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Density Functional Study of Sequential H₂ Dissociative Chemisorption on a Pt₆ Cluster

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The dissociative chemisorption of dihydrogen on a Pt₆ cluster with an octahedral configuration was studied with density functional theory. The on-top site was identified to be the most favorable chemisorption site for dihydrogen followed by the bridge site and the 3-fold hollow site. It was found that the dissociative chemisorption process is dictated by the charge transfer from the Pt cluster to H₂ molecules via the overlap of 5d orbitals of Pt₆ and $1\sigma^*$ orbital of H₂ and that the cluster achieves its full saturation with H atoms at the Pt/H ratio of 1:4. The effect of H coverage on the Pt cluster catalytic activities was discussed.

Introduction

Precious metals have long been used as catalysts in many heterogeneous catalytic reactions. Platinum, in particular, is one of the most valuable catalysts that has been widely used to catalyze dissociative chemisorption of molecular hydrogen. The hydrogen atoms then desorb from the metal surfaces under controlled conditions to attack other molecular species nearby to form hydrogenated products. This technique, known as hydrogen spillover, has been widely utilized in many applications since the 1960s.[1] The hydrogen bronze materials (e.g., H_xWO_3 and H_xMoO_3), potential hydrogenation catalysts, can be prepared via hydrogen spillover in the presence of a Pt catalyst.[2−4] However, the detailed mechanism of hydrogen bronze formation remains unclear. Recent studies by Yang and co-workers have shown that hydrogen atoms generated via dissociative chemisorption of hydrogen on Pt surfaces are capable of spillover onto carbon materials to form C−H bonds, giving rise to a significant storage capacity for hydrogen in these nanostructured materials.[5,6] The calculated adsorption energies of atomic hydrogen on carbon materials are reported to be in the range of 0.6−1.4 eV,[7−9] which is an order of magnitude higher than that of physisorbed molecular hydrogen.[10,11] The supported Pt catalyst plays a vital role as a source of hydrogen atoms upon dissociative chemisorption of H₂. It is hypothesized that the hydrogen atoms on the Pt catalyst can spill over to the receptor surface via diffusion across a physical "bridge".[12] Typically, the reported desorption energy of atomic hydrogen from a Pt single-crystal surface (as an atom, not as a dihydrogen) is approximately 2.65 eV,[13] significantly higher than the formation energy of the C−H bonds in these carbon materials. This of course would not facilitate spillover of atomic hydrogen from catalyst to the nanostructured carbons with favorable thermodynamics. The fact that hydrogen spillover does occur experimentally in materials such as MoO_3 and some carbon-based nanostructures suggests that the desorption energy of atomic hydrogen from the catalyst might be considerably smaller than what is reported in literature. As the first step to unravel the spillover mechanism, it is important to understand the desorption properties of atomic hydrogen on the Pt catalyst.

Theoretically, a Pt catalyst is often modeled with a single, pristine crystalline surface.[13−16] However, it has been shown that chemical reactivity of a gas species on the catalyst depends strongly on surface structures and defects of the catalyst structure. In a heterogeneous catalytic system, a catalyst is usually dispersed on support materials as nanoclusters and thus exhibits a wide variety of surface structures. Studies on the effect of coverage on the desorption energies of gas species are rare. Under typical catalytic conditions (i.e., high gas pressures), the surfaces of the catalyst are fully covered by gas species. As an alternative to the conventional theoretical approach to represent the surface of a catalyst with a single crystalline surface, we utilize a cluster model to describe the interplay between H₂ molecules and the Pt catalyst with the hypothesis that clusters with an appropriate size would be an excellent representation of catalyst particles. It has been shown that physicochemical properties of clusters can differ significantly from those of bulk materials.[17] Platinum clusters, in particular, have been widely studied mainly due to their importance in catalysis. A large number of structural variations of these clusters have been reported.[18−22] Unfortunately, theoretical studies based on quantum-mechanical first-principles have been primarily limited to clusters at subnano scale due to the computational complexity of dealing with a large number of d-electrons and increasingly complicated structural growth patterns.[23] In particular, studies on H₂ dissociative chemisorption on Ptₙ clusters have focused primarily on the dissociation of a single or just a few H₂ molecules on small subnano clusters.[24−30] To adequately address the cluster catalytic reactivity, however, it is very critical to understand the chemical behavior of the clusters that are saturated by H atoms since under typical catalytic hydrogenation conditions an adequate, generally high, H₂ pressure is maintained and the catalytic particles are always at or near a full saturation state. Unfortunately, to date, very little has been reported about the saturation effects on cluster catalytic reactivity.

