— Article —

DFT Study for CO and H₂ Adsorption and Related Reactions on Pt alloy Electrode

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Received June 30, 2004 ; Accepted September 20, 2004

The density functional theory (DFT) calculation has been applied to investigate CO and H₂ adsorption onto Pt-Ru, Pt-Rh, Pt-Pd, Pt-Ag alloys as well as Pt metal modeled by Pt₅M_{10-x} (M = Ru, Rh, Pd, Ag, and x = 3, 5, 7) clusters. The most durable catalysts for CO poisoning were searched using the criteria that adsorption of CO should be weakened compared to pure Pt but adsorption of H₂ should not be weakened, or activation energy for the H-H bond fission is not increased. Pt₅Ru₅ and Pt₇Ru₃ were the best catalyst in conformity with many experimental works. Slab calculation showed that Pt is more localized in the surface layer than the bulk content in Pt-Ru alloy. Energy profiles calculated for the two reactions, CO + OH → COOH and H₂O → OH + H were compared between Pt and Pt-Ru alloy. No significant advantage for Pt-Ru alloy was found for the former reaction, but OH formation was more facile for the Ru site of Pt-Ru alloy.

Key Words : DFT Calculation, Pt-Ru Alloy, CO Poisoning, Shift Reaction

1 Introduction

Research on fuel cells has wide spectrum from basic laboratory experiments to practical uses in industrial plants. Coping CO poisoning is one of the most urgent problems, and Pt-Ru alloy has been thought as the best promising electrode. Many experimental works have been devoted to find the reasons improved by alloying.¹⁻⁴⁾ Gasteiger *et al.* pointed out surface enrichment of Pt atoms in Pt-Ru alloy.¹⁾ The alloying effects are so far interpreted in terms of ligand and bifunctional effects.²⁻³⁾ For methanol decomposition reaction, Watanabe and co-workers gave clear understanding that dehydrogenation occurs at Pt sites and oxidation of CO proceed at Ru sites with easily formed OH species.¹⁾ Another direction of challenge will be to find new alloy systems using cheaper elements, and such efforts are made continuously.⁵⁾

In an early work by Anderson and Grandscharova, they treated qualitative aspects on methanol oxidation on Pt-Ru alloy clusters by their modified extended Hückel method.⁶⁾ Recently a few much more elaborate calculations based on the periodic density functional theory (DFT) methods have been reported.^{5,7-9)} Strasser *et al.* investigated the third component in Pt-Ru-M alloy catalysts.⁵⁾ Other three papers dealt with the interactions between CO and OH in common.⁷⁻⁹⁾ We have examined adsorption of CO and H₂ for the thirteen binary alloy clusters modeling Pt-M alloys, (M = Ru, Rh, Pd, and Ag). Surface enrichment of one metal over the other is simulated by the slab model calculations. Furthermore energy

profiles are investigated for the two reactions, CO + OH → COOH and H₂O → OH + H between Pt and Pt-Ru alloy.

2 Methods and Models of Calculation

Pt₁₀ cluster modeling the local structure of (111) surface was used. It consists of seven atoms in the first layer and three atoms in the second layer. For alloys, the similar shape, *i.e.*, the same symmetry of clusters was employed by changing the nearest-neighbor distances. The nearest-neighbor distances are 2.65, 2.69, 2.75, 2.89, and 2.77 Å for Ru, Rh, Pd, Ag, and Pt, respectively, and the averaged values of 2.71, 2.73, 2.76, 2.83 Å are adopted for Pt₅Ru₅, Pt₅Rh₅, Pt₅Pd₅, Pt₅Ag₅ clusters, respectively. That is, the M₅N₅ (M, N = Ru, Rh, Pd, Ag, and Pt) clusters are built from Pt₁₀ cluster by uniform swelling or shrinking. For Pt₇M₃ and M₇Pt₃ clusters, the nearest-neighbor distance of major component metal is adopted without averaging. Although Rh, Pd, Ag, and Pt build the fcc lattice and Ru builds the hcp lattice, the local structures up to the second layer are the same except for a small difference of the nearest neighbor distance vs. interlayer spacing ratio, *i.e.*, $\sqrt{3}/\sqrt{2} = 1.225$ for fcc metals and $2a/c = 1.266$ for Ru, where *a* and *c* are the lattice constants. Therefore a common shape of clusters can be used. For each alloy represented by Pt-M, adsorption to the two different sites, *i.e.*, Pt and M sites was studied. For example, when the Pt site is considered, five or seven atoms in the first layer are set to Pt atoms as shown in Fig. 1. CO and H₂ molecules are adsorbed with

