# Influence of CO Poisoning on Hydrogen Chemisorption onto a Pt<sub>6</sub> Cluster

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We present a systematic study on the reactivity of a  $Pt_6$  cluster toward  $H_2$  dissociative chemisorption in the presence of CO molecules using density functional theory (DFT). The sequential adsorption and threshold desorption energies of H at varying CO coverage were identified. It was found that the main influence of CO molecules is to block the available active surface sites for  $H_2$  dissociative chemisorption. In addition, our population and density of states analysis indicate that the poisoning effect is partially due to the loss of Pt(5d) electrons upon CO adsorption. The hydrogenation of CO is found to be endothermic.

#### I. Introduction

Fuel cells convert chemical energy of a fuel into electricity directly with great efficiency and are one of the key technologies for enabling a hydrogen economy.<sup>1-3</sup> The cells produce power with minimal emission of pollutants by bypassing combustion. Carbon supported Pt-based nanoparticles are widely utilized as anode electrocatalysts due to their outstanding catalytic reactivity toward hydrogen dissociation and oxidation. However, carbon monoxide, which commonly exists in fuel gas, has long been recognized as a source of poison to the Pt-based electrocatalysts and can severely reduce the catalyst efficiency.<sup>4,5</sup> The poisoning effect is especially significant for fuel cells operating at relatively low temperatures, such as proton exchange membrane (PEM) fuel cells.<sup>5</sup> Hence, CO tolerance is of extreme importance in the development of PEM fuel cell anode catalysts since most reformate fuels contain a substantial amount of CO. Indeed, the presence of CO is one of the obstacles and is particularly challenging for the successful development of fuel cells. Unfortunately, hydrogen feed streams produced from steam reforming of methane, which is the dominant fuel source, followed by water gas shift reaction, commonly contain an appreciable amount of CO (0.5-2%). In order to avoid catastrophic poisoning of the fuel cell anode, CO concentrations generally need to be reduced.

The CO poison mechanisms have been extensively investigated experimentally and theoretically.<sup>5–17</sup> Several theoretical models, ranging from atomistic scale to macroscopic engineering scale, have been proposed. The general consensus is that CO molecules can bind more strongly than dissociating H atoms on Pt catalysts and thus block the available binding sites. The reported dissociative chemisorption energy of hydrogen on the Pt(111) surface, for example, is between 0.7 and 0.83 eV,<sup>18-20</sup> while the CO binding energy on the Pt(111) surface ranges from 1.49 to 1.8 eV.<sup>12,13</sup> Wanatabe and co-workers have concluded that each linear-adsorbed CO molecule on the Pt surface can block one H atom, while the bridge-bonded CO molecule can block more than one H site.<sup>9</sup> Very recently, Kumar et al.<sup>16</sup> studied and compared the adsorption strength of individual CO or H on Pt- and Co-doped Pt subnanoclusters using density functional theory (DFT) calculations. They specifically investigated the effect of Co doping on the Pt catalytic activity. These reported atomistic scale studies addressed only part of the poisoning mechanisms such as the relative reactivity of the Pt catalyst toward adsorption of a single CO molecule or H atom. The reactivity of the Pt cluster toward H<sub>2</sub> dissociative adsorption in the presence of CO and the interplay between CO and H species has not yet been systematically studied. In addition, most theoretical studies have employed single crystalline surface models at low coverage of CO or H species to represent the catalyst surfaces. However, it has been widely recognized that heterogeneous catalytic reactions usually take place at the more reactive sites such as defects, kinks, and steps.<sup>21–23</sup> Furthermore, Pt catalytic reactivity is coverage dependent<sup>24,25</sup> and, in a practical catalytic process, the Pt catalyst is usually fully covered by H atoms and/or CO molecules. In this paper, we attempt to quantitatively elucidate the poisoning mechanism of CO on a model Pt cluster. Computationally, rigorous quantum-mechanical modeling of chemistry on Pt catalyst nanoparticles with a realistic size is prohibitively difficult for the following reasons: (1) the catalyst nanoparticles usually contain thousands of atoms, (2) there are a large number of structural configurations for a

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given size of nanoparticles, and (3) there are numerous unpaired d-electrons in the nanoparticles. We thus chose a Pt<sub>6</sub> subnanocluster to represent the Pt catalyst. While such an unrealistically small cluster size may not adequately represent the detailed structures and properties of actual Pt catalyst nanoparticles, it does allow us to systematically perform DFT calculations on CO and H coadsorption at high coverage, which may mimic the catalytic process well enough to provide useful insight into the poisoning mechanisms. We also note that, based on our previous studies, some of the important chemical properties may not change drastically with the cluster size.<sup>24,25</sup> We show in the present study that the sequential H<sub>2</sub> dissociative chemisorption and H desorption energies are highly dependent on the coverage of CO and H and the catalyst poisoning arises from the loss of Pt(5d) electrons upon CO adsorption. In addition, we further investigated the feasibility of hydrogenating an adsorbed CO on the selected Pt<sub>6</sub> cluster.

