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High CO tolerance of Pt/Ru nanocatalyst: Insight from first principles calculations

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Density functional theory based calculations of the energetics of adsorption and diffusion of CO on Pt islets and on the Ru(0001) substrate show that the CO has the lowest adsorption energy at the center of the islet and its bonding increases as it moves to the edge of the island and further onto the substrate. Activation energy barriers for CO diffusion from the islet to the Ru surface are found to be lower than 0.3 eV making the process feasible and leading to the conclusion that this hydrogen oxidation catalyst is CO tolerant because of the spillover of CO from active Pt sites to the Ru substrate. The rate of CO oxidation by OH is found to be substantially enhanced when the former is adsorbed on the edge of Pt islands and the latter on nearby Ru sites. © 2009 American Institute of Physics. [DOI: [10.1063/1.3088843](https://doi.org/10.1063/1.3088843)]

I. INTRODUCTION

Fuel cells are clean energy conversion devices which can be used in a wide variety of applications. However, there are significant obstacles to their large scale implementations. For example, proton exchange membrane fuel cells (PEMFCs) operate with prereformed hydrogen, which is usually obtained from hydrocarbons and therefore inevitably contains carbon monoxide. Even small traces of CO remaining in the gas after purification poison the commonly used Pt anode by blocking its active site, thereby suppresses hydrogen oxidation. At the same time, in direct methanol fuel cells (DMFCs) the anode is used as a catalyst for both methanol reforming and for oxidation of the hydrogen so obtained. Although carbon monoxide released in the course of this reaction is supposed to be oxidized with OH obtained from admixed water, it still severely poisons the Pt anode. Both PEMFC and DMFC thus suffer from CO poisoning, which is a major impediment in the efficient use of these fuel cells.

It is known that alloying of Pt with a second (and even third) element may reduce this poisoning tendency. For instance, PtRu alloys are found to be more tolerant to CO than pure Pt.¹ Alloying Pt with Sn (Ref. 2) and Mo (Ref. 3) may improve the anode performance to some extent. However, these alloy anodes are also eventually affected by CO poisoning. Another disadvantage of these materials is high loading of expensive platinum. Not surprisingly the report that nanoclusters of Ru with submonolayer of Pt (PtRu₂₀) are much more tolerant to CO poisoning than commercial PtRu catalysts^{4,5} has been welcomed with optimism. It is also important that the content of Pt in these novel materials is much lower than that in PtRu alloys. From estimate of the average diameter of Ru nanoparticles (2.5 nm) and Pt/Ru ratio, the authors conclude that the deposited Pt forms small islands (islets) on the facets of the Ru nanoparticles. The mechanism underlying the high CO tolerance of these particular nano-

structures is yet to be understood, although attempts have been made to gain insight from related systems.^{6–8} For example, Koper *et al.*⁶ calculated from first principles CO adsorption energy $E_{ad}(\text{CO})$ on clean Pt(111) and Ru(0001) surfaces, as well as on a Pt monolayer on Ru(0001) and a Ru monolayer on Pt(111). Since $E_{ad}(\text{CO})$ is found to be the lowest for the case of a monolayer of Pt on Ru(0001) (Pt_{ML}/Ru(0001)), Koper *et al.*⁶ proposed it to be the rationale for high CO tolerance for this system. First principles study of alloying effects on CO adsorption on Pt^{7,8} suggests that strain induced by the second element modifies the electronic states of Pt in such a way that it causes a decrease in CO adsorption energy. Subsequent studies^{5–10} have also upheld the view that enhanced Pt tolerance to CO poisoning is associated with a decrease in $E_{ad}(\text{CO})$, as although reduction in $E_{ad}(\text{CO})$ implies removal of CO from Pt active sites. Note that E_{ad} for CO on these Pt surface alloys is still such that one expects CO to adsorb on the surface. In the case of Pt_{ML}/Ru(0001), in which only Pt atoms are exposed to the surface, CO removal can be achieved only through enhancement of CO desorption. Desorption rate R can be estimated using the transition state theory

