Hydrogen atom quantum migration on platinum

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We have reexamined hydrogen-platinum systems, giving emphasis on the atomic migration on the metal surface. The ideal (111) surface was firstly revisited, with the model potential energy surface for the motion of hydrogen created from calculations using a slab of platinum atoms fixed at the bulk separation obtained from experimental measurements. Calculated hydrogen hopping states in an adiabatic approximation are presented, with the lowest of these found at only 30 meV above the ground state. Effects of the presence of vacancies on the atomic migration are discussed from a potential energy surface constructed using a similar model. [DOI: 10.1380/ejssnt.2006.619]

Keywords: platinum; ab initio quantum chemical methods and calculations; adsorption kinetics; diffusion and migration

I. INTRODUCTION

Put simply, diffusion comprises an essential aspect of catalytic processes as it bridges the initial adsorption of reactants with eventual reactions at other locations. In the context of fuel cells for example, hydrogen, upon reaching the anode, would require moving along the catalyst surface, say that of platinum or its alloys, and traveling through a proton conducting membrane before reacting with ambient oxygen at the other end to complete the process. It is primarily in light of describing these processes at the atomic scale, particularly those involved at the anode, that the H-Pt system has created its own following (see for instance Refs. [1–5]), with a quantum mechanical picture of the behavior of a hydrogen atom on the ideal Pt(111) surface examined as well [6–12]. Previous studies from our group [6–8] showed the importance of such a treatment in accurately describing the system, e.g. in correctly determining the stable adsorption sites, as well as on other metal surfaces. Independent of these studies, at least two other groups [9–11] worked on similar problems, with their quantum treatments of hydrogen motion weighed against available experimental data. More recently, Olsen et al. [12] have considered systems of stepped (211) surfaces, identifying states for hydrogen adsorbed at the step edge.

In line with this we have in this paper extended previous investigations on a full quantum mechanical picture of hydrogen’s behavior on a rigid catalyst surface, as the small mass of hydrogen makes a departure from a classical analysis no less than a necessity. Here we setup groundwork on describing hydrogen motion on a specific defective surface, but we firstly give another look at the benchmark (111) surface of platinum for comparison.

II. ON THE IDEAL (111) SURFACE

The computations work on an adiabatic description of the atom motion on the substrate, and can thus be seen as divided into two parts: the construction of a model potential energy surface for the motion of hydrogen in three dimensions, and solving the Schrödinger equation for H atom motion under the periodic boundary conditions of the surface. For this section we return to the ideal (111) surface, here represented by a five-layer slab with all Pt atoms fixed at bulk separation (2.77 Å), and using a hydrogen surface coverage of one-fourth, i.e. the unit cell contains twenty Pt atoms and a single H. In essence, the number of layers used to represent the surface is the key difference from our group’s previous calculations, with the increased H-Pt interaction energy point sampling as a secondary addition. Energy calculations were performed in a periodic supercell approach to density functional theory (DFT), employing pseudopotentials. For this particular system we used a 508 eV cutoff for the expansion of the electron wave functions, generalized gradient approximation [13] for electronic exchange-correlation effects, and a 4 × 4 × 1 Monkhorst-Pack [14] mesh for the Brillouin zone sampling, which showed good adsorption energy convergence.

Eighty-one total energy surface-normal scans across the 1 × 1 surface primitive cell, encompassing the 9 × 9 grid shown in Fig. 1(a), were the bases of the potential energy surface (PES) constructed. Figure 1(c) shows the minimum-energy corrugation along the surface (i.e., curve depth D(x,y)), with the corresponding trace along indi-
FIG. 1: (a) Lateral positions of the H atom, (b) potential energy along the paths indicated by the broken line in (c), (c) potential energy minimized along the z-direction for the (111) surface of platinum, sampled on a 6 Å×6 Å area. Contour lines are separated by 0.02 eV, and lighter shades denote regions of stronger adsorption.