Our purpose in the present study is not to deal with the cluster structural evolution itself; instead, we examine the reactivity of a selected Pt cluster structure toward dissociative chemisorption of molecular hydrogen using density functional theory. Our particular attention is placed on the effect of sequential dissociative chemisorption on the desorption properties of atomic hydrogen to gain insight into the spillover mechanism. Accordingly, we selected a Pt₆ cluster with an octahedral configuration to represent the catalyst and systematically examined the dissociative chemisorption of H₂ molecules on this cluster until

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the cluster is fully saturated with atomic hydrogen. We subsequently calculated the average H$_2$ dissociative chemisorption energies and the sequential desorption energies of H atoms followed by detailed analyses of electronic structures.

Computational Method

All calculations were performed using density functional theory under the generalized gradients approximation (GGA) with the Perdew−Wang's exchange-correlation functional (PW91)[31] as implemented in the DMol^3 package.[32] The spin-polarization scheme was employed throughout to deal with the electronically open-shell systems. A double numerical basis set augmented with polarization functions was utilized to describe the valence electrons with the core electrons described with an effective core potential, which also accounts for the relativistic effect that is important for heavy elements such as platinum. Full electron calculations were also performed for several selected Pt clusters previously,[23] and no significant differences in cluster structures, relative stability, and chemisorption energies were found. To avoid computational bias, the cluster and H$_2$ chemisorption geometries were fully optimized without imposing symmetry constraints until the energy is converged to less than 2×10^{-4} eV, the maximum force is less than 0.05 eV/Å and the maximum displacement is less than 0.005 Å. Population analysis was performed based on the Hirshfeld charge division scheme.[33] The Mulliken population distribution failed to give the correct direction of charge flow due to its indiscriminative division scheme to divide the charges at the middle of a bond.

The average chemisorption energy is evaluated from the calculated energies of cluster with adsorbate, E(Pt$_6$H$_n$), the bare cluster, E(Pt$_6$), and the H$_2$ molecule, E(H$_2$), using the following equation

$$\Delta E_{CE} = 2[E(Pt_6) + n/2E(H_2) - E(Pt_6H_n)]/n \quad (1)$$

where n is the number of H atoms on the cluster. We note that the average chemisorption energy is not the energy required to desorb an H atom from the cluster. In a realistic catalytic process, desorption of H atoms occurs from nearly fully saturated metal clusters. The release of the H atoms should be sequential rather than simultaneous. Understanding the desorption energy associated with the sequence is important to gain insight into the hydrogen spillover process since it provides the threshold desorption energy required for an H atom to leave the cluster. Accordingly, we define the sequential desorption energy per atom as

$$\Delta E_n = [E(Pt_6H_n) - E(Pt_6H_{n-2})]/2 - E(H) \quad (2)$$

where $E(H)$ is the energy of H atom and $n = 2, 4, 6$, etc. The threshold H desorption energy is defined as the desorption energy when the Pt$_6$ cluster is fully saturated.

