Reentrant Mechanism for Associative Desorption: H_2/Pt(110)-(1 × 2)

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Calculations of the desorption of hydrogen from Pt(110)-(1 × 2), a surface used to model nanoparticle edge sites, show the activation energy varying strongly with hydrogen coverage, from 0.8 to 0.3 eV. The predicted temperature programed desorption spectra agree well with experiments, but the formation of the hydrogen molecules occurs only at two types of sites on the surface even though three peaks are observed. The lowest and highest temperature peaks result from desorption from the same strong binding sites at the ridge, while desorption from the weakest binding trough sites is insignificant.

An understanding of the factors that control the reactivity of adsorbed atoms and molecules on transition metal surfaces can help develop improved heterogeneous catalysts, a task that is vital for designing processes with higher energy and atom efficiency in the chemical industry. The atomic scale design of surfaces of crystals or nanoparticles can make it possible to obtain specific catalytic properties that lower the cost and environmental impact of chemical processes. Theoretical calculations have proved to be useful in this design effort, as has been demonstrated in several cases [1]. The interaction of hydrogen with the surface of platinum metal is of fundamental importance to a wide range of technologies including various reduction reactions, electrolysis, and fuel cells. The hydrogen-platinum system has, furthermore, become a model system where a great deal of effort in surface science has been focused. In practical applications, the Pt catalyst is often finely dispersed in small particles embedded in a matrix and the active sites can be of various types, for example, edges where crystal facets meet. The missing row reconstructed Pt(110)-(1 × 2) surface is a convenient model for edge sites between the most stable facets, Pt(111). It involves three types of binding sites for H atoms and, therefore, can also serve as a model for the interplay between different types of sites in reactive processes.

We present here results of density functional theory (DFT) calculations of the binding, diffusion and desorption of hydrogen on the Pt(110)-(1 × 2) surface, which show a remarkable coverage dependence of the binding and desorption energy. As a result, the desorption mechanism is the same at high and low temperatures, but not at an intermediate temperature—a reentrant behavior. The calculations made use of the revised Perdew-Burke-Ernzerhof (RPBE) functional [2], plane wave basis set with an energy cutoff at 450 eV and ultrasoft pseudopotentials [3] as implemented in the VASP software [4]. Minimum energy paths and activation energy for transitions were calculated using the climbing-image nudged elastic band method [5].

Previous DFT calculations have shown that H adatoms prefer to sit at bridge sites on top of the ridge formed at the edge between the two (111) microfacets [6]. (The inset in Fig. 1 shows the various types of sites on the surface: ridge, facet, and trough.) This came as a surprise, normally H atoms prefer high coordinated sites [7] and several workers have assumed the trough sites to be preferred. He-atom scattering measurements had previously shown that corrugation increases from 1.5 Å for a clean surface to 2.0 Å when H-atoms are adsorbed up to a coverage corresponding to the ridge sites, but the precise location of the atoms could not be determined [8]. A suggestion that H-atoms sit under the ridge Pt atoms could be ruled out from the lack of Pt-atom relaxation deduced from LEED measurements [6], which, however, are insensitive to the location of H atoms. We have calculated the corrugation of the 0.06 eV energy contour of the He interaction potential using DFT/RPBE and obtained quantitative agreement with the measured corrugation, showing that the prediction of the DFT calculations is indeed consistent with measurements. The measured increase in the work function during the initial phase of H adsorption [9] is, furthermore, well reproduced by the DFT calculations when the slightly negatively charged ($-0.05\ e$ deduced from the electron density [10]) H adatoms are placed at the ridge sites, thereby reducing the surface dipole formed by the protruding Pt atoms on the ridge (with the positive end pointing outward due to the Smoluchowski effect [11]). This brings the work function closer to that of the flat Pt(111) surface. After the ridge sites have been filled, the H-atoms fill sites on the (111) facets and, finally, the trough sites leading to a decrease in the work function, again in agreement with experiments [9]. The prediction of the theoretical calculations regarding the preference for the ridge sites, therefore, appears to be in good correspondence with experimental measurements.