### **II.** Computational Methods

All calculations were performed using density functional theory under the generalized gradient approximation with the revised Perdew-Burke-Ernzerhof (RPBE) exchange-correlation functional,<sup>26</sup> which has been shown to give accurate adsorption structure and energies for CO on Pt surfaces.<sup>27</sup> The spin-polarization scheme was employed throughout to deal with the unpaired electrons inherent to Pt clusters. 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 important for heavy elements such as platinum. To avoid computational bias, full geometry optimizations were performed without imposing symmetry constraints until the energy was converged to less than  $2 \times 10^{-4}$  eV. The tolerance of the maximum force was 0.05 eV/Å, and the maximum displacement was allowed to be less than 0.005 Å. Population analysis was performed based on the Hirshfeld charge division scheme.<sup>28</sup> The computational method used in the present study is implemented in the DMol<sup>3</sup> package.<sup>29,30</sup>

The average chemisorption energy of CO is evaluated using the following equation:

$$\Delta E_{\rm CO} = [E({\rm Pt}_6) + mE({\rm CO}) - E({\rm Pt}_6 m{\rm CO})]/m \qquad (1)$$

where *m* is the number of CO molecules and  $E(Pt_6)$ , E(CO), and  $E(Pt_6mCO)$  are the energies of the bare  $Pt_6$  cluster, single CO molecule, and  $Pt_6mCO$ , respectively. Similarly, the average chemisorption energy of H<sub>2</sub> in the presence of *m*CO molecules is defined as

$$\Delta E_{\rm H_2} = 2[E({\rm Pt}_6 m {\rm CO}) + (n/2)E({\rm H_2}) - E({\rm Pt}_6 m {\rm COH}_n)]/n$$
(2)

where *n* is the number of H atoms adsorbed on the cluster and  $E(H_2)$  is the energy of an H<sub>2</sub> molecule. In addition, understanding the desorption energy associated with the sequence is critical to gaining insight into the real catalytic process since the release of the H atoms should be sequential rather than simultaneous. We thus define the sequential desorption energy as

$$\Delta E_{\text{DE}} = E(\text{Pt}_6 m \text{COH}_{n-2}) + 2E(\text{H}) - E(\text{Pt}_6 m \text{COH}_n) \quad (3)$$

where E(H) is the energy of a H atom.

#### **III. Results and Discussion**

The structures and energetic stability of various small Pt clusters have been widely studied theoretically using both



**Figure 1.** Optimized structures of  $Pt_6$  clusters poisoned by *n*CO (*n* = 1-6).

empirical and first-principles methods. In the present study, we attempt to model the chemistry of a Pt nanoparticle with an octahedral subnano  $Pt_6$  cluster. The small  $Pt_6$  cluster provides a useful representation of the active sites such as sharp edges and corners, deemed to be essential in many realistic catalytic reactions.