A critical question here is in what circumstances the cluster can be viewed as fully saturated. Obviously, H$_2$ physisorption on the cluster should be ruled out since we are interested in desorption of only H atoms not H$_2$ molecules. Since H$_2$ chemisorption on the Pt$_6$ cluster always occurs before physisorption due to its favorable thermodynamics, we can readily identify whether the cluster reaches its saturation by performing ab initio molecular dynamics (MD) simulations to check if the MD run yields a physisorbed H$_2$ molecule. The MD simulations were performed at room temperature for typically 2 ps with a
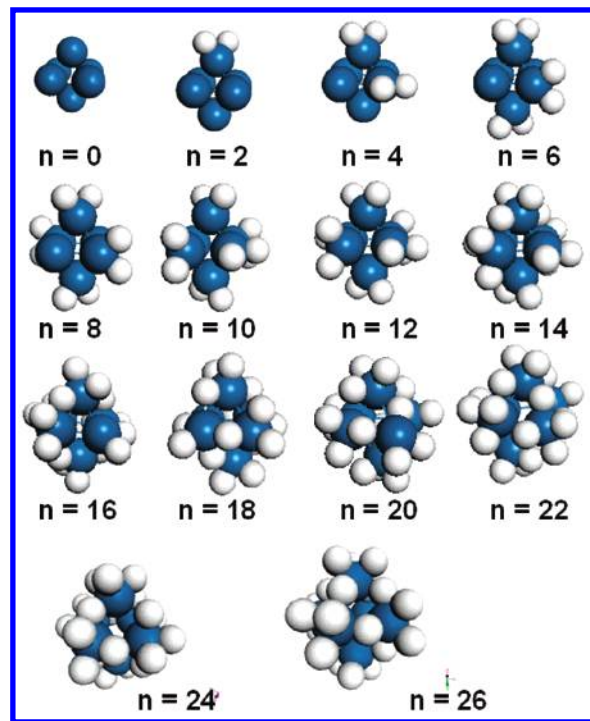

Figure 1. The optimized geometries of the bare Pt$_6$ cluster and Pt$_6$/H$_n$.

time step of 1 fs in a NVT canonical ensemble using the Nosé−Hoover chain[34] for temperature control.

Results and Discussion

The structures and energetic stability of various Pt clusters have been widely studied using both empirical and first principles methods. Gronbeck and co-workers[21] found that the planar structures are the most favorable for small Pt clusters in size of less than five atoms. In contrast, Fortunelli[18] found the lowest-lying isomer for the tetramer is a tetrahedron by using density functional theory (DFT) methods. In a recent DFT study, Nie et al. reported that the most stable structure of Pt$_6$ is an equilateral triangle.[28] However, a nearly degenerate configuration of octahedral geometry was also found. For larger Pt clusters containing icosahedral magic numbers, it is still being debated what structural configurations are energetically most favorable.[17−20] In the present study, we choose the octahedral Pt$_6$ as the cluster model since a 3-dimensional cluster is a more realistic representation of catalytic particles than a 2-dimensional structure. The optimized bare Pt$_6$ structure is shown in Figure 1. The calculated nearest neighbor Pt−Pt bond length in the cluster is 2.72 Å, about 0.06 Å shorter than in bulk platinum.

For dissociative chemisorption of H$_2$ on the chosen Pt cluster, there are three possible adsorption sites: 1-fold on-top, 2-fold edge, and 3-fold hollow site. Accordingly, we placed two H atoms on top of a Pt atom, on two neighboring edges and on two adjacent hollow sites, separately. Calculations of dissociative chemisorption of a H$_2$ molecule at these sites yielded chemisorption energies of 1.71, 1.50, and 1.31 eV, respectively, indicating that the on-top adsorption configuration is energetically most stable. A recent desorption experiment of H/D from a Pt$_{12}$ cluster, which was prepared in NaY zeolite, yielded an H$_2$ dissociative chemisorption energy of 1.36 eV.[30] The H atom was assumed to be adsorbed at the bridge site. Our results are consistent with the experimental observations. Our calculated H$_2$ dissociative chemisorption energies on the Pt$_6$ cluster are also nearly twice the values on a Pt(111) surface that are reported
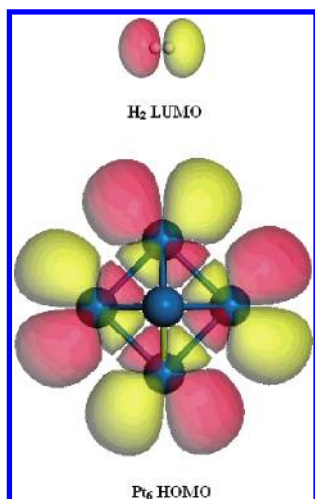
Figure 2. The calculated HOMO of the Pt$_6$ cluster and the LUMO of H$_2$.

