Determining the adsorptive and catalytic properties of strained metal surfaces using adsorption-induced stress

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We demonstrate a model for determining the adsorptive and catalytic properties of strained metal surfaces based on linear elastic theory, using first-principles calculations of CO adsorption on Au and K surfaces and CO dissociation on Ru surface. The model involves a single calculation of the adsorption-induced surface stress on the unstrained metal surface, which determines quantitatively how adsorption energy changes with external strain. The model is generally applicable to both transition- and non-transition-metal surfaces, as well as to different adsorption sites on the same surface. Extending the model to both the reactant and transition state of surface reactions should allow determination of the effect of strain on surface reactivity. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1688317]

I. INTRODUCTION

Surface properties play an important role in controlling the materials catalytic behavior.[1,2] A central theme in surface catalysis has been to tune the chemical properties of surfaces to enhance their catalytic activity. One effective method to do so is by applying external strain. For example, surface adsorption has been observed to change noticeably when thin films are strained by either pseudomorphic growth on lattice-mismatched substrates[3] or by implantation of inert gas bubbles[4,5] and also in strained metal particles on oxide surfaces.[6] First-principles calculations also show changes in molecular adsorption energies on strained surfaces.[7–10]

Although it has become clear that the adsorptive and catalytic properties of metal surfaces depend strongly on external strain, our understanding on such an important effect is incomplete. A model has been proposed suggesting that strain changes adsorption by shifting the center of d states of transition-metal surface because molecules bond to surfaces mainly through the hybridization between frontier molecular orbitals of adsorbate and surface states of the metal.[7] The model has been used to explain observations in quite some systems,[1,2,7] but it has some limitations and has been shown not to work in some instances.[9,10] First, the model is insensitive to adsorption sites and different sites on the same surface may respond to external strain differently. Second, it is based on *arguments* that do not to apply to transition metals with half-filled or fully filled d bands and such systems show important catalytic behavior.[9–11] Last but not least, the model is not applicable to non-transition-metal surfaces, some of them exhibiting important surface chemistry,[12–14] and also in systems where the s band may play an important role in chemical activity.[15]

In the present work, we take an alternate view to elucidate the effect of strain on the adsorptive and catalytic properties of metal surfaces, based on linear elastic theory. We show that the change of chemisorption energy under external strain can be determined by a single calculation of adsorption-induced surface stress (AIS). We show that the sign of AIS controls the qualitative effect of strain on chemisorption, while the quantitative change is determined by the magnitude of AIS. This AIS model is generally applicable to chemisorption on any surface within the regime of linear elasticity, not only for transition metals of any d-state configurations, but also for non transition metals. It is also applicable to different sites on the same surface. We show that the response of chemisorption to external strain is site dependent and different sites may even behave in a qualitatively different manner. Furthermore, we illustrate the possibility of extending the model beyond surface adsorption to surface reaction pathways, which will allow us to determine the catalytic properties of surfaces under external strain.

II. THEORETICAL MODEL

We consider a general case of chemisorption on a solid surface, with the adsorbates arranged in a square lattice with a coverage of $n = 1/d^2$, as shown in Fig. 1. This configuration simplifies the calculation of lattice summation for adsorbate–adsorbate interactions and comparison to first-principles calculations, which use the supercell technique of periodic boundary conditions with a square surface unit cell of dimension $(d \times d)$, representing the same configuration and coverage.

Stress and strain are two conjugate physical quantities, and hence the way that external strain changes surface energy must be mediated by surface stress. The surface energy per unit area of a strained clean surface is expressed, by definition, as

$$\gamma = \gamma_0 + \sigma_{\alpha\beta}\varepsilon_{\alpha\beta}, \tag{1}$$

where σ is the intrinsic surface stress and ε is the external strain. Upon adsorption, the surface energy changes to

$$\gamma^a = \gamma_0^a(n) + \sigma_{\alpha\beta}^a(n)\varepsilon_{\alpha\beta}, \tag{2}$$

where $n = d^{-2}$ is the density (coverage) of adsorbates. So the adsorption energy per unit area is[14]
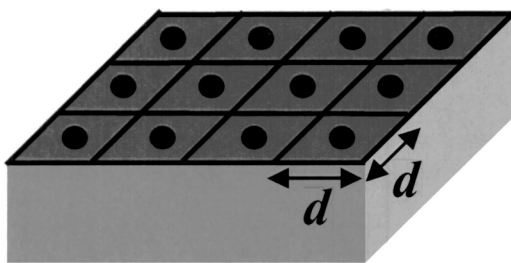
FIG. 1. Schematics of surface adsorption, assuming a square pattern of adsorbates of density (coverage) $n = 1/d^2$.

