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Effects of Alloyed Metal on the Catalysis Activity of Pt for Ethanol Partial Oxidation: Adsorption and Dehydrogenation on Pt₃M (M=Pt, Ru, Sn, Re, Rh, and Pd)

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Abstract

The adsorption and dehydrogenation reactions of ethanol over bimetallic clusters, Pt₃M (M = Pt, Ru, Sn, Re, Rh, and Pd), have been extensively investigated with density functional theory. Both the α -hydrogen and hydroxyl adsorptions on Pt as well as on the alloyed transition metal M sites of PtM were considered as initial reaction steps. The adsorptions of ethanol on Pt and M sites of some PtM via the α -hydrogen were well established. Although the α -hydrogen adsorption on Pt site is weaker than the hydroxyl, the potential energy profiles show that the dehydrogenation via the α -hydrogen path has much lower energy barrier than that via the hydroxyl path. Generally for the α -hydrogen path the adsorption is a rate-determining-step because of rather low dehydrogenation barrier for the α -hydrogen adsorption complex (thermodynamic control), while the hydroxyl path is determined by its dehydrogenation step (kinetic control). The effects of alloyed metal on the catalysis activity of Pt for ethanol partial oxidation, including adsorption energy, energy barrier, electronic structure, and eventually rate constant were discussed. Among all of the alloyed metals only Sn enhances the rate constant of the dehydrogenation via the α -hydrogen path on the Pt site of Pt₃Sn as compared with Pt alone, which interprets why the PtSn is the most active to the oxidation of ethanol.

Keywords

Ethanol electro-oxidation reaction; bimetallic catalyst; ligand effect; bifunctional mechanism; thermodynamic and kinetic control

1. Introduction

In the recent years, direct ethanol fuel cell (DEFC), a promising alternative power source, is attracting much attention because of much less toxic than methanol, natural available and renewable. In addition, DEFC theoretically provides an attractive mass energy density, 8.1 kW·h/kg, which is much greater than that of 0.42 kW·h/kg for hydrogen fuel cell (H₂ 1.5 wt % storage) and that of 6.1 kW·h/kg for direct methanol fuel cell.¹

However, on the other hand, ethanol is difficult to be completely oxidized because the C–C bond cleavage needs to overcome a quite high energy barrier that leads to a poor cell performance. Thus, it has been a challenge to find an efficient electro-catalyst to increase the

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Supporting Information Available: Figure S1–S6 display the optimized geometries for all of the involved systems. This material is available free of charge via the Internet at <http://pubs.acs.org>.

electro-reactivity of ethanol. There have been a few review papers on the recent progress on the electro-catalysts for DEFC.^{2–4} Pt-based alloy catalysts have been recognized to better catalyze the oxidation of ethanol than Pt alone. Of the Pt-based alloy catalysts PtM (M=Ru, Sn, Ir, Bi, Pd, Ru, Rh, etc.), PtSn/C (the bimetallic deposited on carbon materials) is the most active toward the ethanol electro-oxidation reaction (EER) with increasing current density and decreasing the onset potential of ethanol oxidation by approximately 0.2 V compared to Pt alone.^{1, 5–8} However, the experimental result shows that ethanol is not completely oxidized to CO₂ at the PtSn/C anode yet,⁽⁹⁾ because the oxidation products are measured to be acetaldehyde, acetic acid, and CO₂ by the percentages of 22.8%, 74.7%, and 2.5%, respectively.

The bi-functional mechanism proposed by Watanabe and Motoo^{10,11} has been widely applied to interpret the enhancement of EER on Pt-based alloys, where the dissociative adsorption of ethanol occurs on Pt sites while the other metal primarily promotes adsorption and dissociation of water to form OH for oxidizing the intermediates from ethanol decomposition.^{12,13} Other researchers suggested rather similar mechanisms for the EER.^{2,8,14} Although some interesting assumptions have been made, several essential issues still remain uncertain. For example, for water dissociative adsorption although Re is more active than Sn and Ru has similar activity to Sn,^{17,19} PtRu/Re is not as active as PtSn to the EER.¹³ Thus, Sn should have other effects like ligand and electronic structure that promote the EER on PtSn. Otherwise, PtRu/Re should display almost the same activity as PtSn.

Consequently, it is very important to further understand the electro-catalytic enhancement of Pt-based alloys in order to design more efficient catalysts for the EER. The essential problem is to investigate the behavior of the adsorption and dissociation of both water and ethanol on the Pt-based alloy catalysts at a molecular level. The mechanism of the adsorption and decomposition of water on Pt-based alloys has been investigated theoretically with the density functional theory (DFT).^{15–19} It was established that Ru, Re and Sn sites of PtM (M=Ru, Re, and Sn) are more active to water decomposition than Pt sites. There are a few articles referring to the electro-catalytic mechanism of ethanol on pure Pt metal and Pt-M bimetallic alloys,^{20–23} which employed periodic, plane-wave expansion PW91 DFT method. They mainly concentrated on the bond cleavages of ethanol, initiated by the hydroxyl adsorption complex of ethanol on platinum atom. To the best of our knowledge, there are few reports on the adsorptions of ethanol over PtM through -CH₂,²¹ not to mention the detailed mechanism for the consequent bond cleavages. In addition, there is lack of understanding about the ligand effect of the alloyed metal M on the activity of Pt to the EER.