to range from 0.70 to 0.83 eV.[13,35−37] The difference clearly indicates a finite size effect. Balasubramanian and co-workers reported the chemisorption energy of H$_2$ on smaller Pt$_2$ and Pt$_3$ clusters to be 0.93−1.33 eV using the multiconfiguration self-consistent field theory (MCSCF).[26,27] Okamoto reported a chemisorption energy of 1.4 eV for H$_2$ on the on-top sites of Pt$_{13}$ cluster using the DFT/GGA method.[28] Our calculated H$_2$ chemisorption energies are in a reasonable agreement with those reported values despite different computational methods used in these studies. The calculated Pt−H distance for the on-top adsorption configuration is 1.56 Å, also consistent with previous studies.[13,28] The H−H is well separated with a distance of 1.9−2.0 Å. The fully optimized structure is displayed in Figure 1.

The dissociative chemisorption of H$_2$ can be readily understood from the orbital interaction between the lowest-unoccupied molecular orbital (LUMO) of H$_2$ and the highest-occupied molecular orbital (HOMO) of the Pt$_6$ cluster. Figure 2 displays these two orbitals. The HOMO of the Pt$_6$ cluster consists of d orbitals from each of the atoms with a symmetry that matches well with the LUMO of H$_2$, which is an antibonding σ^* orbital. Charge transfer from the Pt$_6$ cluster to H$_2$ occurs upon H$_2$ interaction with the cluster due to the HOMO−LUMO overlap, leading to the dissociation of the molecule.

We next allowed additional H$_2$ molecules to undergo dissociative chemisorption on the Pt$_6$H$_2$ cluster. The H atoms first populate on the on-top sites with each Pt atom adsorbing two H atoms since chemisorption at these sites is energetically most favorable. Upon saturation of all the on-top sites at $n = 12$, the bridge sites, at which chemisorption of H is less stable than at the on-top sites but more stable than at the 3-fold face sites, could also be populated until $n = 24$. No H adsorption at the 3-fold face sites was found. At $n = 24$, the Pt$_6$ cluster appears to reach full saturation with atomic H. The Pt/H ratio at $n = 24$ is 1:4. Indeed, attaching two more H atoms to the Pt$_6$H$_{24}$ cluster yielded a H$_2$ molecule weakly bonded to the cluster upon running ab initio molecular dynamics simulation at room temperature for 2ps, suggesting that no more H atoms on the cluster can be accommodated. All the fully optimized chemisorption structures are displayed in Figure 1. Considerable structural distortion of the Pt$_6$ cluster from the original symmetric octahedral geometry was observed upon dissociative chemisorption of H$_2$. At a low H coverage, the bond lengths of H-bonded Pt−Pt are elongated by 0.05−0.2 Å, while the bond lengths of non-H-bonded Pt−Pt are shortened by 0.05−0.1 Å.

At a high H coverage, all Pt−Pt bond lengths are elongated by 0.01−0.3 Å since all Pt atoms are directly bonded with hydrogen atoms.