From this sequential filling of surface sites, it seems reasonable to assume that the lowest temperature peak in the temperature programed desorption (TPD) corresponds to associative desorption of atoms sitting at trough sites. When atoms or molecules desorb intact, the position of peaks in TPD are directly related to the binding energy to the surface and such experiments are frequently used to
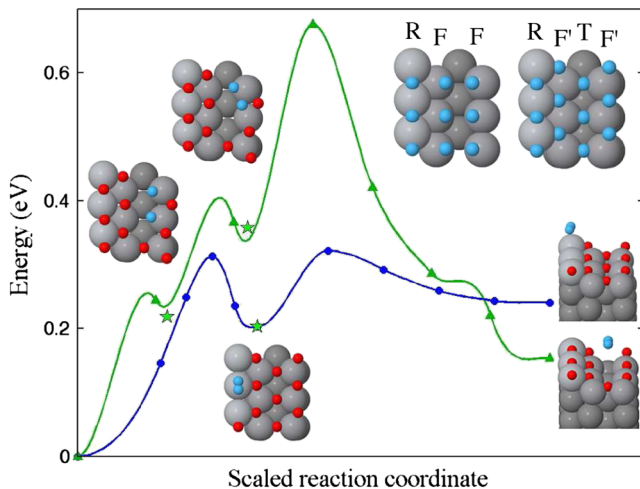
FIG. 1 (color online).   Minimum energy paths for H_2 desorption from the fully hydrogen covered Pt(110)-(1 × 2) surface comparing two different mechanisms: (1) The two H atoms coming from trough sites [green (light grey) line and dots representing discretization points in the climbing-image nudged elastic band calculation] and (2) the 2 H-atoms coming from ridge sites [blue (black) line and dots]. While the second mechanism leads to higher final state energy, it turns out to involve lower activation energy. Even though the trough adatoms are more weakly bound, the activation energy for forming the H_2 molecule there is higher. The energy is plotted as a function of the total displacement of atoms along the minimum energy paths scaled by the total length of 10.6 Å for (1) and 5.5 Å for (2). The insets in the upper right corner show the labeling of the surface sites (when H atoms fill trough sites the atoms at facet sites move from F to F'). The insets along the minimum energy path show configurations at intermediate local minima [green (light grey) stars] obtained by the minimization starting from the nearest climbing-image nudged elastic band discretization point and at the end points when a H_2 molecule has formed. The local minimum on the blue (black) curve corresponds to a Kubas complex [17] where a H_2 molecule binds as a ligand to the ridge. The minimum energy path for H_2 desorbing from facet sites is not shown in the figure since the activation energy for a full H coverage is much larger, 0.97 eV, as can be seen from Fig. 2.

determine the number of different types of binding sites and determine the binding energy at each one. When desorption involves additional bond breaking or bond formation, however, the desorption process can involve an additional activation energy barrier beyond the increase in energy between the bound and gas phase species. The association between peak positions in TPD and the binding energy is then not as direct. Figure 1 shows the calculated minimum energy path for desorption of a H_2 molecule formed from two H adatoms from trough sites. The additional activation barrier is indeed large, giving an activation energy of 0.7 eV in this case, and the path involves large displacements of the neighboring atoms. Two local minima corresponding to rearrangements of the neighboring H adatoms are found before the maximum energy

configuration is reached. The H_2 molecule is finally formed over a Pt atom on the (111) microfacet. The reason for this complex path and high activation barrier is lack of catalytic activity of the highly coordinated and inaccessible trough Pt atoms. If, however, two H adatoms at ridge sites, stronger binding sites, form a H_2 molecule, the activation energy is lower, 0.3 eV; see Fig. 1. The energy of the final state is 0.1 eV higher for desorption from ridge sites compared with trough sites, but surprisingly, the activation barrier is 0.4 eV lower. Clearly, the activation energy for desorption is not correlated with the H-adatom binding energy when these two different mechanisms are compared.

