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Effect of Strain on the Reactivity of Metal Surfaces

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Self-consistent density functional calculations for the adsorption of O and CO, and the dissociation of CO on strained and unstrained Ru(0001) surfaces are used to show how strained metal surfaces have chemical properties that are significantly different from those of unstrained surfaces. Surface reactivity increases with lattice expansion, following a concurrent up-shift of the metal *d* states. Consequences for the catalytic activity of thin metal overlayers are discussed. [S0031-9007(98)07198–1]

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The ability to grow and characterize one metal on top of another has developed rapidly over the last few years. In a number of cases it has become possible to epitaxially grow several layers of one metal on top of another. If the lattice constants of the two metals differ, *strained* overlayers are formed. It has been shown experimentally that such strained overlayers can have chemical properties that are significantly different from those of the pure overlayer metal [1–3]. Most recently strain in the surface region has been introduced not just by growing one metal epitaxially on another, but by local deformation of a single metal phase [4]. Such strain has been shown to modify the chemisorption properties of the metal considerably. If strain generally induces changes in the ability of a surface to form bonds to adsorbed atoms or molecules, the possibility arises of using strain to manipulate the reactivity of a metal.

In the present Letter we investigate the generality of the effect of strain on surface reactivity and its origin by performing a set of density functional (DFT) calculations. We study a metal [Ru(0001)] slab under compressive or tensile stress and show that both molecular (CO) and atomic (O) chemisorption energies as well as barriers for surface reactions (CO dissociation) vary substantially on strained lattices. We further proceed to show that this effect can be explained on the basis of shifts in the metal *d* bands induced by the stress. This allows us to develop a model for the effect which can be readily extended to several catalytically important systems.

We used a three layer slab of Ru periodically repeated in a super cell geometry with five equivalent layers of vacuum between any two successive metal slabs. O adsorption and CO dissociation were treated within a (2×2) unit cell, whereas CO chemisorption was studied on a $\sqrt{3} \times \sqrt{3}$ unit cell. These specific choices represent the most stable overlayer structures for the corresponding systems, as determined by experiments [5,6]. Adsorption is allowed on only one of the two surfaces exposed and the electrostatic potential is adjusted accordingly [7]. The top surface layer was relaxed for the atomic and molecular chemisorption problems, but kept fixed at its initial

position for the calculation of the CO dissociation barrier. Ionic cores are described by ultrasoft pseudopotentials [8] and the Kohn-Sham one-electron valence states are expanded in a basis of plane waves with kinetic energies below 25 Ry. The surface Brillouin zone is sampled at 18 special **k** points. The exchange-correlation energy and potential are described by the generalized gradient approximation (PW91) [9,10]. The self-consistent PW91 density is determined by iterative diagonalization of the Kohn-Sham Hamiltonian, Fermi population of the Kohn-Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density [11]. All total energies have been extrapolated to $k_B T = 0$ eV.

We first examine the effect of changing the lattice constant parallel to the surface of the Ru(0001) slab on the chemisorption properties of the surface. In this way we focus directly on the strain effects. For thin layers of one metal on top of another it can be difficult to isolate the strain effects because they are folded with the effects due to the interaction of the overlayer with the substrate. We will later return to the overlayer structures. The calculated equilibrium lattice constant (d_{eq}) for bulk Ru(0001) was found to be 2.74 Å, in reasonable agreement with the experimental value of 2.70 Å [12]. The equilibrium c/a value used for Ru is 1.582 [12]. For the purposes of the present study, we vary the lattice constant (d) parallel to the surface between 2.70 and 2.80 Å corresponding to a maximum absolute value of relative strain ($\Delta d / d_{eq}$) of ca. 2%. All the results shown here were obtained from calculations on a three-metal-layer slab, where the distance between the middle and bottom metal layers was kept fixed at the value of the interlayer distance corresponding to the equilibrium structure (d_{eq}). We have also tested an alternative model, where the interlayer distance between these two layers is changed with in plane strain according to Ru's Poisson ratio [13] of 0.29. We found no significant difference between the results of these two approaches. Furthermore, additional test calculations performed with up to six metal layers show that the results presented here remain practically invariant with the number of metal layers used.

First, consider the adsorption of CO and O. Figure 1 shows the calculated adsorption energy

$$\Delta E_{ads} = E(ads/metal) - E(ads) - E(metal) \quad (1)$$

as a function of the surface strain $\Delta d/d_{eq}$. The geometry of adsorption is illustrated in Fig. 2. O is chemisorbed on its preferred hcp site in a 2×2 overlayer structure as suggested by several experiments, including LEED studies [5]. CO on the other hand, preferentially adsorbs on an atop site in a $\sqrt{3} \times \sqrt{3}$ overlayer structure, in accord with experimental evidence [6]. The results for O and CO adsorption on the unstrained surface are in good agreement with previous DFT calculations [14,15].

