CO Oxidation Process on Pt-M(111) Alloys (M = Ru, Sn): An *ab initio* Study

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Direct Methanol Fuel Cell (DMFC) have attracted attention in recent years because they are very energy-efficient. However, there is a serious problem in that Pt, which is the usual anode electrocatalyst, is poisoned by CO. Therefore, it is very important to develop new materials for use as electrocatalysts that exhibit good tolerance to CO. The aim of this study is to examine the mechanism of CO oxidation and of the CO+OH combination reactions in the CO oxidation process by calculating the adsorption energies and the activation barriers. In the case of Pt-Ru alloys, the activation barrier for the H2O dissociation reaction is almost the same as it is for pure Pt. The activation barrier for the CO+OH combination reaction on the Pt-Ru alloy is larger than that on pure Pt. Nevertheless, the adsorption energy of H2O is larger than that on pure Pt. On the other hand, the activation barrier and adsorption energies of H2O on the Pt-Sn alloy are very close to the corresponding values on pure Pt. Moreover, the activation barrier for the CO+OH combination reaction on the Pt-Sn alloy is lower than that on pure Pt.


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1. **Introduction**

The Direct Methanol Fuel Cell (DMFC) method is a potential candidate for replacing conventional batteries in cell phones and laptop PCs, because fuel cells can be made sufficiently small to realize full portability, although their output voltage is still low. From an applications stand-point, the main problem is still functionality. When pure Pt is used as the material for the anode electrocatalyst, functionality is reduced due to poisoning by CO, which arises from the oxidation of methanol. Recently, several experimental and theoretical studies have reported their work on counter-measures to prevent this degradation.1,2)

CO can be adsorbed on a pure Pt surface in a stable manner. This adsorbed CO can then be oxidized by OH from the dissociation of H2O, after which it is desorbed as CO2. Several groups have proposed the use of alloys as surface electrocatalysts in order to solve the problem of CO poisoning. Binary Pt alloys that include Ru and Sn as a second element show good properties in terms of CO tolerance.3,4)

Alloys in the Pt-Sn binary system initially show better properties in respect of CO tolerance than Pt-Ru alloys, but they have lower durability than Pt-Ru, and their properties become comparable to those of pure Pt after prolonged usage.5) Moreover, the Pt-Sn system does not exhibit activity for the oxidation of methanol, in contrast to Pt-Ru.6) On the other hand, Pt-Ru is stable and exhibits improved properties in terms of CO tolerance, so these alloys are becoming popular electrocatalyst materials for commodity applications. Morimoto *et al.* reported on the differences between the mechanisms for CO oxidation in the Pt-Sn and Pt-Ru systems by using a technique known as cyclic voltammetry.7) In the case of CO on a Pt (111) surface, adsorption on the top-site is favored over other sites such as the bridge-sites, but if the coverage is increased, CO can also be adsorbed on the bridge sites. This behavior has been observed by means of LEED.8) Morimoto *et al.* reported that only the CO peak on the top-site of Pt-Ru shifts to lower energy with respect to pure Pt, while only the peak for CO on the bridge-site of Pt-Sn shifts to lower energy. From these results, they insisted that a Pt-Sn surface promotes the oxidation of CO on the bridge-site, and that a Pt-Ru surface promotes the oxidation of CO on the top-site.

These experimental results suggest that Sn and Ru have different mechanisms for achieving improved CO tolerance. Therefore, it is important to answer the following question: “What is the origin of the different properties that are observed for Sn and Ru?”

Over the past two decades, theoretical approaches to the field of fuel cells have been important tools for investigating chemical reaction processes on electrocatalyst surfaces. Recently, Ishikawa and co-workers examined the oxidation process of methanol on pure Pt and on other transition metal surfaces by using first principles calculations, and then attempted to determine the reaction path.9) They reported that the dissociation of H2O is the rate-determining step in the anode process. Koper *et al.* also investigated differences in CO and OH adsorption for CO oxidation on pure Pt and on a Pt-Ru alloy by using a theoretical approach.10)

In the present study, we apply DFT calculations using a slab model to investigate accurate electronic structures for various electrocatalyst surfaces; this approach prevents the intrinsic errors due to size effects that are encountered when using cluster models.

In these discussions, we chose to use pure Pt, Pt-Ru, and Pt-Sn as the electrocatalyst surfaces. We then investigated theoretically the respective adsorption sites, the absorption energies and the reaction energies for the oxidation reactions of CO (which are the rate-determining step on the anode electrocatalyst during DMFC) in order to determine the total process. Moreover, we investigated and compared the origins and changes in these energies that are caused by alloying, and we discuss these issues as follows:

1) Why does the Pt-Ru alloy promote the oxidation of CO on
the top-site, whereas the Pt-Sn alloy promotes the oxidation of CO on the bridge-site?
(2) What are the differences in the electrocatalyst surfaces in terms of the dissociation process for H₂O and the activation barriers of the combination process between CO and OH?