Fig. 1 Optimized structures for CO on Pt_5Ru_5 and H_2 on Pt_7Ru_3 clusters. ΔE is the adsorption energy, and the negative values mean stabilization.

the end-on and side-on configurations, respectively, to the on-top site on the central atom. Only the adsorbate was optimized and the structure of $\text{Pt}_x\text{M}_{10-x}$ clusters is fixed.

All the cluster calculations were carried out with Gaussian 98 program package.¹⁰⁾ The Becke three-parameter Lee-Yang-Parr hybrid functionals are employed.^{11–14)} The Los Alamos model core potential (MCP) are used for the transition metal atoms.¹⁵⁾ For Pt, the 1s through 4d atomic orbitals (AO's) are replaced by the MCP, and the 5s, 5p, 5d, 6s, 6p AO's are explicitly treated as the valence orbitals. For Ru, Rh, Pd, and Ag, the 4s, 4p, 4d, 5s, 5p AO's are explicitly treated. The valence orbitals are represented by the double zeta quality basis sets.¹⁶⁾

The DFT calculation with the periodic boundary condition has also been performed to examine which element is more localized in the surface layer. The plane wave based program Castep¹⁷⁾ was used together with the ultra-soft core potentials.¹⁸⁾ The kinetic energy cutoff was set to 240 eV. Four layer slab model was adopted, as shown in Fig. 2. For each Pt-M alloy, two types of unit cells, $\text{Pt}_2\text{M}_2\text{-Pt}_2\text{M}_2$ and $\text{M}_2\text{-Pt}_2\text{-Pt}_2\text{-M}_2$ are employed. Outer layers and inner layers correspond to the "surface" and "bulk" of alloys. The averaged lattice constants were adopted similar to the cluster models. For the direction perpendicular to the surface, each slab was separated by a vacuum region of 10 Å.

In the present calculation, the gas/solid interface model is employed instead of the liquid/solid interface. The electric field and electrode potential are not considered.

3 Results and Discussion

3.1 CO and H_2 adsorption onto alloy clusters

Figure 3 shows CO and H_2 adsorption energies for the pure Pt and thirteen models of alloys calculated in this work. For six systems, the energies of transition state (TS) structures for the H-H bond fission are also shown. The abscissa represents the alloy composition and adsorption site. For example, the models where molecule is

Fig. 2 $\text{Ru}_2\text{Pt}_2\text{Pt}_2\text{Ru}_2$ (top) and $\text{Pt}_2\text{Ru}_2\text{Ru}_2\text{Pt}_2$ (bottom) unit cell structures for slab calculation. Open and full circles represent Pt and Ru atoms, respectively.

Fig. 3 CO and H_2 adsorption energies to Pt_xM_y , Pt_xM_y , and Pt_3M_7 clusters. Full and open circles represent adsorption energies for CO and H_2 , respectively. Open triangles indicate the TS energies for H-H bond fission. Three horizontal dashed lines show those for Pt_{10} cluster. Vertical arrows indicate the alloy systems with smaller CO adsorption energies than that for Pt.