$$R = D_0 e^{-\Delta E/kT}, \quad (1)$$

where D_0 is the prefactor and, for this particular process, $\Delta E = E_{ad}(\text{CO})$. Setting $D_0 = 10^{12} \text{ s}^{-1}$, which is a typical value for the prefactor $T = 350 \text{ K}$ (operation temperature for PEMFC) and taking $\Delta E = 1.11 \text{ eV}$ from Ref. 6, we obtain $R \approx 10^{-4} \text{ s}^{-1}$. The desorption rate is thus quite low for Pt_{ML}/Ru(0001) and it is expected to be even lower for other anodes because of higher $E_{ad}(\text{CO})$. Missing from this analysis is the consideration of CO diffusion rates which for anodes with inhomogeneous surfaces such as the PtRu₂₀ nanoparticles⁴ may be the main factor contributing to the CO removal from Pt sites. Spillover of CO from Pt islands to the Ru substrate is mentioned in Ref. 9 as a possible mechanism for the high CO tolerance, but the argument contrives to be

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based on the assumption of weakened CO adsorption. Weak adsorption, however, does not necessarily guarantee high spillover. Conclusion about efficiency of the CO spillover needs to be based on more direct information such as the magnitude of the activation energy barriers for CO diffusion in the system. One way of obtaining such information is through accurate first principles calculations of the system energetics based on density functional theory (DFT). In this work we have carried out such calculations of the energetics of adsorption and diffusion of CO on and off Pt nanoislands and the Ru(0001) substrate. Rationale for the obtained energetics is drawn from the calculated local densities of electronic states (LDOSs) of the systems. In Sec. II we provide some details of the computational method that we use. This is followed by results and discussion in Sec. III.

II. COMPUTATIONAL DETAILS

The first principles calculations reported in this paper have been carried out within the DFT^{11,12} using the plane wave pseudopotential method¹³ as embodied in the code VASP (Ref. 14) with ultrasoft pseudopotentials.¹⁵ To maintain periodicity of the systems we used supercell comprising of a 5 layer Ru(0001) slab with a four, seven, or nine Pt-atom islands on one side and a vacuum layer of 15 Å. All layers were allowed to relax. Most calculations also included the CO molecule adsorbed either on the island or on the Ru(0001) substrate. To diminish interaction between the periodic images of Pt islands, the supercell was extended along the (0001) surface making up the (4×4) superstructure. With such geometry the shortest distance between edges of neighboring Pt islands equaled two Ru–Ru bond lengths. The supercell thus contained 80 Ru atoms plus Pt atoms forming the island and a CO molecule. Brillouin zones were sampled with the $(3 \times 3 \times 1)$ Monkhorst–Pack k -point meshes.¹⁶ We used a kinetic energy cutoff of 400 eV for the wave functions and 700 eV for the charge density which provided sufficient computational accuracy for the oxygen containing structures. The Perdew–Wang¹⁷ generalized gradient approximation has been used for the exchange–correlation functional.

To achieve structural relaxation, a self-consistent electronic structure calculation was followed by calculation of the forces acting on each atom. Based on this information the atomic positions were optimized to obtain equilibrium geometric structures in which forces acting on atoms do not exceed 0.02 eV/Å.

III. RESULTS AND DISCUSSION

We present here the results for the seven-atom Pt islet on the Ru(0001) surface (7Pt/Ru(0001)). The Pt atoms in our model take the hcp hollow sites of Ru(0001) since such configuration has the lowest energy (although the difference from the configuration with Pt on the fcc sites is quite small: 0.09 eV). We have calculated the energies of CO adsorption (E_{ad}) on all nonequivalent sites of the system including the top of the central (c -Pt) and edge (e -Pt) platinum atoms and on two nonequivalent (fcc and hcp) hollow sites, as well as on the Ru substrate site neighboring the Pt islet (n -Ru) and the next neighbor Ru site (nn -Ru). In addition, activation

FIG. 1. (Color online) Schematic of energetics of CO diffusing from the center of Pt islet (c -Pt site) to its edge (e -Pt) and further to Ru substrate (n -Ru and nn -Ru sites). Large balls: blue (dark) and grey represent Pt and Ru, respectively, while small balls: red (dark), yellow, and smallest light blue ones denote O, C, and H, respectively. Negative and positive numbers correspond to CO adsorption energies and CO diffusion energy barriers, respectively.

energy barriers have been calculated for CO diffusion from c -Pt to e -Pt between two e -Pt (along the island edge) from e -Pt to n -Ru and from n -Ru to nn -Ru sites. Figure 1 shows the energetics calculated for the system with CO moving along the c -Pt– e -Pt– n -Ru– nn -Ru path.