$$\Delta \gamma(n) = \gamma^a - \gamma = \Delta \gamma_0(n) + \Delta \sigma_{\alpha\beta}(n) \varepsilon_{\alpha\beta}. \qquad (3)$$

Alternatively, we may calculate the adsorption energy *per adsorbate* as the interaction energy between the adsorbate and surface:

$$E(n) = E_b + \frac{c\mu^2}{d^3} G(s) + \mu_{\alpha\beta}\varepsilon_{\alpha\beta}. \qquad (4)$$

E_b is the "chemical" binding energy between a single adsorbate and surface. The second term is the elastic adsorbate–adsorbate interaction energy:[16] c is a constant related to the modulus and Poisson ratio of the substrate, μ is the elastic force dipole induced by adsorbate, and $G(s)$ is a geometric factor, which equals 9 for the square lattice of adsorbates we consider. The last term is the additional strain energy of adsorption representing the work done by the elastic force dipole of adsorbate under external strain. In general, there may be also a direct electrical dipole–dipole interaction between adsorbates,[17] which is neglected in this elastic model for simplicity. From Eq. (4), the adsorption energy per unit area can be readily calculated as

$$\Delta \gamma(n) = nE_b + \frac{cn\mu^2}{d^3} G(s) + n\mu_{\alpha\beta}\varepsilon_{\alpha\beta}. \qquad (5)$$

Comparing Eqs. (3) and (5), we have

$$\Delta \gamma_0(n) = nE_b + \frac{cn\mu^2}{d^3} G(s) \qquad (6)$$

and

$$\Delta \sigma(n) = n\mu_{\alpha\beta}. \qquad (7)$$

Clearly, Eqs. (3)–(7) show that the effect of strain (ε) on adsorption is completely determined by the nature of the elastic force dipole introduced by the adsorbate and AIS, $\Delta \sigma(n) = \sigma^a(n) - \sigma$. For any given coverage of adsorbates, the adsorption energy will increase or decrease *linearly* with external strain, depending on the sign and magnitude of the AIS. Thus we derive a simple model to determine the effect of strain on adsorption, for a given coverage, by a single calculation of the AIS on the *unstrained* surface. Furthermore, if the force dipole μ remains a constant (a good approximation at low coverages), Eq. (7) indicates that the AIS is proportional to coverage. Thus, for complete coverage dependence, one needs only to perform first-principles calculations of the AIS down to the lowest coverage, below which μ

becomes constant.[18] This is practically very useful, because the low-coverage calculations require large supercells and are computational demanding.

III. COMPUTATIONAL RESULTS AND DISCUSSION

To validate our model, we have performed first-principles calculations of CO chemisorption on unstrained and strained Au(001) and K(001) surfaces. Both systems cannot be handled *in principle* by the previous model[7] as the model is not applicable for completely filled *d*-band transition metals (based on *arguments* of the previous model, the *d*-band center should not change on application of external strain for completely filled *d*-band metals) and for nontransition metals. We choose CO chemisorption on metal surfaces as the model systems, partly because they have been extensively studied before and the adsorption of CO on unstrained metal surfaces is well understood.[1,3–5,13] For simplicity, we use the unreconstructed Au(001) and K(001) surfaces with a CO coverage adsorbed in C-(1×1) geometry. It has also been shown that the fcc metal (001) surfaces remain unreconstructed with small addition of adsorbates.[19] *However, we emphasize that the principle concepts of our proposed model established by the model calculation will not depend on the surface reconstruction and molecular coverage used.*