For CO adsorption on the Pt<sub>6</sub> cluster, four possible adsorption modes were investigated: the on-top site (O), the 2-fold edge (E), the 3-fold hollow site (H), and the side-on configuration on the edge (L). Upon full geometry optimizations, the H and L modes were found to be unstable. In both cases, the CO molecule migrates to the on-top site. The CO bond lengths at the O and E modes are elongated by 0.04 and 0.03 Å, respectively, and the corresponding adsorption energies are 2.73 and 2.40 eV, indicating that the on-top adsorption configuration is energetically most favorable. We next allowed the Pt<sub>6</sub> cluster to be further poisoned sequentially by CO molecules. The CO molecules were placed on the on-top sites until all six Pt ontop sites are occupied, as shown in Figure 1. The Pt<sub>6</sub> structure remains nearly intact upon structural relaxation. The calculated CO bond distances are stretched by about 0.04–0.06 Å from the gas-phase value. According to the Blyholder model,<sup>31</sup> electrons are transferred from the  $CO(5\sigma)$  state into the Pt(5d) band and then back-donated from Pt(5d) to CO  $\pi^*$ -orbitals upon CO adsorption. Figure 2 displays the calculated projected density of states (PDOS) of the CO-poisoned Pt<sub>6</sub> cluster. In all cases shown in Figure 2, the calculations yield no unpaired electrons and thus the electronic structure of each system becomes closed shell. Figure 2 indicates that the Pt(5d) bands below the Fermi level are enhanced with CO loading on the cluster as the CO(5 $\sigma$ ) orbital donates electrons to the d-band. In parallel, the  $\pi^*$ -bands of CO molecules move downward roughly into the range between -6 and -8 eV upon receiving back-donation of d-electrons from the Pt<sub>6</sub> cluster. Based on the Hirshfeld charge analysis, the net result is that electron flow from Pt(5d) to CO  $\pi^*$ -orbitals dominates the binding process and the Pt\_6 cluster acts as an electron donor. The calculated electron loss per CO decreases monotonically as the CO loading increases. Correspondingly, the average binding energies also drop from 2.73 to 2.13 eV (see Table 1). The electron back-donation from the d-band of the Pt<sub>6</sub> cluster to the antibonding  $\pi^*$ -orbital of CO gives rise to a looser C-O bond and consequently the C-O bond length is elongated.

We next turn to the  $H_2$  chemisorption on  $Pt_6$  in the presence of CO. For convenience, we first choose the cluster with



**Density of States** 

Figure 2. Calculated density states of bare  $Pt_6$  cluster and  $Pt_6/nCO$  (n = 1-6).

TABLE 1: Calculated Adsorption Energies of CO and  $H_2$ on the  $Pt_6$  Cluster and Associated Electron Transfer

	Pt <sub>6</sub> /						
	1CO	2CO	3CO	4CO	5CO	6CO	H <sub>2</sub>
$\overline{E_{ad} (eV)}$ electron transfer	2.73	2.47	2.46	2.44	2.28	2.13	1.65
	0.107	0.158	0.176	0.199	0.213	0.239	0.10

adsorption of one CO molecule as an example to show CO poisoning effects on the sequential H2 dissociative chemisorption. It was found that the most favorable binding site for H<sub>2</sub> is also the on-top site; however, it has a chemisorption energy of 1.65 eV, which is much lower than that of CO. As expected, the stronger binding strength of CO leads to the preferential adsorption of CO over H<sub>2</sub>. Our previous study indicates that hydrogen adsorption on the Pt cluster is dictated by the overlap between Pt(5d) and H(1s) orbitals.<sup>24</sup> Pt also serves as an electron reservoir which transfers electrons to H atoms. It is thus expected that the charge transfer from Pt(5d) electron to H atoms upon CO poisoning is reduced, leading to the degradation of catalytic reactivity toward hydrogen chemisorption. Indeed, the calculated H adsorption energy on the Pt atom on which CO is adsorbed is considerably reduced by 0.4 eV, and the electron transfer from Pt<sub>6</sub> to the H atom is only 0.06 e, which is 0.04 e smaller than on the bare Pt<sub>6</sub> cluster. However, this weakening effect is localized and has little influence on H<sub>2</sub> adsorption at the other on-top sites. A transition state search shows the H<sub>2</sub> molecule can still readily dissociate on other on-top sites with an extremely low barrier of 0.05 eV with an adsorption energy that is nearly the same as for bare Pt<sub>6</sub> clusters. Furthermore, we note that the calculated CO and H<sub>2</sub> adsorption energies on the Pt<sub>6</sub> cluster are around 1.0 eV higher than the values on the Pt(111) surface at low coverage. The stronger bonding strength highlights the extraordinary reactivity of active sites on clusters.