As illustrated in Fig. 1, CO bonding increases as the molecule moves from the center of Pt island to its edge and further to the Ru(0001) substrate. This negative gradient of $E_{\text{ad}}(\text{CO})$ along the c -Pt– e -Pt– n -Ru– nn -Ru path already indicates that the CO molecule adsorbed on 7Pt/Ru(0001) would prefer to leave the islet for the Ru substrate. Furthermore, we find $E_{\text{ad}}(\text{CO}) = -1.94$ eV for CO on clean Ru(0001). This value is lower than those for CO adsorption on the n -Ru and nn -Ru sites suggesting that CO tends not only to leave the Pt islet but also move away from it.

The activation energy barrier for CO diffusion from c -Pt to e -Pt through the bridge site is found to be as low as 0.06 eV. The barriers for the rest of the considered path are also quite low. The highest n -Ru– nn -Ru barrier is 0.3 eV resulting in a diffusion rate of $R \approx 5 \times 10^7 \text{ s}^{-1}$ from Eq. (1) with $D_0 = 10^{12} \text{ s}^{-1}$ and $T = 350 \text{ K}$. Clearly, this rate is much higher than that for CO desorption. Furthermore, the potential energy surface for CO in the central region of the island is found to be quite flat: $E_{\text{ad}}(\text{CO})$ adsorption on the hcp hollow sites in the Pt island is only a few meV lower and on the fcc hollow site a few meV higher than that on c -Pt. This allows the molecule to move easily from c -Pt to e -Pt not only through the Pt–Pt bridges but also through the hollow sites, which increases its total rate of diffusion. We thus find the spillover of CO from Pt islets to Ru substrate to be a favorable process, which keeps active Pt sites available for hydrogen oxidation and hence provides high CO tolerance of the PtRu₂₀ nanostructure. Interestingly, we find CO bonding to the Pt island atoms to be significantly stronger than its bonding to Pt_{ML}/Ru(0001) [we obtain $E_{\text{ad}}(\text{CO}) = -1.15$ for Pt_{ML}/Ru(0001), which differs slightly from -1.08 eV reported in Ref. 6]. For the edge Pt atom it is even stronger than CO bonding to Pt(111) (-1.6 eV). Nevertheless, this system provides very efficient mechanism for CO removal from active Pt sites and this mechanism originates not from weak CO bonding to Pt atoms but from the negative adsorption energy gradient and low energy barriers for CO moving

from the center of Pt island to its edge and further to the Ru(0001) substrate. The calculations have also been performed for a four-atom Pt islet on Ru(0001) in which all Pt atoms belong to its edge. It is thus not surprising that the obtained $E_{\text{ad}}(\text{CO}) = -1.78$ eV is almost the same as for the edge Pt atoms in 7Pt/Ru(0001) (-1.76 eV). We can thus expect the same spillover scenario for smaller islands.

Since we consider here CO adsorption on a Pt-containing system, we should address the issue called by Feibelman *et al.*¹⁸ the “CO/Pt(111) puzzle.” As they noticed, DFT calculations suggest the Pt(111), Cu(111), and Rh(111) hcp hollow sites to be preferred for CO adsorption while experiments show preference for on-top adsorption. Subsequent DFT calculations with the revised Perdew-Burke-Ernzerhof exchange-correlation functional¹⁹ resulted in the correct (top) adsorption site for Rh(111). Grinberg *et al.*²⁰ find the error to originate mostly from the exchange-correlation approximations that overestimate CO binding to the hcp sites while the top sites adsorption is treated correctly. Kresse *et al.*²¹ suggest that such behavior is caused by the underestimation in DFT of the gap between the highest occupied and lowest unoccupied states of CO. In the present calculations, the CO binding energy is found to be much higher for the top *e*-Pt site than for the hollow sites, suggesting that for this system “the puzzle” is not in effect. This may be caused by significant modification of the Pt *d*-states as a result of their hybridization with the Ru *d*-states. Furthermore, the pathway for the CO spillover found in our calculations goes through the top adsorption sites for which DFT calculations are expected to be accurate.²⁰

The rationale for the hierarchy in the CO energetics presented in Fig. 1 may be traced to the LDOS of 7Pt/Ru(0001). Of course, it is impossible to express directly the total energy through LDOS within DFT because the energy also depends on the Hartree integral as well as the exchange-correlation potential and energy integrals.¹² However, some qualitative models appear to be quite useful for description of the CO adsorption on metal surface in terms of LDOS.

