [1], the ionic cores are described by soft pseudopotentials [9], and for the chemisorption energies reported, we use the non-local Perdew–Wang (GGA) exchange–correlation functional applied to local density approximated (LDA) densities and geometries [10]. The method allows full structural optimization, which is done for all Pt atoms within a 4 Å range of the surface plane and for all the adsorbate degrees of freedom.

We have considered two different adsorption sites

[1] For the details of the calculational method see ref. [8]. Plane waves up to a kinetic energy of 40 Ry are included at $\boldsymbol{k}$-point grids of approximately the same density for the different systems; Pt(211)-p(2 × 1): 16, Pt(11,8,5): 16, Pt(100)-(2 × 5)-hex: 12, Pt(111)-p(2 × 2): 54, Pt(100)-p(2 × 2): 36 $\boldsymbol{k}$-points in the complete Brillouin zones.

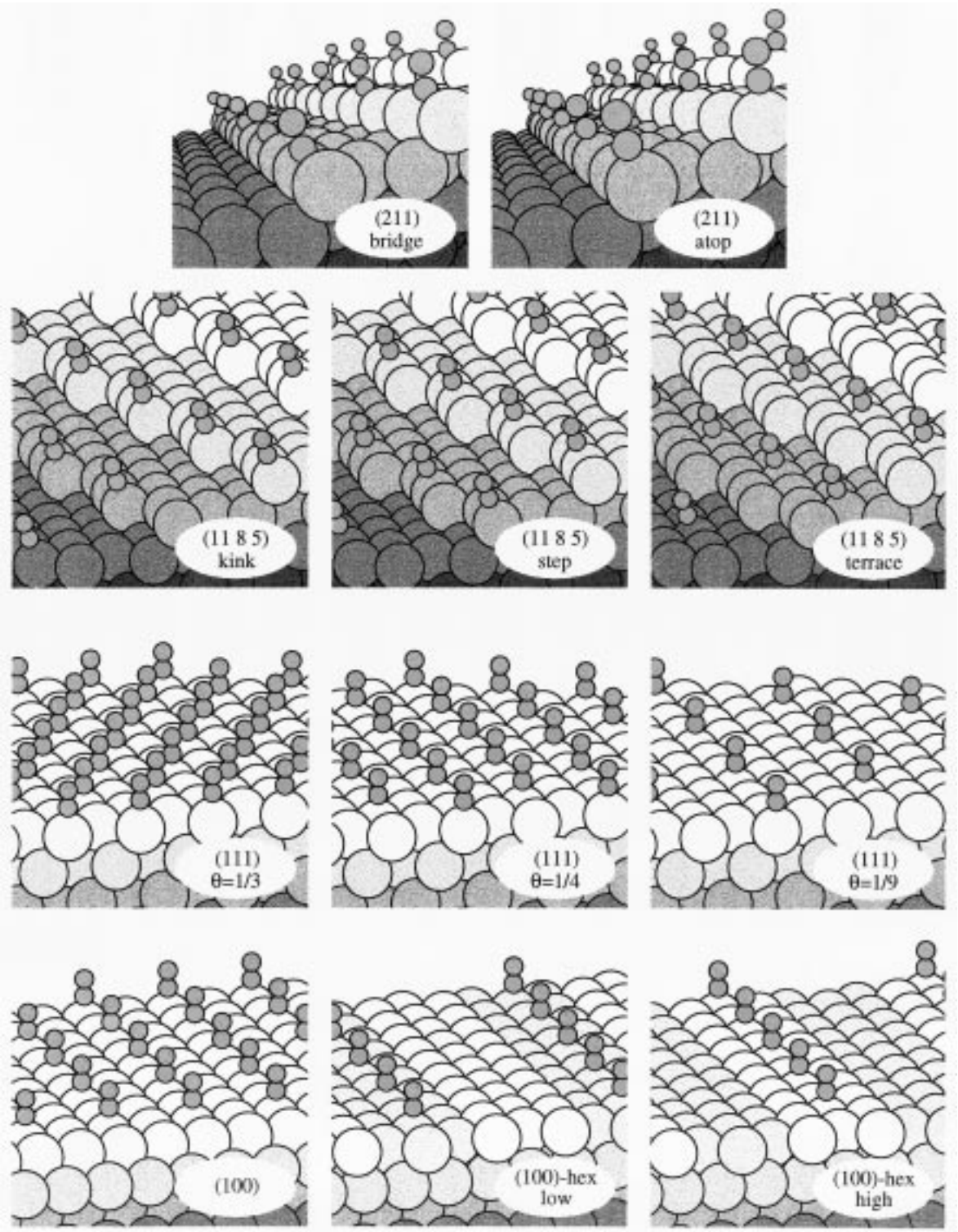

Figure 1. Structure and adsorption sites for the different surfaces considered. A full structural minimization is done for CO adsorption on the (211) surface. For the other surfaces only the atop sites are considered, a fixed CO–Pt configuration is used and the Pt atoms are kept in the positions whereto they relax in the absence of the CO, except for CO at the (11,8,5) kink and step sites, where the Pt are put at the truncated bulk positions. The Pt(11,8,5), Pt(111), $\theta = 1/3$ and $\theta = 1/9$ slabs consist of four (111) type layers, while the other systems have six (111) or (100) type layers. The robustness of the results against slab thickness was tested for the Pt(111), $\theta = 1/4$ and Pt(211) systems. The Pt(111), $\theta = 1/3$, $1/4$ and $1/9$ chemisorption energies agree within 0.01 eV, indicating very small CO–CO interactions, as also reported in ref. [21].

shown in figure 1. The equilibrium binding energies at the two sites are 2.19 and 2.07 eV, considerably larger than the fully relaxed value of 1.49 eV on the flat Pt(111) surface. The equilibrium bond lengths of adsorbed CO are 1.18 and 1.16 Å, the C–Pt separations are 2.01 and 1.85 Å, and the CO axis is close to normal to the macroscopic (211) surface with a very weak confining potential for the rotation. The C–O vibrational frequencies at the two sites are 1860 and 2080 cm^{-1}, the latter value slightly lower than at the flat (111) surface where the frequency is calculated to be 2120 cm^{-1}. The Pt atoms at the step are substantially relaxed towards the neighbors in the absence of the CO (the Pt–Pt bond lengths are smaller by 3% than for bulk Pt). Adsorption of CO reverts the Pt atoms at the step almost back (75% of the way) to the unrelaxed position.