Figure 3 shows the sequential  $H_2$  dissociative chemisorption on the  $Pt_6$  cluster poisoned by one CO molecule. At a low coverage, the H atoms, resulting from  $H_2$  dissociation, first populate on the on-top sites far from the CO molecule. After all on-top sites are filled, H atoms begin to occupy the less favorable sites (2-fold edges) until the cluster reaches its full adsorption capacity. To ensure that the cluster is really saturated, we performed ab initio molecular dynamics (MD) simulations for 2 ps at 300 K with a time step of 1 fs in the NVT canonical ensemble using the Nosé–Hoover chain thermostat.<sup>32</sup> As shown in the H–H distance distribution analysis (Figure 4), the H–H distances are well separated by at least 2.0 Å when 22 H atoms are chemisorbed. When two additional H atoms are introduced



**Figure 3.** Optimized structures of  $H_2$  sequential dissociative chemisorption on  $Pt_6$  cluster poisoned by one CO molecule.

into the system, a sharp peak at around 0.75 Å is observed, which corresponds to the formation of a H<sub>2</sub> molecule. Hence, the Pt<sub>6</sub> cluster can only accommodate 22 H atoms in the presence of one CO molecule. The calculated sequential H<sub>2</sub> dissociative chemisorption energy ( $E_{H_2}$ ) is shown in Figure 5(a1). It decreases monotonically as the H loading increases, indicating that the Pt<sub>6</sub> catalytic reactivity is coverage-dependent. Upon H saturation, the calculated average chemisorption energy drops to 0.94 eV, which is around 0.7 eV less than at low coverage.

The minimum energy required for desorption of H atoms is an important property that determines how easily the H atoms can be released from the catalyst. In a heterogeneous catalytic hydrogenation process, the surfaces of catalyst particles are always fully covered by H atoms at a given H<sub>2</sub> pressure. The desorption of an H atom from the cluster would make a site available to accommodate another atom resulting from H<sub>2</sub> dissociative chemisorption. Because the release of the H atoms is not simultaneous, the threshold H desorption energy is neither



**Figure 4.** Calculated H–H distance distribution g(r) for Pt<sub>6</sub>/1CO/H<sub>22</sub> and Pt<sub>6</sub>/1CO/H<sub>24</sub>, respectively.

the average desorption energy of H atoms nor the desorption energy at zero coverage. Instead, it is defined to be the sequential H desorption energy at full H coverage. As shown in Figure 5(b1), the calculated sequential H desorption energy ( $E_{DE}$ ) decays gradually from 3.15 eV at zero coverage to 2.45 eV at full coverage. This threshold H desorption energy in the presence of one CO molecule is considerably lower than the average desorption energy of 2.83 eV. Figure 5(c1) displays the sequential charge transfer from Pt<sub>6</sub> to H atoms. Again, the results clearly indicate that the  $Pt_6$  cluster serves as an electron donor for both CO and H. Similar to the calculated average chemisorption energies, the electron loss decreases monotonically as the H loading increases.

We now address the effects of higher loading of CO molecules sequentially adsorbed at the O sites on dissociative chemisorption of H<sub>2</sub> molecules. The calculated average H<sub>2</sub> dissociative chemisorption energies, the sequential H desorption energies, and the charge transfer are displayed in Figure 5. Like the case with only one CO adsorption, the general trend is that they all decline as the H coverage increases, except some fluctuation exhibited in the sequential H desorption energy due to the stable adsorption structure of the preceding cluster. At low H coverage, the dissociative chemisorption energies decrease as the CO coverage increases (from roughly 1.6 eV for Pt<sub>6</sub>/1CO to 1.27 eV for Pt<sub>6</sub>/6CO with two H atoms). However, at full H saturation, the calculated dissociative chemisorption energies vary in a very small range around 0.9 eV regardless of the amount of CO loading. A similar observation can also be made for the threshold H desorption energy, which ranges approximately between 2.4 and 2.5 eV. This result suggests that the H threshold desorption energy, an important catalytic property, may not be sensitive to the CO concentration in the hydrogen feed. We note that the calculated threshold  $H_2$ dissociative chemisorption energy and H desorption energy in the presence of CO molecules are similar to the corresponding values on small bare Pt clusters.<sup>24</sup> Furthermore, it is also interesting that the calculated H threshold desorption energies



Figure 5. (a) Calculated  $H_2$  dissociative chemisorption energy; (b) H desorption energy; (c) loss of Hirshfeld charges of Pt cluster vs H coverage.



**Figure 6.** Optimized structures of fully H-saturated  $Pt_6$  clusters poisoned by CO molecules.



Figure 7. Number of H atoms adsorbed vs number of CO molecules.

are roughly half the  $H_2$  formation energy (4.74 eV), indicating that recombination of H atoms to form  $H_2$  is thermochemically facile. The optimized structures of H-saturated  $Pt_6$  clusters at varying CO coverage are displayed in Figure 6.