2. Numerical Method

All of the calculations were performed using density functional theory, as implemented in the VASP code. The Kohn-Sham equation was obtained by a self-consistent approach. The core electrons and nuclei of the atoms were described by their ultrasoft pseudopotentials. The cutoff energy was 350 eV. The GGA PW91 function was used to describe the exchange correlation term. The electronic energies were calculated using a 5 × 5 × 1 k-point grid mesh. All of the calculations were performed using a 3 × 3 unit cell within a periodic boundary. Three kinds of 5-layer metal slabs were considered, including a (111) Pt surface, a Pt-Ru(2:1) alloy and a Pt-Sn(2:1) alloy; these slabs were separated by vacuum layers of about 11 Å in thickness. The lattice constants are 3.99 Å, 3.95 Å, and 4.03 Å, respectively. The corresponding experimental data for pure Pt, the Pt-Ru alloy, and the Pt-Sn alloy are 3.99 Å, 3.95 Å, and 4.03 Å, respectively.

The adsorption energies and geometric parameters for each adsorbate at various sites on pure Pt and on Pt-Ru and Pt-Sn alloys are listed in Table 1. Sites and angles are indicated in Fig. 1 and the most stable structures for various adsorbates are shown in Fig. 2. Table 2 lists the adsorption sites, and the dissociation, combination and activation barriers for the dissociation process of H₂O and the combination process between CO and OH.

3. Results and Discussion

The adsorption energies and geometric parameters for each adsorbate at various sites on pure Pt and on Pt-Ru and Pt-Sn alloys are listed in Table 1. Sites and angles are indicated in Fig. 1 and the most stable structures for various adsorbates are shown in Fig. 2. Table 2 lists the adsorption sites, and the dissociation, combination and activation barriers for the dissociation process of H₂O and the combination process between CO and OH.

3.1 CO

Other experimental groups have reported that the adsorption positions for CO can be both the top- and the bridge-sites. For CO on a Pt (111) surface, the top-site is favored over the bridge-site under low-coverage conditions, but if the coverage increases, CO can also be adsorbed on the bridge-sites: therefore, the top-site is favored over the bridge-site. However, our calculation method cannot reproduce and evaluate the adsorption sites and adsorption energy of CO, though other adsorbates can be properly evaluated. Many papers have been published to discuss this issue of why conventional DFT cannot predict the correct adsorption site. Therefore, in the present study, we cannot compare CO adsorption sites on the same surface, and we merely investigate differences in adsorption energies on the same adsorption site for different surfaces.

We would like to stress that the CO adsorption energy at the top-Sn site for the Pt-Sn alloy is quite low (0.04 eV), so we determine that CO almost fails to adsorb on the top-Sn site.

Shubina et al. reported that the adsorption energy of CO is 1.63 eV on the top-site, while it is 1.75 eV on the bridge-site for pure Pt. Our calculation results are in good agreement with the previous results obtained by using the slab model.

Koper et al. reported that the adsorption energy of CO is 1.27 eV on the top-Pt site and is 2.07 eV on the top-Ru site for the Pt-Ru alloy. In the present study, our results are in good agreement with the previous results. Liu et al. reported that the CO adsorption energy is 0.98 eV on the top-Pt site and is nearly zero on the top-Sn site when using the Pt₃Sn alloy. There is only a small discrepancy between the previous results and our present results. Our calculation results for the top-Pt site are within the range of the respective theoretical values from the previous reports, since we used Pt₃Sn as our Pt-Sn alloy in the present study. Moreover, we discovered that the adsorption energy is almost zero on the top-Sn site.

3.2 H₂O

From Table 1, the adsorption energy of H₂O is 0.22 eV on the top-Pt site for pure Pt. The adsorption energies on the top-M sites for the two different alloys are larger than the value for pure Pt. In particular, the Pt-Ru alloy exhibits a value that is three times larger than that of the top-Pt site for pure Pt. From these results, we can conclude that H₂O is more easily adsorbed on an alloy than on pure Pt, and especially on the top-M site.

Desai et al. reported that the adsorption energy of H₂O is 0.31 eV on the top-Pt site of pure Pt, whereas it is 0.35 eV on the top-Ru site of the Pt-Ru alloy. Our results are not in
good agreement with the previous paper in this instance, due to differences in the coverage rate. In the present study, we use a 1/9 coverage rate for the H$_2$O adsorbate, whereas the Desai group used 1/4 as the H$_2$O adsorbate coverage rate. Therefore, the distance between the H$_2$O adsorbates in the Desai et al. calculation is much smaller than it is under our calculation conditions. Their calculation conditions may arise when hydrogen bonds are formed between H$_2$O adsorbate, and these stabilize the adsorbates on the surface.