The increased bond energies and lowered vibrational frequencies at the step edge are in good agreement with experimental evidence [4–7]. Experimentally, both the atop and bridge-bonded adsorption species are found by some investigators at intermediate coverages, but the atop species seem more abundant in the experiment while the present calculation suggests the bridge-bonded species to be most stable. This may be a sign that CO–CO interactions play a role in determining the most stable overlayer structure (we have only considered a single structure with one CO per two step atoms) or it may be an artifact of the GGA approximation for exchange and correlation. The small difference in bridge and atop binding energies is, however, not important on the scale of the difference between step and terrace binding energies which is the main topic of the present letter.

We now turn to the question why the Pt atoms at the step have such a different ability to bond to CO. To investigate this we consider CO adsorption on a number of other Pt surfaces. We consider the Pt(11,8,5) surface which has steps and (111) terraces like the (211) surface, but also even more under-coordinated kink sites. We also consider the Pt(100) surface and the reconstructed Pt(100)-hex(1×5) surface, which is an otherwise flat Pt(100) surface covered by a hexagonally packed, buckled Pt overlayer. The reconstruction is observed [11] as an intermediate structure in the formation of the larger but otherwise similar Pt(100)-hex(5×20) structure [12]. In the Pt(100)-hex(1×5) surface the outermost Pt atoms are "over-coordinated", the Pt density in the first layer being 4% larger than in the (111) surface. The structure and unit cells used are illustrated in figure 1. For adsorption at the step and kink sites of the Pt(11,8,5) surface we only consider the unrelaxed surface, which we expect to be close to the final state in the presence of CO as it was found to be for CO/Pt(211) in the fully relaxed calculations presented above. For the hex reconstructed surface we have relaxed the two first layers. A buckled surface results and we adsorb CO at a low and a high site, respectively. In all these cases we adsorb in the atop position and fix the CO bond length to 1.14 Å and the C–Pt distance to 1.94 Å.

In figure 2 we show the calculated CO chemisorption energies as a function of the center of the d bands for the surface atom to which the CO bonds. The correlation is seen to be striking – the CO chemisorption energy varies by as much as 1 eV from the most densely packed to the most open surface site and so does the d-band center. It is seen that the hex reconstructed surface binds CO even weaker than the close-packed (111) surfaces, in good agreement with recent experiments [18], while the binding to kinks is even stronger than to the steps.

In figure 3 we show the d density of states projected onto selected adsorption sites in the absence of CO. It is seen that the widths of the d bands vary considerably, being larger for the higher coordinated Pt sites as would be expected from tight-binding theory. In response to this variation the whole d band moves substantially, while the amount of empty d states ("d holes") is essentially constant.