The coverage dependence of the desorption activation energy for three different desorption mechanisms is shown in Fig. 2. At high coverage, desorption from ridge sites has the lowest activation energy. After clearing ridge sites, H adatoms from facet sites then diffuse to fill the ridge sites and finally, H adatoms from trough sites fill the vacant facet sites. The activation energy for diffusion is calculated with the climbing-image nudged elastic band method to be 0.25 eV for the highest coverage, whereas it gets lower for lower coverage, down to 0.1 eV. When all trough sites have been cleared in this way, the direct desorption from facet sites becomes the preferred mechanism. Finally, when only the ridge sites are filled, the desorption occurs again from there. This reentrant mechanism results from remarkably strong coverage dependence in the activation energy, the energy barrier increasing from 0.3 eV at high
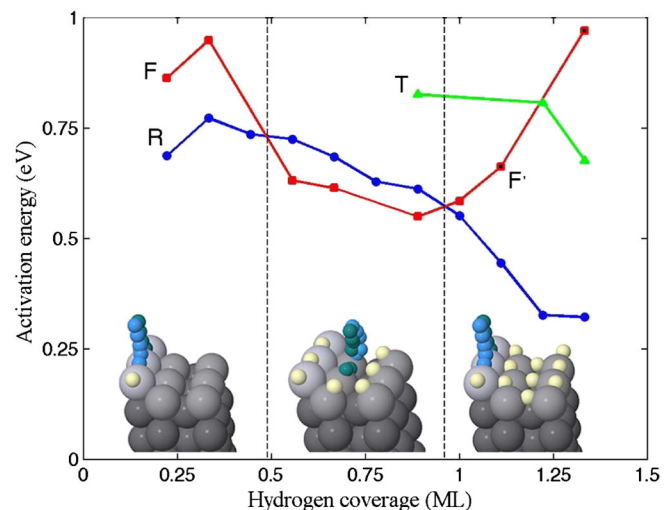

FIG. 2 (color online).   Coverage dependence of the calculated desorption activation energy for three different desorption mechanisms: (1) the mechanism involving adatoms at ridge sites (blue, black), (2) the mechanism involving adatoms at facet sites (red, dark grey), and (3) the mechanism involving adatoms at trough sites (green, light grey). The dotted black lines mark a crossover from one mechanism to another. The insets at the bottom show the calculated minimum energy paths for each of the three cases.

coverage to 0.8 eV at low coverage—desorption from the same two ridge sites. (Such a difference in activation energy corresponds to the 8 orders of magnitude difference in the rate at room temperature.) Various other desorption mechanisms were studied, such as the combination of atoms from R and F' sites, and the combination of atoms from F' and T sites; however, these did not give the optimal desorption mechanism at any coverage.

The question then arises, how well the calculations compare with measured TPD spectra. The activation energy for desorption and diffusion obtained from the DFT calculations was fitted to a polynomial function of the hydrogen coverage at various types of sites and adjusted to within 0.1 eV of the calculated values so as to reproduce the measured peak positions. First order kinetic equations are used for ridge desorption, which is consistent with the strong attractive interaction between H adatoms on the ridge obtained in the DFT calculations [12], but second order equations are used for facet desorption since there is slight repulsive interaction between the H adatoms [12]

$$\frac{d\theta_R}{dt} = [-2k_{R,H_2} - k_{R,F}]\theta_R(t) + k_{F,R}2\theta_F(t), \quad (1)$$

$$\frac{d\theta_F}{dt} = [-2k_{F,H_2}\theta_F(t) - k_{F,R} - k_{F,T}]\theta_F(t)$$
$$+ k_{R,F}\frac{1}{2}\theta_R(t) + k_{T,F}\frac{1}{2}\theta_T(t), \quad (2)$$

$$\frac{d\theta_T}{dt} = -k_{T,F}\theta_T(t) + k_{F,T}2\theta_F(t). \quad (3)$$

Here, θ_i is the coverage of H adatoms at binding sites of type i and the factors 2 and $1/2$ in front of θ come from counting different adsorption sites. $k_{X,Y}$ is the rate constant for transition from initial state X to final state Y given by the Arrhenius equation with preexponential ν and activation energy E_a,

$$k(\tau, \theta_R, \theta_F, \theta_T) = \nu e^{-E_a(\theta_R,\theta_F,\theta_T)/k_B\tau}. \quad (4)$$