cated paths connecting the minima at the top and hollow sites. The top site ($D = 2.609$ eV) is found to be only very slightly more stable than the fcc threefold-hollow site ($D = 2.607$ eV), which in practical terms makes the two sites energetically equivalent. The slight energetics differences as compared with related computational literature, especially on the relative adsorption strength on the hollow and top sites, arises from factors including adsorbate coverages used, differences in the slab thickness, and the choice of equilibrium bulk lattice constants. The three-dimensional PES for hydrogen motion on Pt(111) was built using a similar procedure outlined in Ref. [8]. Surface-normal Morse fits were used with $D$, $\beta$ and $z_0$ parameters dependent on the H atom lateral coordinates $x$, $y$, i.e. expressing the full potential energy term as

$$V(x, y, z) = D(x, y) \left\{ \left[ e^{-\beta(x,y)[z-z_0(x,y)]} - 1 \right]^2 - 1 \right\},$$

(1)

with intermediate points interpolated through Fourier transforms. Working within variation methods, the eigenstates describing hydrogen motion were numerically determined based on wave functions expressed as a linear combination of 720 Gaussian orbitals centered at $(x_i, y_i, z_i)$, i.e.

$$\psi(x, y, z) = \sum_i c_i \phi_i(x, y, z)$$

$$= \sum_i c_i e^{-\frac{1}{2} \sigma_{xy} [(x-x_i)^2+(y-y_i)^2]} e^{-\frac{1}{2} \sigma_z (z-z_i)^2}.$$  

(2)

The orbitals are placed at a $12 \times 12 \times 5$ grid right above the first layer of Pt atoms, spanning the area of a surface primitive cell, and the 5 surface-parallel 'layers' of orbitals used were placed at $0.9 \text{Å} \leq z \leq 1.7 \text{Å}$.

The ground state ($E = -2.461$ eV, Fig. 2(a)) of hydrogen for these calculations show similarities with our previous results for a coverage of 0.25 on the Pt(111) surface modeled through three-layer slabs, except that the ground state wavefunction is clearly more localized in the vicinity of the fcc threefold hollow site in the current calculations, arising from slight differences in the potential energy surfaces constructed. Comparing our results to that reported in Refs. [9, 10], agreement is found with regard to the character of the ground state wave function. While being more close to [10], results deviate starting from the first excited state, which isn’t unexpected from the differences in the systems studied, if not from approximations used in obtaining the wave functions. The first excited state (Fig. 2(b)) is 30 meV above the ground state, and while...
FIG. 2: Hydrogen motion eigenstates on Pt(111), plotted on a $2 \times 2$ surface cell. (a) Ground state ($E = -2.461$ eV), (b)-(e) first to fourth excited states, which have eigenenergies of 30 meV, 32 meV, 34 meV, and 34 meV above the ground state, respectively. Representations of nearest first-layer atoms (grey spheres) are shown for reference.

primarily located at the hcp site, already exhibits significant delocalization, having vibrational peaks at all three high-symmetry sites. This then suggests that, assuming the system is initially at the ground state, migration is likely to occur even at half the barrier obtained straight from the PES, as the H atoms can be widely distributed along the surface. The second excited state (Fig. 2(c)) has its vibrational peaks at the top and hcp sites, while bridge sites are accessed in the degenerate 3rd and 4th excited states (Figs. 2(d) and 2(e)), which as well show considerable delocalization. As we go higher from these states, vibrational states expectedly get more complex, e.g. locations of vibrational peaks are more spread out, attributed to the intrinsic anharmonicity of the potential.

Laser-induced thermal desorption (LITD) measurements [16] of the barrier to the diffusion of H on the flat Pt surface showed values in the range of 300 to 520 meV for coverages of 0.33 to 0.001 ML, although it has been pointed out that defects created on the surface may have significantly affected the reported results. Data from quasielastic helium atom scattering [17] yielded an average activation energy of $68 \pm 5$ meV at a coverage of 0.1 ML, while linear optical diffraction results [18] yielded values ranging from 104 to about 185 meV for the entire spectrum of coverages studied (around 157 meV for $\Theta = 0.1$), found generally higher than those observed on stepped surfaces, and exhibiting a different coverage-dependence trend when compared with the previous two studies mentioned. At this point we can at most discuss our results with the dissimilar data at a finite coverage of 0.1 ML from the latter two studies, although we are pursuing further modeling in order to arrive at any finality on this subject.