adsorbed to the Pt and Ru sites of the Pt-Ru alloy clusters are represented by Pt_5Ru_5 and Ru_5Pt_5 , respectively. Three horizontal lines show the energies of the local minima for CO and H_2 adsorption and of the TS for H_2 dissociation on pure Pt. Generally CO adsorption to metal surfaces is very strong. To reduce CO poisoning, the alloys with weaker interaction energy than pure Pt must be searched. On the other hand, adsorption of hydrogen molecule and the H-H bond fission on the alloy surfaces is an important elemental reaction of the fuel cell. We adopted three criteria to select CO durable catalyst: (1) CO adsorption energy must be smaller than that for pure Pt, and (2) H_2 adsorption energy must not be smaller than that for pure Pt, or (3) activation energy for the H-H bond fission must not be larger than that for pure Pt. Among the models, the six models, Pt_7Ru_3 , Pt_5Ru_5 , Pt_7Pd_3 , Pt_5Ag_3 , Ag_5Pt_5 , and Ag_7Pt_3 , satisfied the first criterion, which are designated by arrows in Fig. 3. Applying the second criterion, we found that the adsorption energies of H_2 are almost the same. Then we applied the third criterion instead of the second. All the four models,

Table 1 Total energies for plane wave DFT slab calculations with experimental surface tension values(σ).¹⁹⁾

	Pt ₂ -M ₂ -M ₂ -Pt ₂ ^a	M ₂ -Pt ₂ -Pt ₂ -M ₂ ^a	ΔE^b	σ (dyn cm)
Pt	—	—	0.00	1865
Ru	13316.80	13313.37	330.9	2250
Rh	-5322.65	-5321.03	-156.3	2000
Pd	-6095.45	-6095.15	-28.9	1500
Ag	-7007.61	-7008.02	+39.6	921

^aTotal energy for the slab models in eV unit.^bDifference energy between the two slab models in kJ mol⁻¹ unit.

Pt₇Ru₃, Pt₅Ru₅, Pt₇Pd₃, and Pt₇Ag₃, show smaller activation energy than that of pure Pt, whereas those for Ag₅Pt₅ and Ag₇Pt₃ are much larger than that of pure Pt. The reason is ascribed to an inert character of Ag metal, which also reduced the CO adsorption energy remarkably. Thus Ag-Pt alloy is eliminated from the candidate. Pt₅Ru₅ and Pt₇Ru₃ models show a reduction of CO adsorption energy and almost the same activation energy for the H-H bond fission compared to pure Pt. Besides the well known Pt₅Ru₅ and Pt₇Ru₃ systems, two promising systems are suggested by the present calculation. Pt₇Pd₃ and Pt₇Ag₃ also show both reductions of the CO adsorption energy and activation energy for the H-H bond fission.

3.2 Slab model calculation on surface concentration

Total energies of the slab models calculated by the plane wave DFT method were shown in Table 1. Negative values in the difference energy (ΔE) mean that the alloy configuration is more stabilized when the Pt atoms are located at the surface rather than bulk. We compare this quantity with experimental values of surface tension,¹⁹⁾ which are also tabulated. Ru and Rh have larger values of surface tension than Pt, and these metals tend to be localized in the bulk. Thus the calculated negative values of ΔE are consistent with an expectation by the surface tension. The positive values of ΔE are obtained for Pd and Ag. The ΔE for Ag is consistent with the sur-

face tension, but that for Pd is not. We think that other subtle factors not considered here are responsible for this discrepancy since the absolute value of ΔE and the difference between the surface tension are the smallest among the four alloys.

The slab model calculation for Pt-Ru alloy suggests that Pt atoms are more localized in the surface layer, and local configurations like Pt₇Ru₃ and Pt₅Ru₅ clusters are more often realized than that like Ru₅Pt₅ cluster, which have been suggested by experimental papers.¹⁾ Second consequence is less probability of appearance for the Pt₇Ag₃ model since Ag metal has larger trend to be localized in the surface layer. However if the configuration like Pt₇Ag₃ is stabilized at the alloy surface, such a site is expected to show a good performance. Finally the present calculation suggests that Pt₇Pd₃ model is easily realized from the view point of surface localization, and shows a performance similar to pure Pt metal.