To show that all the H atoms are indeed chemisorbed and the cluster is fully saturated, we calculated the radial distribution functions (RDF) of the H−H bonds and H−Pt bonds for Pt$_6$H$_{24}$ and Pt$_6$H$_{26}$ using the trajectory files of the MD runs. The results are shown in Figure 3. For Pt$_6$H$_{24}$, the H−H distances on the cluster are well separated with the shortest distance around 1.8 Å. For Pt$_6$H$_{26}$, however, the shortest H−H distance in the cluster is about 0.75 Å, close to the gas-phase H−H bond distance in dihydrogen, indicating some physisorption character of molecular hydrogen in additional to hydrogen chemisorption. The results show that the Pt$_6$ cluster reaches its full saturation by H atoms at $n = 24$. The RDF of the H−Pt distance peaks at a very short distance of 1.6 Å, indicating strong hydride formation in these two clusters.

Upon sequential H$_2$ dissociative chemisorption, the average adsorption changes with the H atom coverage. Figure 4 displays the calculated average chemisorption energy vs the number of H atoms on the cluster. It shows that the chemisorption energy decreases monotonically with the H-atom coverage, indicating that as the H loading on the cluster increases the driving force for the cluster to dissociate H$_2$ decreases. At a low coverage, the chemisorption energy is nearly twice of the reported heats of adsorption determined from thermal desorption spectroscopy for the dissociative chemisorption of H$_2$ on the Pt(111) surface that range from 0.70 to 0.83 eV.[35−37] Only at full coverage do the calculated average chemisorption energies become comparable to the experimental heats of formation. It is understood that the experimental values here are for H$_2$ chemisorption on the Pt(111) surface and will vary at a different crystalline surface. The metal atoms in the cluster exhibit sharp corners and steps and thus are more exposed to H$_2$, leading to generally higher average adsorption energies even upon H saturation.