The total desorption rate per surface site is then

$$r(\tau, t) = k_{R,H_2}(\tau)\theta_R(t) + 2k_{F,H_2}(\tau)\theta_F(t). \quad (5)$$

This set of rate equations was solved using the finite difference method. An experimental estimate of the prefactor for desorption was used [9], $\nu = 10^{11}$ s^{-1}. The TPD experiment of Minca *et al.* [6] was simulated by setting $\tau = \tau_0 + \gamma t$ where τ_0 is the initial temperature and γ is the heating rate of $\gamma = 3$ K/s; see Fig. 3. The calculated activation energy and the deduced crossover in the mechanism is clearly in good agreement with the measurements. When starting with the highest initial coverage, $\theta = 1.33$, the α peak is reproduced quantitatively by desorption from the *ridge* sites, not the trough sites as could be expected from the binding energy. This illustrates the danger in interpreting peaks in TPD spectra for associative desorption in
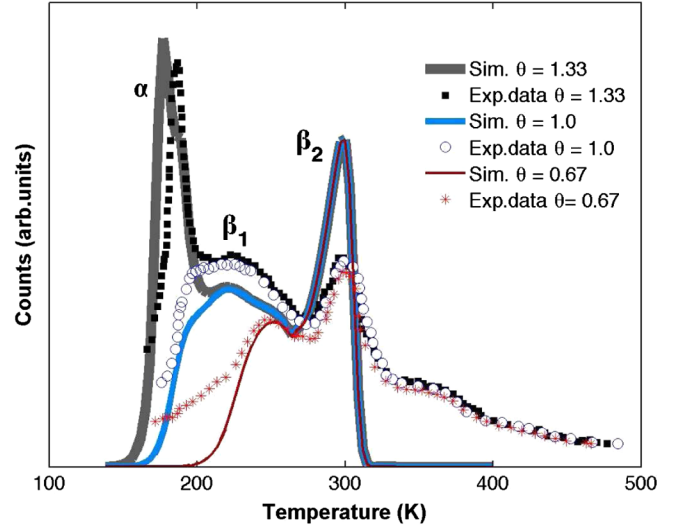

FIG. 3 (color online). Comparison of simulated (solid lines) and measured [6] (symbols) temperature programed desorption spectra for D_2 desorption from the Pt(110)-(1 × 2) surface starting from high, intermediate, and low coverage. Both the lowest (α) and the highest (β_2) temperature peaks correspond to desorption from ridge sites, but the intermediate peak (β_1) corresponds to desorption from facet sites. TPD spectra for H_2 desorption from the Pt(110)-(1 × 2) surface have a similar shape [18] but the positions of the peaks are approximately 10–20 K lower in temperature.

terms of binding energy of the adatoms to the surface. The sharpness of the peak is due to attractive interaction between the H adatoms on the ridge. The β_1 peak is due to desorption from the facet sites. When starting with a coverage of $\theta = 1.0$, this is the lowest temperature peak observed since even though H atoms are present at ridge sites at this coverage, the desorption activation barrier has become greater than that of desorption from facet sites. Starting with even lower coverage, gives a β_1 peak at a higher temperature. Finally, the highest temperature peak, β_2, corresponds to desorption from ridge sites, the same as the lowest temperature α peak.