In the present paper, we focus on the reaction mechanism of the initial adsorption and dehydrogenation steps of ethanol on Pt₃M (M=Pt, Ru, Sn, Re, Rh, Pd) through both α -hydrogen atom and hydroxyl group approaching the Pt and M atoms of Pt₃M. The adsorption complex and the dehydrogenation transition state of each reaction pathway will be clarified in detail by the density functional theory. The calculated results will elucidate the most favorable adsorption and dehydrogenation reaction pathway of ethanol on each bimetallic catalysts as well as the ligand effects of the alloyed metal, and eventually provide a new understanding about the mechanism by which the alloying of Sn most effectively enhances the electro-catalytic activity of Pt for the EER.

2. Computational Methodology

Tetrahedral Pt₃M (M=Pt, Ru, Sn, Re, Rh, and Pd) was applied to model sub-nanoscale particle catalysts. The geometric parameters of the ethanol adsorption complexes on Pt₃M have been fully optimized with the B3PW91 density functional theory^{24,25} as implemented

in Gaussian 03.²⁶ The LANL2DZ type of effective core potential (ECP) and the corresponding double- ξ basis set were employed for all of the involved metal atoms,²⁷ while the basis sets for H, C and O are 6-311++G(d, p).²⁸ Spin multiplicities for the predicted ground electronic state of Pt₃M for M = Pt, Ru, Sn, Re, Rh, and Pd are 3, 5, 3, 8, 4, and 3, respectively. The transition states (TS) for dehydrogenations of the adsorbed ethanol were directly searched for by the eigenvector following with the Berny algorithm.²⁹ Frequency analysis for Pt₃M-ethanol system was done at the same level as optimization for all stationary points to characterize the stationary points and make the zero point energy (ZPE) corrections. The dissociation transition state (TS) structures of adsorbed ethanol were confirmed by the vibrational mode with a unique imaginary frequency. Ethanol adsorption energy (E_{ads}) was defined as the difference between the energy of the adsorption complex and the energy summation of the cluster at ground state and ethanol, $E_{\text{ads}} = E(\text{CH}_3\text{CH}_2\text{OH-Pt}_n\text{M in ground state}) - [E(\text{CH}_3\text{CH}_2\text{OH}) + E(\text{Pt}_n\text{M in ground state})]$. The more negative E_{ads} , the stronger the ethanol adsorbs on the PtM. The energy barrier (E_a) and the dissociation energy (E_{diss}) refer to the energies of transition state and the dehydrogenation product relative to the adsorption complex, respectively.

3. Results and Discussion

Figures 1–6 display the potential energy profiles of C₂H₅OH+Pt₃M (M=Pt, Ru, Sn, Re, Rh, and Pd) including ZPE correction. The optimized geometries of all stationary points of the six reaction systems are summarized in Figures S1-S6 of Supporting Material. Adsorption energy (E_{ads}), dissociation energy (E_{diss}), energy barrier (E_a), and imaginary frequency (ν/cm^{-1}) of transition state for all reaction channels of C₂H₅OH + Pt₃M (M=Pt, Ru, Sn, Re, Rh, and Pd) are listed in Table 1.

Pt₄ + CH₃CH₂OH

Two kinds of adsorption of ethanol on the metallic cluster Pt₄ are shown in Figure 1. The first one is α -hydrogen adsorption, for which CH₃CH₂OH is adsorbed via the α -hydrogen atom (H_α) on Pt. The distances of H_α -Pt and C_α -Pt are predicted to be 1.829 and 2.516 Å, respectively. The adsorption energy is -0.37 eV relative to the separated Pt₄ and CH₃CH₂OH. The dehydrogenation from this adsorption complex (Pt₄-a) to the product (Pt₄-a-p) can take place via a atop transition state (Pt₄-a-ts). At the TS, the H_α -C $_\alpha$ bond elongates to 1.432 Å and the C_α -Pt and H_α -Pt are shortened to 1.599 and 2.245 Å, respectively. The imaginary frequency of this transition state is $i605\text{ cm}^{-1}$. The relative energy of the transition state (Pt₄-a-ts) is -0.35 eV, only slightly higher than Pt₄-a by 0.02 eV, which shows that the dehydrogenation readily occur once ethanol is adsorbed via the H_α . The product complex (Pt₄-a-p) is rather stable because of its significantly lower energy of -1.19 eV relative to the reactants. Figure 1 shows that the adsorption/dehydrogenation process initiated by the H_α is rather favorable in both kinetics and thermodynamics.