III. THE (111) SURFACE WITH VACANCIES

We compare our results to a (111) surface of Pt wherein one atom in four at the first layer is removed, creating a surface with an ordered arrangement of vacancy defects - a simplification done solely for computational practicality. From the symmetry of the system, total energy calculations were performed to build 324 surface-normal scans on a $2 \times 2$ area, i.e., on the $18 \times 18$ grid shown in Fig. 3(a). All computational parameters are held the same as with the discussion in the previous section, save for the choice of the functional [15] and the energy cutoff, which was done to optimize calculations without compromising accuracy. Figure 3(c) shows the potential energy minimized along the $z$ (surface normal) direction, while Fig. 4 shows the corresponding stable-position corrugation $z_0(x, y)$ for this system, which essentially follows the contours of the surface itself.

A quick inspection of Fig. 3 shows the following key details/trends. First, strongest adsorption occurs at the bridge centers on vacancy step edges (Fig. 5), with that on the (100) step slightly preferred over (111). The adsorption energy from DFT, i.e., without zero-point correction, at this position is 2.96 eV - stronger than that on the flat surface, which is to be expected from the lower stability of the rough surface modeled in this study. Adsorption at high-symmetry sites (and at all points directly above the first layer) is stronger as compared to data shown in Fig. 1, although the relative stability of the top site is noticeably decreased.

Second, there is a clear difficulty in entering the vacancy. This process requires surmounting a wall at least 840 meV high, and is thus expected to prevent hydrogen from settling at the positions left vacant by the removed substrate atoms. The slight stability of the vacancy center from its immediate surroundings is to be expected partially from being a site of high-symmetry on the second layer of the (111) surface, but the magnitude of the barrier is worth noting. This wall arises from the relative stability of the second layer atoms at the vacancy, associated with their higher coordination, and is expected to http://www.sssj.org/ejssnt (J-Stage: http://ejssnt.jstage.jst.go.jp) 621
FIG. 3: (a) Lateral positions of the H atom, (b) potential energy along the paths indicated by the broken curves in (c), (c) potential energy minimized along the z-direction for the (111) surface of platinum with vacancies, sampled on a 6 Å×6 Å area. Contour lines are separated by 0.05 eV, and lighter shades denote regions of stronger adsorption.

FIG. 4: H atom surface normal (z) position at energies corresponding to Fig. 3(c). Contour lines are separated by 0.12 Å, and lighter shades being farther from the Pt surface.

Third, the diffusion barrier as obtained straight from the PES is higher (at 208 meV) for the defective system. The path of least potential along the surface passes through the top site, as compared with the honeycomb canal network connecting only hollow sites in the ideal (111) surface, which has a 60 meV barrier. As our interest is the quantum migration of the adsorbates on the catalyst surface, calculations on the hydrogen eigenstates are currently ongoing. However, from the perspective of the obtained PES, it won’t be surprising to find out that the diffusion states for the defective surface would be less accessible.

IV. CONCLUSION

Hydrogen behavior on ideal and defective Pt(111) surfaces were examined, giving emphasis on the atomic migration on the catalyst surface. A quantum mechanical treatment of H on the ideal Pt(111) surface showed delocalization of the first excited state, suggesting an effective barrier of 30 meV, a value worthy of note in view of available experimental data. On the defective surface, from calculations within density functional theory, hydrogen is seen to be preferably adsorbed on bridge sites at the step edges of a vacancy, and is expected to have a higher migration barrier. For a comprehensive picture on the hydrogen motion we are pursuing dynamics studies based on
FIG. 5: Most stable location of hydrogen on the surface, from the obtained PES. The H atom (white) is at the bridge center of the edge of a (100) step.

the potential energy surfaces that we have constructed.

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