3.3 OH

The adsorption energies of OH on the top-M sites of the
alloys are much larger than that for the top-Pt site in the case of a Pt alloy. Therefore, we summarize that OH is absorbed on the top-M sites of the alloy surfaces. Koper et al. obtained OH adsorption energies of 2.31 eV on the top-site and of 2.24 eV on the bridge-site for pure Pt. Our calculation results fall within the ranges of their respective previous values.

### 3.4 COOH

In the case of the Pt-Ru alloy, the adsorption energy of COOH on the top-M site is larger than that of the other sites. On the other hand, the top-Pt sites for pure Pt and for the Pt-Sn alloy exhibit larger adsorption energies than those of the alternative sites. We deduce that the adsorption site for COOH is strongly affected by the adsorption sites for CO and OH, because COOH is synthesized by a combination between CO and OH. We conclude that OH can be adsorbed on the top-M site on a Pt-Ru alloy surface in preference to CO, since the adsorption energy of OH is much larger than that of CO. Therefore, we summarize that CO, which reacts with OH to synthesize COOH, can be adsorbed on the top-Pt and on the bridge-sites. Consequently, COOH is absorbed on the top-Pt site. This result, in which the COOH that arises from the combination of CO with OH is absorbed on the top-

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![Diagram](image)
Pt site, is in good agreement with the calculated results from the Desai group, which take account of the transition states.\textsuperscript{26}

3.5 H$_2$O dissociation process

The dissociation of H$_2$O is a reaction in which H$_2$O dissociates to form OH and H adsorbates. Tremendous theoretical effort has been focused on the dissociation of H$_2$O on Pt-based materials,\textsuperscript{27} because this reaction process is key to the realization of good electrocatalysts. From the above-mentioned adsorption energies, the top-M site is favored over the other sites in the case of H$_2$O and OH. Therefore, we estimated the dissociation and activation barriers for the H$_2$O dissociation process on the top-M site. Figure 3 shows the energy diagram of H$_2$O dissociation. And Table 2 summarizes these values, which are very similar to those for pure Pt and for the Pt-Ru and Pt-Sn alloys. In the case of the Pt-Ru alloy, we conclude that H$_2$O is more easily adsorbed on the alloy surface than on pure Pt from a comparison of their adsorption energies. If a large number of H$_2$O molecules are adsorbed on a surface, then a high concentration of OH exists on that surface. The activation barrier for the H$_2$O dissociation process is around 1.0 eV, which is too large for it to dissociate. Therefore, a large surface concentration of OH is advantageous for the oxidation of CO.

3.6 CO and OH combination process

The combination reaction of CO and OH is a process in which CO is oxidized by OH to synthesize a COOH adsorbate. We determined that the adsorption site for OH is the top-M site, and that the adsorption site for COOH is the top-Pt site for both the Pt-Ru and Pt-Sn alloys. From previous experimental results, we conclude that CO absorbs on both the top-Pt and the bridge sites. The combination and activation barriers for the combination process of CO and OH are listed in Table 2. And Figure 4 shows the energy diagram of CO and OH combination process. If CO is absorbed on the top-Pt site in the Pt-Ru alloy, then the activation barrier is larger than that for pure Pt. On the other hand, in the Pt-Sn case, the activation barrier is almost the same as that for pure Pt. If CO is absorbed on the bridge-site of the Pt-Ru alloy, then the activation barrier is larger than that for pure Pt. In the case of the Pt-Sn alloy, the activation barrier is smaller than that for pure Pt. From these results, we can point out that the combination reaction of CO and OH hardly occurs on the Pt-Ru alloy when compared with pure Pt. Meanwhile, the adsorption of CO on only the bridge-site of the Pt-Sn alloy promotes the oxidation and synthesis of COOH.

4. Conclusion

The adsorption and activation barriers for the reaction process in CO oxidation have been determined from first principles calculations. The theoretical approach predicts that H$_2$O is easily adsorbed on a Pt-Ru alloy, because the activation barrier for the H$_2$O dissociation reaction is almost the same as that for pure Pt. If H$_2$O can easily adsorb on the activation surface of the electrocatalyst, a large amount of OH (which is necessary for the oxidation of CO) can be produced. Consequently, the occurrence of this phenomenon at the Pt-Ru alloy surface improves its tolerance to CO poisoning. Meanwhile, the activation barrier for the combination process of CO and OH on a Pt-Ru alloy is larger than that for pure Pt.

On the other hand, the adsorption of CO on a bridge-site on the Pt-Sn surface can facilitate the combination reaction between CO and OH. The adsorption energy of H$_2$O is almost the same as it is for pure Pt. For this reason, Pt-Sn exhibits a high tolerance to CO poisoning. Our theoretical study to identify the most stable sites and the adsorption and reaction energies on pure Pt, Pt-Ru and Pt-Sn alloys has provided necessary information for understanding the CO oxidation process for various surfaces.

REFERENCES