From figure 2 it appears that the d band center provides a good quantitative measure of the electronic effects caused by the surface structure. The question is why? A key to the answer is an understanding of the change in the electronic structure of a CO molecule during chemisorption. The CO adsorption on transition metal and alloy surfaces can be described in a transparent molecular orbital language, where the adsorption is viewed as taking place in two steps [13–17]. First, the coupling between the adsorbate levels and the itinerant

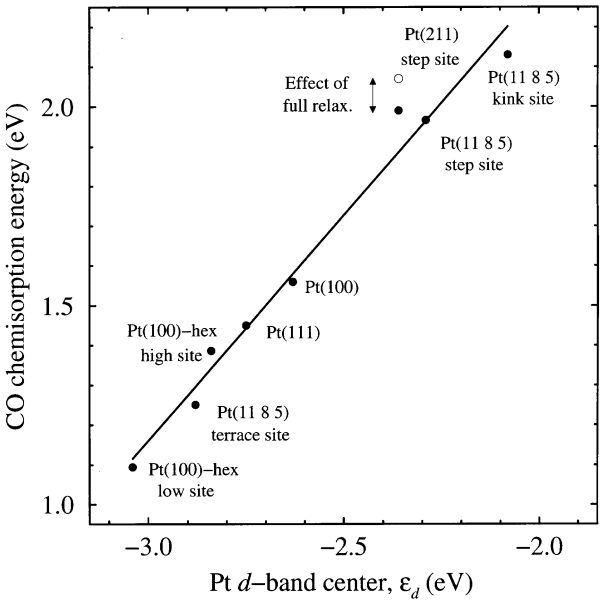

Figure 2. Calculated CO binding energy shown as a function of the d band center for the adsorption site. The solid circles are for CO in the fixed adsorption geometry over the rigid surfaces. Also included as and open circle is the result for CO over Pt(211) vs. the d band center at the step of bulk truncated Pt(211). However, note that this result cannot be compared directly to the solid points as it is calculated with a full structural relaxation and therefore gives somewhat more stable bond.

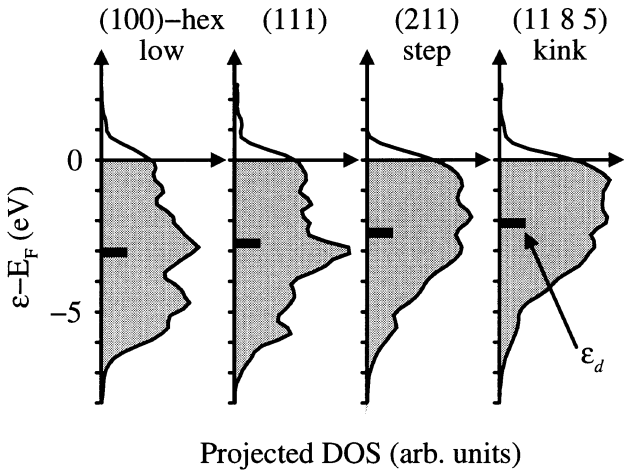

Figure 3. The d density of states before the chemisorption of the CO at selected adsorption sites.

sp electrons of the metal leads to new adsorbate levels that are broadened into resonances and shifted down in energy (''renormalized'') by the surface potential. The process is illustrated schematically in figure 4 for the highest occupied (HOMO) and lowest unoccupied (LUMO) CO molecular orbitals, 5σ and $2\pi^*$. For a simple metal like Al this is the only contribution, but for transition metal and noble metal surfaces, the presence of d bands in the electronic structure causes an additional splitting of the renormalized adsorbate levels into bonding and anti-bonding levels [15,16] as shown in figure 4. This is the second step, where e.g. the coupling of the initially unoccupied $2\pi^*$ LUMO to the metal d states thus gives rise to a down-shift of the almost filled metal d states and a similar up-shift of the empty $2\pi^*$ states. In a simplified description where the width of the d band is neglected, the size of the shift is given by the matrix element V and the difference $\Delta\epsilon = |\epsilon_d - \epsilon_{2\pi}|$ in energy between the metal d and adsorbate levels. In the limit $|V| \ll \Delta\epsilon$ the shift is given by the second-order perturbation result:

$$\Delta = \frac{V^2}{\epsilon_{2\pi} - \epsilon_d} . \qquad (1)$$

The energy shifts due to the coupling between the molecular 5σ state and the metal d states are of the same order of magnitude, but here the anti-bonding states around the top of the d bands are almost filled and the net result is only a weak energy gain due to hybridization.

When considering the difference in CO chemisorption energy from one Pt site to another, we therefore first concentrate on the $2\pi^*$–d coupling[2]. The simple model explains qualitatively the effect observed in figure 2. If the center of the d bands ϵ_d is shifted towards the Fermi level and $\epsilon_{2\pi}$, eq. (1) shows that the energy denominator $\epsilon_{2\pi} - \epsilon_d$ becomes smaller and the energy shift Δ increases. This means that the higher the d band, the stronger the CO bonding, which is exactly what the figure shows.