3.3 Reaction of CO with H₂O

Adsorbed CO is assumed to be removed through interactions with H₂O or OH. If the alloying effects work to promote CO desorption, the activation barrier is expected to be lower than that for pure Pt. Reaction mechanisms between CO and two H₂O molecules are compared among Pt₁₀, Pt₅Ru₅, and Ru₅Pt₅ clusters. Figure 4 shows the optimized structures for reactant and transition state (TS) on Pt₁₀ clusters, and similar structures are obtained for Pt₅Ru₅ and Ru₅Pt₅ clusters. Configuration for the reactant is Pt₁₀(CO)(H₂O), whereas that for the TS is Pt₁₀(COOH)(H₃O). So for the energetics, the energy of isolated H₂O is added to that of the reactant. Activation energies for the TS measured from the corresponding reactant are evaluated 74, 85, and 133 kJ mol⁻¹ for Pt₁₀, Pt₅Ru₅, and Ru₅Pt₅, respectively. Both energies are considered almost the same between Pt₁₀ and Pt₅Ru₅, and the superiority of Pt₅Ru₅ to Pt₁₀ is not obtained. This is not so surprising result since so-called ligand effects by alloying are known to be the secondary importance, as reported by experimental works.³⁾ However, the activation energy for Ru₅Pt₅ is much larger, this means that CO adsorption at the Ru atom site is not favorable to process the shift type

Fig. 4 Reactant and TS structures for the shift reaction with Pt₁₀ cluster. In the reactant, CO and H₂O are adsorbed, and the energy of free H₂O is added for comparison. In the TS, COOH + H₃O complex is formed.

Fig. 5 Reactant and TS structures for OH formation with Ru_5Pt_5 cluster. In the reactant, two H_2O molecules are adsorbed at the center and edge atoms. In the TS, OH species is going to be formed, but another H_2O molecule also releases H atom to Pt atom of the cluster.

reaction, in consistent with the larger adsorption energy of CO to the Ru site of Pt-Ru cluster. (See Fig. 3.)

3. 4 OH formation from H_2O

Another reaction relating the removal of CO is formation of OH species. Although Ru atom has smaller probability exposed on the surface, as mention above, certain area of the surface is even covered by Ru atoms. Figure 5 shows the optimized structures for reactant and TS on Pt_{10} and Ru_5Pt_5 clusters with the configurations of Pt_5M_5 (H_2O)₂. Activation energies for the TS measured from the corresponding reactant are evaluated to be 91 and 64 kJ/mol for Pt_{10} and Ru_5Pt_5 clusters, respectively. The smaller activation energy is consistent with facile formation of OH species at the Ru atom site on Pt-Ru alloy. Since all the calculations are carried out in the gas/solid interface, *i.e.*, without the solvent effects, the oxonium ion is not calculated to be a stable product. Therefore, in the TS structures, the H_2O molecule which accepts H atom, again releases other H atom to the surface metal atom. We think this reaction mechanism is also reasonable. When the solvation effects are taken into account, the H-Pt bond will be easily cleaved, and the H atom will be released as the oxonium ion.

4 Conclusion

In this article, CO durable electrode catalysts were searched from computational chemistry. Among the four alloys, Pt-Ru, Pt-Rh, Pt-Pd, Pt-Ag, the calculation suggested Pt_7Ru_3 , Pt_5Ru_5 , and Pt_7Ag_3 as promising candidates. Pt_7Ru_3 and Pt_5Ru_5 confirmed that Pt-Ru was the best catalyst so far with respect to smaller CO adsorption energy and similar H_2 dissociation energy compared to pure Pt. The periodic slab calculation reproduced that Pt atoms are enriched in the surface layer of Pt-Ru alloy, and similarly Ag atoms are enriched in the surface layer of Pt-Ag alloy. If the configuration of Pt_7Ag_3 is stabilized even partially at the Pt-Ag alloy surface, this can also be a good candidate. The energetics of so-called shift reaction and OH formation are compared among the Pt_{10} , Pt_5Ru_5 , and Ru_5Pt_5 clusters and between the Pt_{10} and Ru_5Pt_5 clusters, respectively. Activation energies for the former reaction

are almost the same between Pt_{10} , and Pt_5Ru_5 , but they are considerably smaller than that for Ru_5Pt_5 . On the other hand, for the OH formation, the activation energy on the Ru_5Pt_5 cluster is 27 kJ/mol smaller than that on the Pt_{10} cluster, which is consistent with the trend as expected by experiments.⁴⁾ Thus, the calculated results are in good agreement with the experimental finding that the major role of Ru atom is thought to facilitate the formation of OH species.

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