A central issue in heterogeneous catalysis is what would be the minimum energy required for the H atoms to desorb from the metal catalyst. We argue that, under typical catalytic conditions, this minimum energy, or more precisely, the threshold H desorption energy, is not the average desorption energy of H atoms. Instead, it should be the sequential H desorption energy, defined by eq 2, at the full cluster saturation. This is because desorption of an H atom from the cluster would generate an empty coordination site that is available to accommodate another atom resulting from H$_2$ dissociative chemisorption and, therefore, the metal clusters should always be in the fully saturated state under catalytic hydrogenation conditions. The calculated sequential H desorption energy is shown in Figure 5. Similar to the dissociative chemisorption, the calculated sequential H desorption energy decreases monotonically with the H coverage on the cluster, indicating that as the H loading on the cluster increases the cluster loses the catalytic reactivity. At full saturation, the calculated threshold H desorption energy is 2.44 eV, which is significantly lower than the average H desorption energy of 2.81 eV and the H desorption energy of 3.2 eV at low hydrogen coverage. Watari and co-workers performed local density functional theory (LDA) calculations on H adsorption on a Pt$_{13}$ cluster by placing the H atoms at the hollow sites, which were found to be the least favorable adsorption sites in our studies. They reported the H desorption energies of 2.9−4.5 eV at low coverages.[38] By consideration of the overbinding nature of LDA and the less favorable adsorption at the hollow sites, the reported H desorption energies might not be reliable.
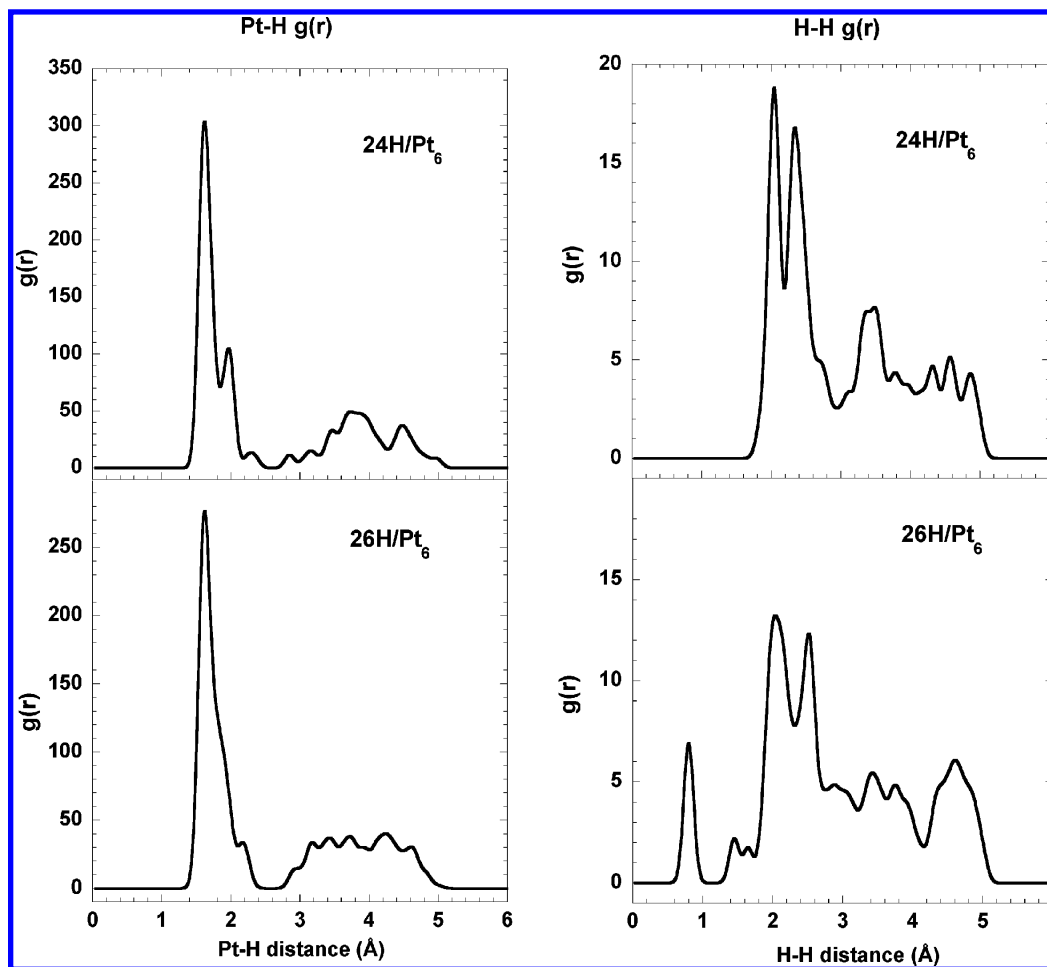
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Figure 3. The calculated radial distribution functions of Pt_6H_{24} and Pt_6H_{26}.
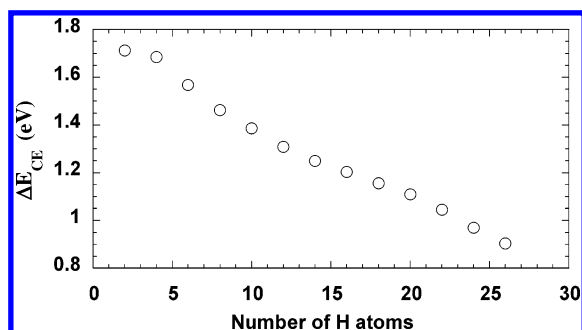

Figure 4. The calculated average dissociative chemisorption energy vs the number of H atoms on the cluster.
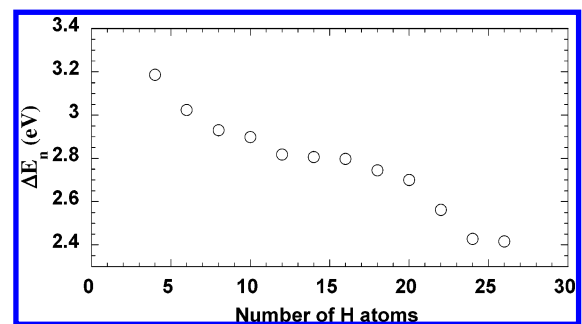

Figure 5. The calculated sequential H desorption energy per atom.