The first-principles total-energy calculations within the density functional theory (DFT) formalism[20] and generalized gradient approximation (GGA) functional[21] are performed using the ultrasoft pseudopotential plane-wave method[22] employing the Nielsen–Martin scheme for calculating stress tensors.[23] A supercell of a five-layer slab was used for modeling the metal surface, with a cell dimension of (5.27 Å ×5.27 Å×42.5 Å) and (4.18 Å×4.18 Å×42.5 Å) for K(001) and Au(001), respectively. A cutoff of 420 eV was used for the plane-wave expansion and 144 k points for Brillouin-zone sampling. All atoms were relaxed using the conjugate-gradient technique for energy minimization, with an electronic energy convergence up to 10^{-8} eV per supercell in most cases. Convergence for energy and stress was tested with respect to the thickness of the vacuum layer, the number of k points, and the energy and force convergence criteria. Typically, for the convergence of surface stress, forces should be determined more accurately and are to be converged to a smaller value, compared to the convergence of the total energy. To avoid computational artifacts it is important to converge the surface stress such that the stress perpendicular to the surface is negligible.

We have considered CO adsorption on the (001) surface of Au (fcc) and K (bcc) at both the hollow site (HS) and top site (TS), to investigate the possible site dependence on application of strain. We have also considered two possible modes of CO adsorption, one with C and the other with O coordinating to the surface. In all cases, the mode of C coordinating to the metal surface is more stable, consistent with previous studies.[1] We first calculate the adsorption energy and AIS on unstrained surfaces, from which we predict adsorption energies on strained surfaces using Eq. (3). In Table I, we list the calculated CO adsorption energies[24] and the AIS on the unstrained Au(001) and K(001) surfaces at both the

TABLE I. Adsorption-induced stress (AIS) and adsorption energy on unstrained surface. Positive and negative signs of AIS indicate tensile and compressive stress, respectively.

Metal surface	Adsorption site	AIS [eV per (1×1) cell]	Adsorption energy (eV)
Au(100)	Hollow site (HS)	−0.10	−0.019
Au(100)	Top site (TS)	+1.40	−0.058
K(100)	Hollow site (HS)	+1.58	−0.743
K(100)	Top site (TS)	−0.06	−0.283

HS and TS for the stable mode of adsorption. On the Au(001) surface, the TS adsorption was preferred over the HS, while the opposite is true on the K(001) surface.

Using the calculated adsorption energy and AIS on unstrained surfaces (data in Table I), we make quantitative predictions of CO adsorption energies on Au(001) and K(001) surfaces under external strain (ε) using Eq. (3). These are shown by the straight lines plotted in Figs. 2 and 3 for Au(001) and K(001) surfaces, respectively. The value at $\varepsilon = 0$ is given by the adsorption energy on the unstrained surface, and the slope of the line is given by the AIS. We then compare the predictions with a series of direct calculations of adsorption energies on strained surfaces by manually straining the surface up to a maximum biaxial strain of ~2%. These results are also plotted in Figs. 2 and 3 as solid dots and squares, in comparison with the model predictions. Excellent agreement has been obtained between the model prediction and the direct calculation in all cases. We have also done some direct calculations at even larger strain beyond 2% where the strain dependence becomes increasingly nonlinear, exceeding the linear regime of the current model. Calculations of the AIS for different coverages also confirm the relation of Eq. (7) that the force dipole of the adsorbate, μ, becomes a constant at low coverages. (Here we can just use results at one coverage to validate our model, because the model is applicable independently of any given coverage. The results of the coverage dependence, in particular varying μ at high coverages, will be presented elsewhere.)
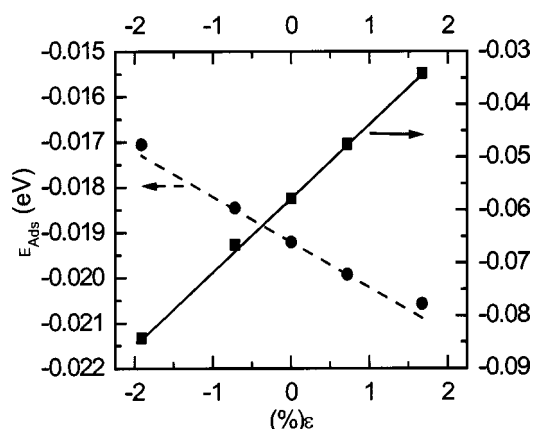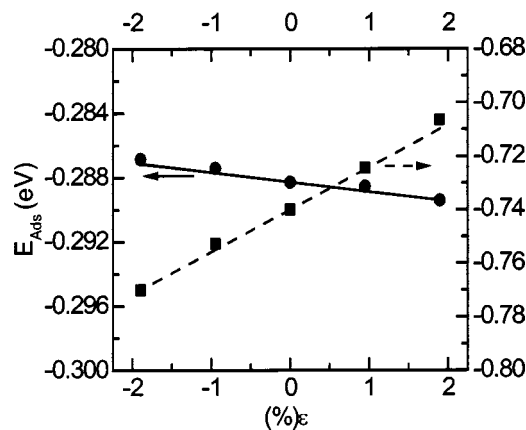