The results illustrated in Fig. 1 suggest that there is a considerable variation in adsorption energy with strain, and in both cases the chemisorption bond gets stronger as the lattice constant increases. However, the effect on O chemisorption strength is about 5 times more pronounced than the corresponding effect for CO. The trend calculated for O adsorption is in accord with scanning tunneling microscopy (STM) observations on a strained Ru(0001) surface [4], where oxygen atoms were found to preferentially adsorb on sites at the expanded regions of the surface. The same experiments suggest two possibilities for CO: (i) either the opposite chemisorption trend with lattice strain holds (i.e., CO prefers sites at the compressed regions of the surface), or (ii) a dense CO overlayer is formed at the expanded regions, rendering
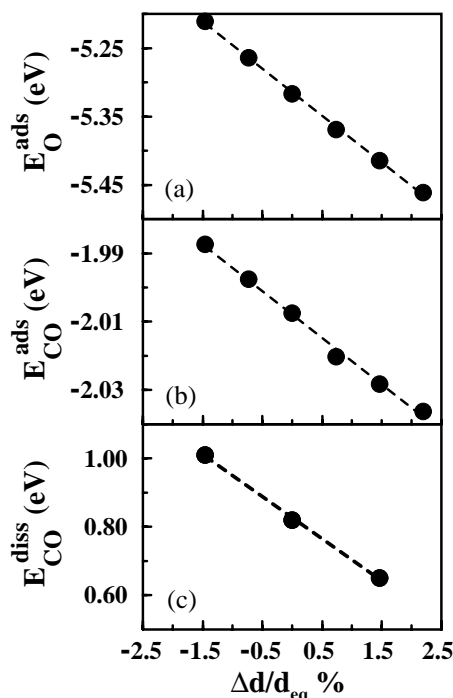
molecules invisible to the STM in these regions. Gsell *et al.* [4] suggest that further experiments are needed to clarify the situation with CO. We believe that the second of the proposed possibilities is most likely describing the actual events. The high mobility of CO molecules on this surface (calculated diffusion barrier of ca. 0.15 eV) adds to the degree of difficulty for the CO experiment. Therefore, the above mentioned room temperature STM experiments had to trace very mobile CO molecules and differentiate between adsorption sites with only slightly different binding energies between each other. Results pertaining to O adsorption are much easier to interpret, since the binding energy difference between competing sites is considerably larger, and the diffusion barrier for O atoms is much higher (calculated ca. 0.40 eV) compared to CO. In support of these arguments, several studies of CO adsorption on strained overlayers show that an expansion of the lattice constant increases the CO binding energy (see, for example, [1]).

We next consider the dissociation of CO on Ru(0001). The barrier for CO dissociation over several metal surfaces has been determined in the past [16]. Extending this work to CO dissociation on Ru(0001), we determined the transition state (TS) for the unstrained surface as shown in Fig. 2. The TS is very stretched compared to the bond length of the gas phase molecule (calculated at 1.15 Å, versus an experimental value [17] of 1.12 Å), and the reaction proceeds almost entirely as a stretch of the CO bond with the C end of the molecule already in its final, hcp site on the surface. When the surface lattice constant is varied, we search for the new transition state by making variations in this reaction coordinate. This is illustrated in Fig. 3, where, as the lattice constant increases, the TS moves slightly towards smaller C-O distances, but the overall trend is not affected significantly. In the bottom panel of Fig. 1 the variation in the energy of the TS, defined similarly to Eq. (1), is also shown as a function of strain. Again the interaction strength increases with increasing tensile strain (ca. 0.15 eV for each 1% of strain, on the average), making the stretched slab considerably more reactive towards CO dissociation.

It seems that molecular and atomic adsorption energies as well as activation energies for dissociation show similar

FIG. 1. Effect of relative change in surface lattice constant $(d - d_{eq})/d_{eq}$ of a Ru(0001) surface on the (a) binding energy of atomic oxygen (E_O^{ads}) (top panel), (b) binding energy of molecular CO (E_{CO}^{ads}) (middle panel), and (c) CO dissociation barrier (E_{CO}^{diss}), referenced to a zero of the clean surface plus a gas phase CO molecule (bottom panel). Dashed lines are drawn as a guide to the eye.