We can quantify this by calculating from eq. (1) the change in the CO bond energy with d band position. From studies of the effect of alloying on the CO bond energy [15] we have the values of the matrix element and the renormalized adsorbate level. For the Pt(111) surface these values give the change in CO adsorption energy due to a shift in the d band center shown in figure 5. Here we show the contribution for the 2π–d interaction in the simple two-level perturbation expression eq. (1). We also include the result of a non-perturbative solution of the Newns–Anderson model [13,19] in which the width of the d band is included. It is clear that the simple perturbation result captures the essence of the effect and that both the full model and the perturbation theory give a slope $\partial E_{chem}/\partial\epsilon_d$ in excellent agreement with the least-squares linear fit in figure 2. The main dif-

[2] The sp electrons do not give rise to so large variations, at least for Al. For CO chemisorption at kink sites in Al(11,8,5) we find a binding energy difference of only 0.15 eV compared to Al(111) – the chemisorption at the flat surface being the more stable.

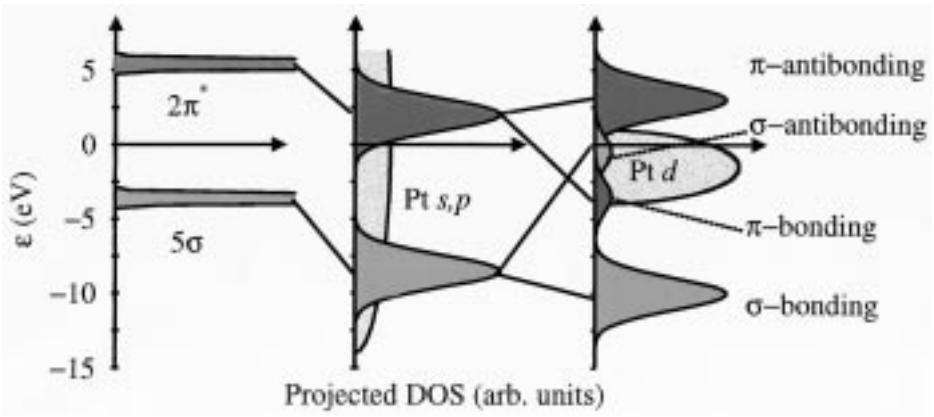

Figure 4. Schematic illustration of the two-step model for CO adsorption on a transition metal surface.

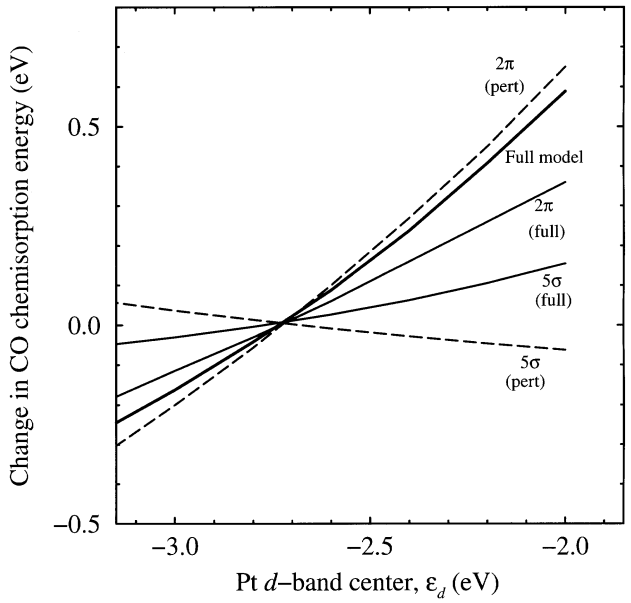

Figure 5. Model calculations of the change in hybridization energy of the 2π and 5σ CO states with changes in the d band position. Both the result of a simple two-level perturbation calculation (marked "pert"), eq.(1), and the full solution of the Newns–Anderson model (marked "full") are shown. The parameters describing CO/Pt are taken from ref. [15].

ference between the two-level perturbation theory and the full model is that the 5σ contribution to $\partial E_{\mathrm{chem}}/\partial\epsilon_{\mathrm{d}}$ is negative in the former and positive in the latter. This is of no consequence here because the 2π contribution dominates. But the full model shows that even adsorbates like NH_3 or the atomic adsorbates (H, O, N etc.), which only have chemically important (renormalized) adsorbate states below the Fermi level [20], will have an increased bonding to under-coordinated metal atoms.

Any catalytic reaction will consist of adsorption, dissociation, recombination and desorption processes, and for transition metal catalysts, there will in general be contributions from the d bands to the binding energy of the atomic and molecular adsorbates, as well as to the height of the reaction barriers along the pathway. We speculate on the basis of the present results that if the contributions are large, the stability of the intermediates and the barrier heights will depend on the local coordination number for the transition metal atoms in the surface through the d band center.

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