FIG. 3. Comparison between predicted and computed adsorption energies (E_{ads}) on K(001) surface under external strain (ε). Notations are the same as in Fig. 2.

There exists a common trend on both surfaces that at the more stable adsorption site (either TS or HS) the CO always induces a positive (tensile) AIS, while at the other less stable site it induces a negative (compressive) AIS. A possible explanation is when the adsorbate induces a tensile surface stress, it implies a net "attractive" force[16] between the adsorbate and surface that leads an overall expansion of the surface, while the other case implies a net "repulsive" force[16] between the adsorbate and the surface. However, attempts to generalize this feature using first-principles chemisorption calculations on other surfaces performed in our group have not been met with success. Furthermore, it has been shown that the adsorption energy decreases with lattice expansion in certain cases,[7,8,10] implying that AIS can be compressive. We also note that in all calculations, the bond lengths of CO remain roughly constant when metal surfaces are strained. This possibly indicates that the change of chemical bonding within the adsorbate is small and contributes little to the strain-induced change of adsorption energy in the range of strain applied.

Therefore, we establish a simple model to determine the adsorption energies of molecules on strained metal surfaces by a single calculation of the AIS on an unstrained surface. The effect of strain on adsorption is completely contained in the AIS within the regime of linear elasticity. If the sign of the AIS is positive—i.e., the adsorption induces a tensile stress in the surface, such as the case of CO at the TS on Au(001) and at the HS on K(001)—then the adsorption energy will increase (decrease) when a tensile (compressive) strain is applied to the surface, as shown in Figs. 2 and 3. The reverse will be true if the sign of the AIS is negative. Also, the larger the magnitude (absolute value) of AIS, the stronger is the strain effect. *These principles apply generally to any adsorbate on any surface at any adsorption site.*

It is particularly interesting that on the same surface adsorption at different sites can respond to external strain in a qualitatively different manner if the AIS has opposite signs at different sites. This is shown by adsorption at the TS vs HS on both Au(001) and K(001) surfaces. We have performed calculations on other surfaces and have found that such a feature exists on other metal surfaces too. It indicates that the

FIG. 2. Comparison between predicted and computed adsorption energies (E_{ads}) on Au(001) surface under external strain (ε). The solid and dashed lines are model predictions for TS and HS, respectively. Solid dots and squares are computed data.
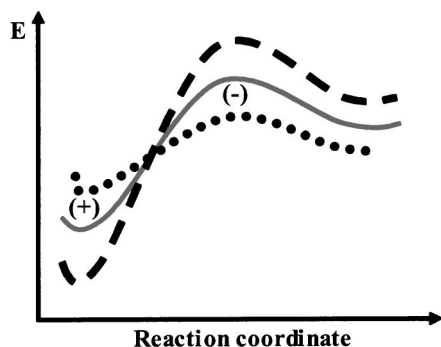
FIG. 4. Schematics illustrating the effect of strain on reaction pathway on surface. The solid line is the path without strain. The positive and negative signs indicate the tensile and compressive AIS at the reactant and transition states, respectively. The dotted and dashed lines show the reaction path under a tensile and compressive surface strain, respectively.

change of adsorption energy can be site sensitive; it is governed by a *local* property like the AIS, which is related to the adsorbate-induced elastic force dipole at a particular site, rather than a *global* property like the center of *d* bands suggested in a previous model.[7] Such site sensitivity is especially important in surfaces where more than one site of comparable adsorption energy is present and in experiments where tensile and compressive strain regions are created simultaneously in the same surface.[4]