Indeed, as has been often discussed, hybridization between the *d*-electron states of surface atom and CO electronic states induces donation of electron density from the occupied bonding CO states to the metal atom and a back donation to the nonoccupied antibonding CO states, which form CO-metal chemical bond.^{22,23} This mechanism together with the Newns–Anderson model²⁴ has been utilized in the widely used *d*-band model.²⁵ The model is essentially based on the narrow *d*-band approximation and it works well in many cases when the band is really narrow (e.g., effects of step or kink in Pt surface on the CO adsorption energy²⁶). In the present case of Pt on Ru(0001), the hybridization of the wider Ru *d*-band with narrower Pt *d*-band enhances the Pt LDOS “tails” above the Fermi level and at the bottom of the band and reduces LDOS around Fermi level (see Figs. 2 and 3). On the other hand, since hybridization depends on energetic overlapping of the metal and molecule states, bonding within the “donation-back donation” mechanism^{22,23} has to be stronger if the density of the metal *d*-states around the Fermi level (E_F) is higher.

Our results confirm such correlation. On the other hand,

FIG. 2. Calculated Pt LDOS. Upper panel: surface atoms of Pt(111) (solid line) and Pt_{ML}/Ru(0001) (dashed line). Lower panel: *e*-Pt (solid line) and *c*-Pt (dashed line).

a visual analysis suggests that some correlation between the *d*-band center and E_{ad} also takes place. The highest absolute values of $E_{\text{ad}}(\text{CO})$ are found for the *n*-Ru and *nn*-Ru sites, which have high LDOS (>1 state/(atom eV)) from both sides of E_F (see Fig. 3). Both the absolute value of $E_{\text{ad}}(\text{CO})$ and LDOS at E_F (see Fig. 3) are much higher for Pt(111) than for Pt_{ML}/Ru(0001). Similarly, LDOS around E_F and $E_{\text{ad}}(\text{CO})$ correlates for the *e*-Pt and *c*-Pt sites in 7Pt/Ru(0001). We can thus conclude that for systems under consideration, LDOS around E_F controls the strength of the CO bonding to the surface.

Characteristics of Pt LDOS in 7Pt/Ru(0001) are mostly governed by the *d*-Pt–*d*-Pt and *d*-Pt–*d*-Ru hybridizations. The Ru *d*-band is wider and has more nonoccupied states than the Pt *d*-band. As a result, *d*-Pt–*d*-Ru hybridization redistributes Pt *d*-states into the region above E_F and reduces the average Pt LDOS. It is clear that this effect is stronger if the Pt site has more Ru neighbors. Another factor affecting the LDOS of Pt is the total number of nearest neighbors: the larger this number, the wider is the *d*-band. Interplay of the above factors results in a variety of shapes and magnitudes of Pt LDOS shown in Fig. 2. In Pt_{ML}/Ru(0001) *d*-states of each Pt atom hybridize with *d*-states of three Ru atoms and have

FIG. 3. LDOS calculated for *n*-Ru (upper panel) and *nn*-Ru (lower panel) sites.

FIG. 4. LDOS calculated for CO adsorbed on the *c*-Pt site.

as many as nine nearest neighbors. This makes the Pt *d*-band wide, LDOS low, and CO bonding relatively weak. The *e*-Pt atoms in 7Pt/Ru(0001) have only six nearest neighbors that make the *d*-band of *e*-Pt narrow and aligned to E_F . In addition, hybridization with three Ru neighbors increases the LDOS of *e*-Pt just above E_F . This causes strong CO bonding to the *e*-Pt sites. On the other hand, the *c*-Pt site has six Pt neighbors, just like Pt atoms in Pt_{ML}/Ru(0001). However, in contrast to the latter, all six are *e*-Pt atoms with the narrow *d*-band. As a result, the *c*-Pt site has both LDOS and $E_{ad}(\text{CO})$ intermediate between *e*-Pt and Pt_{ML}/Ru(0001).