To understand the change of electronic structure of the Pt_6 cluster upon H₂ chemisorption, we further calculated the density of states of the electronic structure. The results are shown in Figure 6, where the Fermi level is shifted to zero and the main

components of atomic orbitals that contribute to the low-lying states are projected. For the bare Pt_6 cluster, the 6s orbitals contribute only slightly in the valence band, which is largely dominated by the d band. Upon H₂ dissociative chemisorption, contribution of the Pt d band to the valence band decreases with the H coverage, while contribution of the H 1s orbital to the valence band increases. In parallel, the d band component in the conduction band increases considerably. The change of the electronic structure suggests that the d electrons from the Pt_6 cluster are partially but sequentially ionized and the H atoms act as the charge acceptor. It is also noteworthy that the valence band and the conduction band become increasingly separated with the H coverage as the bonding nature in the cluster changes from the metal−metal bonding to more covalent metal hydride bonding. The last figure of Figure 6 corresponds to a structure similar to the fully saturated cluster except there is an additional H atom placed at the center of the Pt_6 cluster. The H atom at the center withdraws charges from the surrounding Pt atoms, making the 1s band of H at the far left of the density of states spectrum further down shift.

The partial, sequential charge transfer from the metal cluster to the H atoms is further confirmed from the Hirshfeld population analysis. Figure 7 displays the loss of charge from the Pt_6 cluster. Indeed, as the H coverage increases, more charge from the metal cluster is shared with the H atoms, consistent with the change of electronic structures shown in Figure 6. In particular, the average charge gained per H atom decreases with the H loading, reflecting the diminished capability of the metal cluster to adsorb H atoms as the cluster approaches saturation.
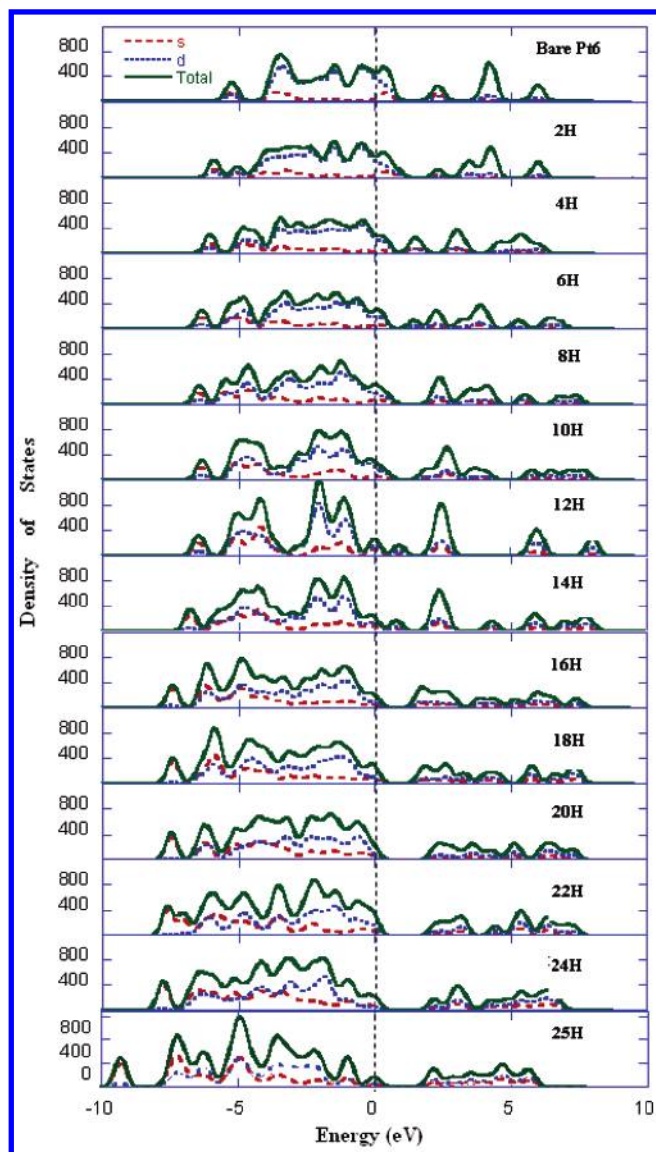
Figure 6. The calculated density of states of the bare Pt_6 cluster and Pt_6H_n. The green solid lines represent the total density of states. The red dashed and blue dotted lines represent the contribution from H 1s and Pt 5d bands, respectively.
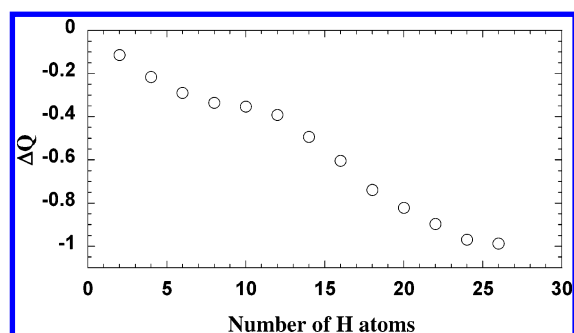