Figure 7 displays the maximum number of H atoms that the  $Pt_6$  cluster can accommodate as a function of the number of adsorbed CO molecules. Each CO can roughly eliminate the chemisorption of one  $H_2$  molecule and thus leads to substantial degradation of the Pt catalyst performance. In light of the fact that the calculated  $H_2$  dissociative chemisorption and H desorption energies at full cluster saturation vary only in a small range regardless of CO loading, we can conclude that the main effect of CO poisoning is to physically block the binding sites for hydrogen. As shown in Figure 6, after poisoning by six CO molecules, the  $Pt_6$  cluster can only accommodate 12 H atoms. Compared to a clean cluster, which can accommodate up to 24 H atoms, the poisoned  $Pt_6$  cluster loses 50% catalytic efficiency.

It has been observed experimentally that the CO poisoning effect can be substantially reduced at high temperature. One possible mechanism would be that the H atoms residing near the poisoning sites on Pt surfaces could migrate from the metal atoms to attack the C atoms to form surface formaldehyde species, which subsequently desorb from the surface at a high temperature. To test this hypothesis, we investigated the hydrogenation of CO on the Pt<sub>6</sub> cluster. As shown in Figure 8, at low coverage, the first H<sub>2</sub> dissociative chemisorption reaction is energetically favorable with a reaction energy of 0.96 eV. However, the interplay between the C atom and H atoms is highly repulsive so that the diffusion of H atoms onto the C atom is nearly prohibited. This is partially because both C and H atoms are negatively charged. As a consequence, the formation of a formaldehyde molecule and then desorption from



the Pt<sub>6</sub> cluster requires 2.75 eV. The overall hydrogenation reaction is endothermic with an energy of 1.79 eV. At higher CO coverage, the Pt-CO bond strength is significantly weakened. Furthermore, the C atom interacting with Pt<sub>6</sub> becomes more reactive and is able to form a C-H covalent bond with the incoming H atom. Therefore, the CO hydrogenation reaction is promoted. On a  $Pt_6/6CO/H_{11}$  cluster, the chemisorption of two additional H atoms requires only 0.45 eV. MD simulations at 300 K indicate that one H atom can form a stable bond with the C atom to give rise to partial hydrogenation of CO. In addition, the second H atom can also readily diffuse onto the C atom. The formation of a formaldehyde molecule and desorption to the gas phase is found to be endothermic with a moderate reaction energy of 0.56 eV. Hence, the overall hydrogenation reaction energy is substantially reduced to 1.0 eV, around 0.8 eV lower than the value at low coverage.

#### **IV.** Conclusions

Platinum nanoclusters play a critical role in many heterogeneous catalytic reactions and in applications such as PEM fuel cell and hydrogen storage. However, catalyst poisoning by CO has been long recognized as one of the major obstacles to the progress and commercialization of these technologies. In this paper, we investigated part of the catalytic processes of molecular hydrogenation by employing a small Pt subnanocluster as a model to understand sequential H<sub>2</sub> chemisorption and H desorption in the presence of CO poisons. Our results indicate that each CO molecule can roughly exclude two H atoms on the Pt<sub>6</sub> cluster. The loss of Pt(5d) electron as well as the physically blocked binding sites upon CO poisoning leads to performance degradation of the Pt catalyst. The calculated dissociative H<sub>2</sub> chemisorption energy is dependent on both CO and H coverage, while the H threshold desorption energy does not appear to be sensitive to the CO concentration. CO hydrogenation on Pt<sub>6</sub> is found to be endothermic.

In practical applications, the challenge and the solution are not merely the removal of CO in the fuel source but also the selective removal of CO from the catalyst. Different CO mitigation techniques have been proposed such as the use of a Pt alloy catalyst and an increase in fuel cell operating temperature. Ideally, the designed new Pt alloy catalyst would have not only the preference for H adsorption but also possess a preferential catalytic reactivity toward CO oxidation. Alloying with a second metal such as Ru is a popular option to develop efficient CO-tolerant catalysts.<sup>4</sup> The second metal is designed to modify the electronic structure of the Pt-based catalysts in order to weaken the CO–catalyst interaction without significantly changing the H-catalyst interaction. In the present study, we focused on a pure Pt subnanocluster. Nevertheless, we expect that it can still provide some insights into the real catalytic process and help design improved Pt-based catalysts.

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