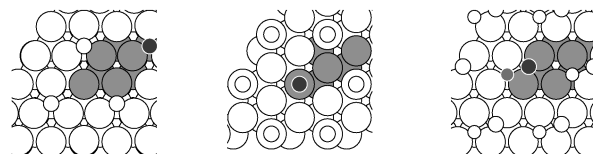## O/Ru(0001) CO/Ru(0001) TS/Ru(0001)

FIG. 2. A top view of the preferred geometry for chemisorbed O and CO, and the TS for CO dissociation on a Ru(0001) surface for the equilibrium (unstrained) lattice constant (2.74 Å). The TS is very close to a center (C)-bridge (O) configuration. Shaded metal atoms illustrate the unit cell used. Smaller circles, above the surface plane, represent the respective adsorbed species.
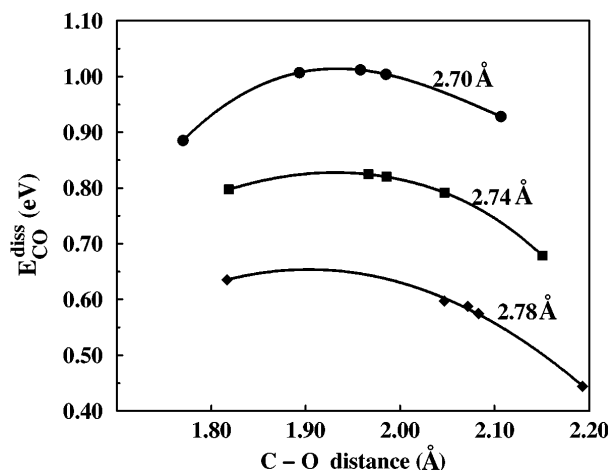
FIG. 3. Calculated energy along the reaction coordinate of C-O distance during CO dissociation over three different Ru(0001) surfaces. The corresponding surface lattice constants are shown as labels to the curves. Continuous lines represent the best fits through the calculated data points shown with circles, squares, or diamonds. Calculated forces along the reaction coordinate have been used for the slopes of these lines. The highest point on each curve is taken as the respective activation energy barrier shown in the bottom panel of Fig. 1. The energy scale is referenced to a zero of the clean surface plus a gas phase CO molecule.

trends. We will now discuss possible explanations for this, trying to elucidate the underlying mechanism leading to the observed behavior. In particular, we will examine if the effect of strain on surface chemisorption and reactivity can be reduced to the strain-induced change in a more fundamental parameter determining these variations. Finally, the generality of the strain effect for different surfaces and adsorbates within the framework of both uniformly strained slabs and thin overlayers is argued.

We will start by postulating that the underlying parameter determining the strain-induced variations shown in Fig. 1 is the position of the center of the metal d bands. There are good reasons for this [18]. The interaction between the adsorbate states and the metal d states is an important part of the interaction energy, and while the sp bands of the metal are broad and structureless, the d bands are narrow, and small changes in the environment can change the d states and their interaction with adsorbate states significantly. The d-band center (ϵ_d) is the simplest possible measure for the position of the d states. In Fig. 4 we show the data of Fig. 1 as a function of the center of mass of the density of states projected onto the atomic d states of the clean surface. For convenience, we use all the d states here, instead of the ones with the correct symmetry for bonding with the various adsorbates. This makes no major difference, when the adsorption geometry remains similar. When the lattice is expanded parallel to the surface, the overlap between the d electrons on neighboring metal atoms becomes smaller, the bandwidth decreases and to keep the d occupancy fixed, the d states
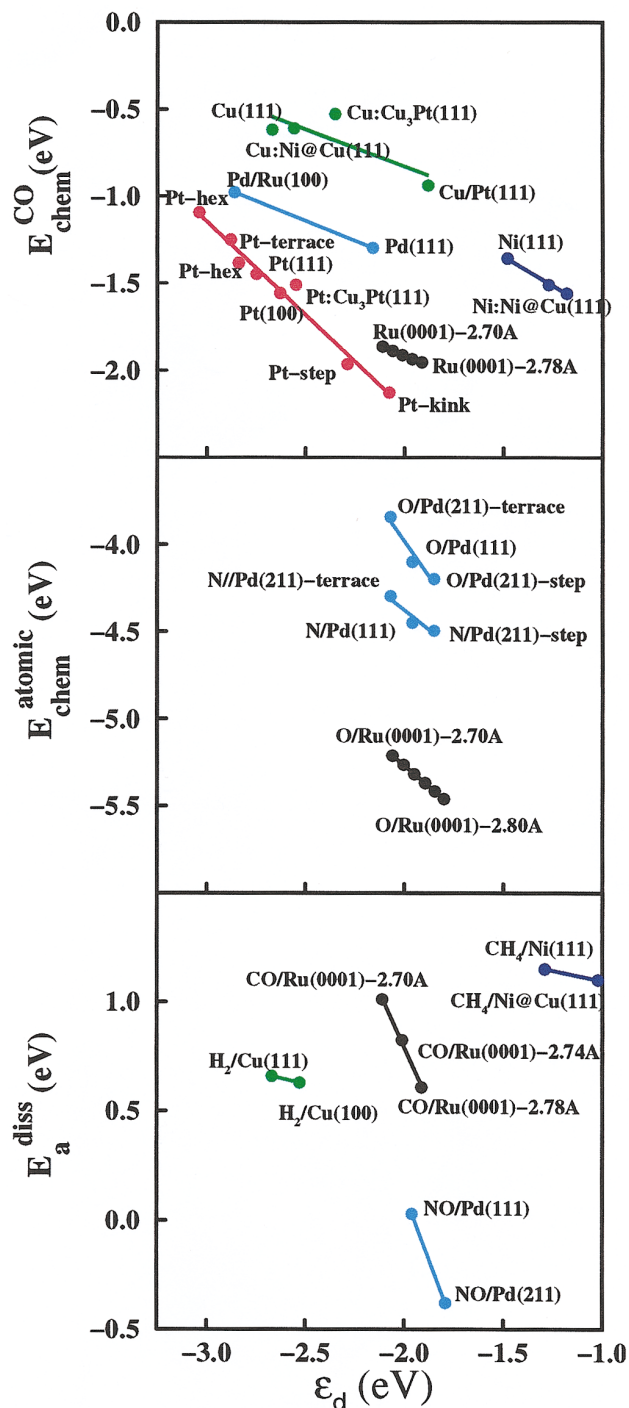