Figure 7. The calculated loss of the Hirshfeld charges of the Pt_6 cluster upon H_2 dissociative chemisorption.

The results highlight the role of Pt clusters as reservoir of electrons in hydrogenation/dehydrogenation reactions.

Summary

Supported platinum nanoclusters play an important role in many heterogeneous catalytic reactions. Detailed catalytic mechanisms of many of these reactions have not been well

understood at the atomic scale. In this paper, we attempt to address part of the catalytic processes of molecular hydrogenation by employing a small Pt subnano cluster as model to understand dissociative chemisorption of dihydrogen and the desorption of atomic hydrogen. While the effect of support on catalytic reactivity is believed to be secondary, the unsupported subnano Pt cluster allows us to study these reactions in details using the state-of-the-art computational method. Our ultimate purpose is to provide mechanistic understanding of the hydrogen spillover phenomenon, which is currently a subject of considerable debate.

We show that H_2 molecules can undergo sequential dissociative chemisorption of the selected Pt_6 cluster up to a Pt/H ratio of 1:4, at which point the cluster is fully saturated. The on-top sites were identified as the energetically most favorable adsorption sites followed by the bridge sites and then the 3-fold hollow sites. Our results indicate that the H_2 dissociative chemisorption is dictated by the charge transfer from the Pt cluster to H_2 molecules via $5d-1\sigma^*$ orbital overlap. The charge transfer increases with the H coverage, revealing the role of the Pt clusters in hydrogenation/dehydrogenation processes as an electron reservoir.

Unlike H_2 dissociative chemisorption on smooth, crystalline Pt surfaces, the reaction on the selected Pt_6 cluster is much more exothermic at a low H coverage with a calculated chemisorption energy nearly twice that on a Pt(111) surface. However, upon saturation of the cluster, the calculated dissociative chemisorption energy is only slightly higher than the value on a Pt(111) surface. This is an important finding because the surfaces of very small catalyst nanoparticles used in practice are not smooth; instead, they exhibit sharp corners, steps, defects, vacancies, etc. In fact, it is widely believed that the catalytic activity arises mainly from these surface defects. One thus expects that H_2 dissociative chemisorption energy and H desorption energy at these sites would differ significantly from those at smooth, low-index surfaces, depending on H coverage. Our results suggest that, under typical catalytic hydrogenation conditions, at which Pt nanoclusters are fully saturated by H atoms, the energetics associated with H_2 chemisorption and H desorption on highly exposed, sharp-cornered Pt clusters are similar to what was reported on a smooth Pt surface. We are currently studying the saturation effects on the activities of catalysts with various sizes of clusters.

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