Next, we illustrate the possibility of extending the AIS model beyond surface adsorption to determine the effect of strain on surface catalytic properties. We may generalize the AIS model to reactants (*not necessarily to just one adsorbent*) that interact with the surface as a whole, residing in different energy states (reactant versus transition state). A similar idea has been applied to study the effect of strain on surface diffusion.[25] The "*generalized* AIS" (which is the surface stress along the reaction coordinate in the case of molecular dissociation on the surface) is then expected to change along the pathway of surface reaction and, in particular, to be different at the reactant and transition states. Consequently, the energies at these two states will respond differently to the applied external strain, leading to a change in the activation energy, the energy difference between the two states. Applying Eq. (3) to both reactant and transition states, we have

$$E_b = E_b^0 + (\sigma_{\alpha\beta}^T - \sigma_{\alpha\beta}^R)\varepsilon_{\alpha\beta}, \tag{8}$$

where E_b is the activation barrier, and σ^T and σ^R are the AIS at the transition and reactant states, respectively. Apparently, the effect of strain will be most pronounced when the AIS has opposite signs at the transition and reactant states.

Figure 4 shows schematically the case when the *generalized* AIS (surface stress in this case) is negative (compressive) at the transition state and positive (tensile) at the reactant state (solid line in Fig. 4). When a tensile strain is applied to surface, the energy at the transition state will decrease, while the energy at the reactant state will increase, leading to a decrease of activation barrier (dotted line in Fig. 4). The reverse will be true when a compressive strain is applied to the surface (dashed line in Fig. 4). Such a sce-

nario, as illustrated in Fig. 4, has indeed been confirmed by our model calculation of CO dissociation on a Ru(0001) surface.

CO dissociation on a Ru(0001) surface has attracted considerable experimental and theoretical interest.[4,5,7,26] The calculation methodology is the same as described above for CO adsorption on Au and K surfaces. For the "surface reaction" of CO dissociation, using the same procedure as in previous works,[7,27] we first determine that the reactant state of CO (the stable configuration of adsorption) with C coordinating to the top site with its molecular axis perpendicular to the surface, while in the transition state, the molecular axis is tilted with the C–O bond greatly stretched, in which C is at the hollow site binding to three Ru atoms, but O moves close to the bridge site binding to two Ru atoms. These are in good agreement with previous calculations.[7,26] We then calculate the *generalized* AIS (surface stress in the present case of molecular dissociation on the surface) at both the transition and reactant states, which are found to be −1.62 and +11.88 eV per (2×2) supercell, respectively, as qualitatively shown in Fig. 4.

With validation of the AIS model by direct computations for both adsorption and surface reactions in the above-mentioned systems, it is tempting to search for qualitative guidelines to rationalize and predict the sign of the AIS on any surface as this might be useful in tuning the chemical activity on surfaces using strain. Many insightful pointers have been proposed in the earlier studies to rationalize the sign of the AIS on both the metal and semiconductor surfaces.[14,16,28,29] Though the origins behind the tensile nature of the clean metallic surface are fairly clear in most cases,[29] the general factors underlying the sign of AIS are unclear and hence a qualitative rationalization and prediction without performing a calculation or an experiment is not possible presently.

IV. CONCLUSIONS

We derive a model to determine quantitatively changes in adsorption energy and reaction barrier on any metal surface when the surface is strained in the elastic regime. The model involves a single calculation of adsorption-induced stress on the unstrained surface. The predictions of the model are in excellent agreement with the results computed from first-principles calculations. The model predictions are quantitative for small strain within the linear regime and are expected to be qualitatively correct at larger strains beyond the linear region. Although the microscopic origins underlying the AIS can be complex and an *a priori* prediction of the AIS without a first-principles calculation may not be possible, the AIS model provides us with an unambiguous parameter to determine changes in adsorption energy for a given molecule (or activation energy for a given reaction) on strained metal surfaces and a rather general scheme for interpreting and analyzing changes in the adsorption (activation) energy under the application of external strain.

ACKNOWLEDGMENTS

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