The surprisingly large coverage dependence for desorption from ridge sites is directly related to strong coverage dependence in the binding energy,

$$\Delta E_{2H^*,R}(n) = E(n) - E(n-2) - E_{H_2}, \quad (6)$$

of two H adatoms at the ridge. The maximum energy along the minimum energy path is, in all cases, only 0.03 to 0.1 eV above the energy of the gas phase molecule at any coverage for this mechanism. So, the binding energy and the activation energy are closely correlated in this case. Figure 4 shows how the binding energy changes as the other sites get occupied by H adatoms. The effect of filling F', F, and T sites is similar in magnitude. Each atom occupying a trough site has, in fact, twice as large effect since there are only half as many trough sites as facet sites.
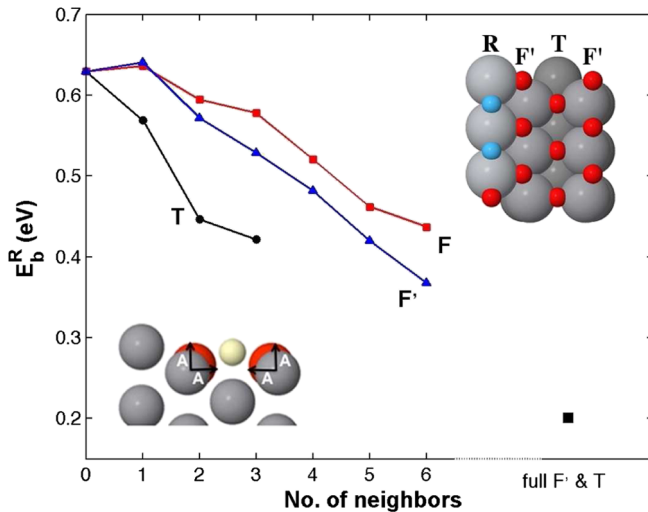
FIG. 4 (color online).   The binding energy of two H adatoms at adjacent ridge sites as a function of the number of neighbors in various types of sites. The black square shows the binding energy when all sites are occupied. The insets show the labeling of sites (top-right), and the structural relaxation that occurs when H atoms bind in the trough sites (bottom-left).

The total shift in the binding energy, over 0.4 eV, is nearly the sum of the shift due to trough and facet sites separately. Adsorption in facet and trough sites results in large structural relaxation. As H atoms bind there, facet Pt atoms are pulled up and toward them, as shown in Fig. 4. The relaxation is particularly strong when a H adatom binds to a T site. The displacement is 0.35 Å, as shown in Fig. 4. This flattens the surface locally and apparently makes the Pt atoms at the ridge less available for bonding. There could also be a long-range electronic effect here involving surface states at the ridge. Such surface states have, in fact, been detected by angular resolved photoemission [13].

The calculated minimum energy paths can also be used to estimate the activation energy for direct adsorption as a function of coverage. The values obtained range from 0.05 eV at low coverage to 0.53 eV at high coverage, which is consistent with the experimental measurements [6] where an exposure of 10^4 L was needed to reach full coverage.

A nanoparticle of Pt has several different facets separated by edges and corners. The lowest energy facet is the (111) facet and the ridge on the Pt(110)-(1 × 2) surface is often used as a model for an edge between such facets. The Pt(110)-(1 × 2) surface is, therefore, sometimes used as a model for nanoparticles [14,15]. The calculations presented here indicate that at high coverage, the H atoms adsorbed at ridge sites are chemically most reactive, not the atoms adsorbed at trough sites, even though the trough adatoms are more weakly bound. This large reactivity at the edges could help design catalysts for reducing rather inert molecules, such as N_2 and CO_2, electrochemically [16].

In summary, we have found a remarkably strong coverage dependence of the binding energy and activation energy for desorption of H_2 from the missing row reconstructed Pt(110)-(1 × 2) surface in DFT calculations. The preferred binding sites on top of the ridge are also the most active desorption sites both at high coverage and at low coverage, thereby giving rise to two different peaks in the TPD spectrum for the same desorption sites. At intermediate coverage, the desorption occurs from sites on the (111) microfacets. The strong coverage effects observed in this study can, in part, be correlated with large surface relaxations, up to 0.35 Å, when H atoms bind to the surface.

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