FIG. 4(color). Molecular (E_{chem}^{CO}) and atomic (E_{chem}^{atomic}) binding energy as a function of the d-band center (ϵ_d) of the metal surface (top and middle panel, respectively). The barrier for dissociation of small molecules, referenced to gas phase zero, as a function of ϵ_d is shown in the bottom panel. Common colors are used for data corresponding to the same metal throughout the three panels. Lines drawn represent best linear fits. $X{:}XY$ reflects chemisorption on or dissociation over atom X in an XY-alloy surface. $X@Y$ means an X atom impurity in a Y surface. Specific data points are taken from: [20] for N, O, and NO on Pd; [23,24] for CO on Pt, Ni, Cu, and Pd; [22,25] for CH$_4$ on Ni; [21] for H$_2$ on Cu. Data for O and CO on Ru are those shown in Fig. 1.

have to move up in energy [19]. According to Fig. 4 this gives a stronger interaction in all cases.

In order to show that the d-band center is the underlying parameter we have included in Fig. 4 a large number of data from the literature [20–25], all extracted from similar DFT calculations. These data represent calculated adsorption energies of atomic and molecular adsorbates as well as activation energies for surface reactions. They all describe a situation, where the adsorbate interacts with the same kind of metal atom(s) in the same local geometry, but the environment varies. In particular, the environment has been changed in several cases by considering different facets and stepped surfaces. Here the local d-projected density of states has not been changed due to strain, but due to a change in the number of metal neighbors, the general rule being that the lower the coordination number, the smaller the local bandwidth and the higher the ϵ_d (for metals with more than half-filled d bands). The fact that these data follow the same trend when plotted as a function of ϵ_d strongly suggests that ϵ_d is the underlying parameter determining reactivity to a first approximation. This data set also includes alloys and overlayers, where a large portion of the change in ϵ_d can be attributed to changes in the metal-metal distances in the surface [26], as is the case for the strained slab.

Data in Fig. 4 also show that the correlation between interaction strength (adsorption energy or activation energy barrier) and ϵ_d holds for many different adsorbates and metals. Similar calculations for H_2 dissociation on transition and noble metals have shown such a relationship to hold also when different metals are compared [18,27]. The generality of this correlation is a simple manifestation of the fact that the coupling to the d states depends on the position of the d states relative to the Fermi level. This tendency is also elucidated by simple models describing interactions between atomic or molecular adsorbates and transition states with metal surfaces [18]. In addition, the correlation between the interaction strength and the d-band center found in the framework of these simple models appears to be independent of the adsorbate and the metal, in agreement with the trends revealed with our large-scale total energy calculations, as illustrated with the data in Fig. 4. The identity of the metal involved shows up only in the *strength* of the effect, that is, the slope of $E(\epsilon_d)$ through the size of the coupling matrix element. The relative ordering in the coupling strength is $5d > 4d > 3d$ following the relative sizes of the d wave functions [18].

In conclusion, we have shown that there is a general correlation between surface strain and adsorption energies and activation energy barriers. We have also shown that this effect can be attributed to a shift in the center of the metal d bands (ϵ_d) with strain. The parameter ϵ_d, which is a property of the local adsorption site of the unperturbed metal surface, also describes variations in reactivity for metal overlayers and for different surface structures. Our results suggest that surface strain can in general be used to tailor the catalytic activity of metals.

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