For CO adsorbed on 7Pt/Ru(0001) we have also calculated the LDOS of the C, O, *c*-Pt, and *e*-Pt atoms. The three narrow low-energy maxima seen in Figs. 4 and 5 between -11 and -6 eV reflect strong *p*-C-*d*-Pt hybridization providing electronic charge donation from CO to Pt for CO adsorbed on both *c*-Pt and *e*-Pt. The main difference between the plots shown in Figs. 4 and 5 is found in the energy region closer to E_F . A broad structure of C *p*-states in this region resulting from *p*C-*d*Pt hybridization is found to be much

FIG. 5. LDOS calculated for CO adsorbed on the *e*-Pt site.

FIG. 6. (Color online) Three configurations of CO-OH coadsorption considered for estimating the rate of CO oxidation around the Pt island (see text). Red, small light blue, yellow, blue, and gray balls represent O, H, C, Pt, and Ru atoms, respectively.

more intensive for CO adsorbed on *e*-Pt than on *c*-Pt. Since these structures reflect the back donation of the electronic charge from Pt to CO, we conclude that as CO moves from *c*-Pt to *e*-Pt, the back donation is enhanced making CO bonding stronger.

The above conclusion that CO tends to diffuse from the center of Pt island to its edge and further to the Ru substrate begs the question: what happens to CO next? One of the options is CO electro-oxidation by OH. The latter can be obtained from water electrodecomposition on Ru with lower potential than on Pt.^{27,28} The rate of CO electro-oxidation by OH can be estimated using a simple model proposed by Nørskov and co-workers.^{29,30} This model is based on the observation that variation in the transition state energy closely follows the adsorption energy of the reaction products. As a result, for given temperature and electrode potential, the change in the electro-oxidation rate δR (due to variation in composition or geometry of the catalyst) can be estimated as $\delta R \sim \exp(-\delta E_{ad})$, where δE_{ad} is a change in the difference $E_{ad}(\text{OH}) - E_{ad}(\text{CO})$ of the adsorption energies of OH and CO. If the electrode potential $U=0$, then $\delta R = \exp(-\delta E_{ad})$.

We have estimated δR with respect to Pt(111) for the following coadsorption configurations: (1) CO on the *e*-Pt site and OH on the *n*-Ru site; (2) CO on *n*-Ru site and OH on the next *n*-Ru site; and (3) CO on *n*-Ru and OH on *nn*-Ru (Fig. 6). The corresponding calculated adsorption energies of CO and OH and the results of estimation of $(\delta)R$ for room temperature with $U=0$ are provided.

As seen from Table I, if CO is adsorbed on the edge of the Pt island and OH is located on the Ru neighbor to the island, the rate of electro-oxidation of CO by OH is estimated to be substantially higher than that on Pt(111). If CO leaves the Pt island for the Ru substrate, the rate is slightly higher than on Pt, although this difference may be within the errors of the model and the adsorption energy calculations.

In summary, the first principles studies presented in this paper show that a fine balance among the number of nearest neighbors, ratio of Pt and Ru neighbors, and *d*-band widths

TABLE I. Adsorption energies and CO oxidation rates calculated for configurations shown in Fig. 6.

Configuration	1	2	3	Pt(111)
$E_{ad}(\text{OH})$ (eV)	-3.01	-2.83	-2.85	-2.35
$E_{ad}(\text{CO})$ (eV)	-1.81	-1.76	-1.84	-1.38
$E_{ad}(\text{OH}) - E_{ad}(\text{CO})$ (eV)	-1.25	-1.02	-1.01	-0.97
δR	7.3×10^4	7.4	5.0	0

of Pt and Ru results in a unique pattern of LDOS in 7Pt/Ru(0001), which causes gradual strengthening of CO bonding along the c -Pt- e -Pt- n -Ru- nn -Ru path. Such a gradient together with low activation barriers for CO diffusion across the system provide favorable condition for CO spillover from Pt islands to Ru substrate. If CO reaches the island edge and meets OH adsorbed on Ru substrate just beside the island, CO oxidation can occur with rate much higher than that on Pt(111). If CO leaves the island for the Ru substrate and then meets OH, the oxidation may take place with the rate slightly higher than on Pt(111). This oxidation removes CO from the system making the catalyst free of CO poisoning.

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