Hydroxyl group of CH₃CH₂OH approaches to Pt atoms to form another adsorption complex (Pt₄-b). The O-Pt distance of complex Pt₄-b is 2.207 Å and the adsorption energy is -0.66 eV, more stable than the H_α adsorption by 0.29 eV (E_{ads} : -0.66 vs -0.37 eV). The ethanol adsorption on Pt(111) through the hydroxyl was widely discussed elsewhere. The predicted O-Pt adsorption bond lengths on Pt(111) are 2.56 and 2.65 Å by Alcalá et al.²⁰ and Wang et al.²², respectively, with adsorption energies, -0.28^{20,21} and -0.18²² eV, much lower than that on the cluster Pt₄. Two dehydrogenation processes from Pt₄-b are predicted, one passing through a four-membered ring transition state (Pt₄-b1-ts, bridge) and another one through a three-membered ring transition state (Pt₄-b2-ts, atop). Their energies are above the reactants by 0.41 and 0.16 eV, respectively. Although the energies of the corresponding dehydrogenation products (Pt₄-b1-p and Pt₄-b2-p) are lower than or close to that of Pt₄-b, these processes are not easy to occur kinetically because of their much higher

dehydrogenation barriers as compared with the α -hydrogen adsorption channel. This basically follows the conclusion reached by Alcalá et al for the EER on Pt(111) that the lowest energy pathway for the formation of acetaldehyde is via the C-H $_{\alpha}$ bond cleavage.²¹

Pt₃Ru + CH₃CH₂OH

Both the α -hydrogen and hydroxyl adsorptions on Pt as well as Ru of Pt₃Ru were located, as shown in Figure 2. The bond lengths of H $_{\alpha}$ -Pt (1.838 Å) and C $_{\alpha}$ -Pt (2.600 Å) of Pt₃Ru-a are very close to those at Pt₄-a, while the adsorption energy, -0.28 eV, is less than that of Pt₄-a by 0.09 eV due to the replacement of Pt with Ru (E_{ads} : -0.28 vs -0.37 eV). The C $_{\alpha}$ -H $_{\alpha}$ breaking via atop transition state Pt₃Ru-a-ts is similar to that of Pt₄, but the dehydrogenation barrier is 0.12 eV, higher than the barrier of Pt₄-a-ts by 0.1 eV. This shows that the alloying of Ru is not able to enhance H $_{\alpha}$ adsorption, and cannot promote the subsequent dehydrogenation on Pt site of PtRu as well.

As for Pt₃Ru-b, the adsorption through the α -hydrogen on Ru is almost the same as that of Pt₃Ru-a in terms of the adsorption energy and dehydrogenation energy barrier. The distance of H $_{\alpha}$ -Ru at Pt₃Ru-b is slightly longer than that of H $_{\alpha}$ -Pt on Pt₃Ru-a, while C $_{\alpha}$ -Ru is slightly shorter than that of Pt₃Ru-a. The dehydrogenation transition state (Pt₃Ru-b-ts) of Pt₃Ru-b also has a similar structure to Pt₃Ru-a-ts. The bond lengths of H $_{\alpha}$ -Ru, C $_{\alpha}$ -Ru, and C $_{\alpha}$ -H $_{\alpha}$ at Pt₃Ru-b-ts are 1.633, 2.139, and 1.467 Å, respectively. The relative energy of Pt₃Ru-b-ts is -0.14 eV and the dehydrogenation barrier is 0.15 eV, only slightly higher than that of Pt₃Ru-a-ts by only 0.03 eV. Both dehydrogenation products (Pt₃Ru-a-p and Pt₃Ru-b-p) also have the same dissociation energy (E_{diss} : -0.75 eV). In spite of no enhancement as compared with Pt₄, the adsorption/dehydrogenation reactions on Pt and Ru sites of PtRu may also readily proceed spontaneously.

Another two adsorption complexes are Pt₃Ru-c and Pt₃Ru-d formed by the hydroxyl approaching the Pt and Ru atoms of the Pt₃Ru cluster, respectively. The respective adsorption energies on Pt and Ru sites are -0.61 eV and -0.59 eV, with O-Pt and O-Ru of 2.220 and 2.261 Å. In the dehydrogenation processes, the relative energies of the transition states are predicted to be 0.42 and 0.20 eV for Pt₃Ru-c-ts and Pt₃Ru-d-ts, respectively. Because of much higher reaction barriers of these two transition states compared with the H $_{\alpha}$ adsorption transition states, the dehydrogenation reactions of the hydroxyl adsorption complexes cannot be able to compete with the α -hydrogen adsorption processes.

Pt₃Sn + CH₃CH₂OH

It can be seen from Figure 3 that α -H is only adsorbed on the Pt site of Pt₃Sn, and the stable adsorption on the Sn site was not located. The stable α -hydrogen adsorption complex (Pt₃Sn-a) is formed by the H $_{\alpha}$ atom approaching one Pt atom. At Pt₃Sn-a, the distances of H $_{\alpha}$ -Pt and C $_{\alpha}$ -Pt are 1.813 and 2.558 Å, respectively, rather close to the corresponding values at Pt₄-a and Pt₃Ru-a. However, due to the alloying of Sn, the adsorption becomes slightly stronger with adsorption energy of -0.44 eV. Following Pt₃Sn-a, the dehydrogenation takes place via a atop transition state, Pt₃Sn-a-ts with a similar structure to Pt₄-a-ts and Pt₃Ru-a-ts and an energy barrier of 0.14 eV, and the dehydrogenation product (Pt₃Sn-a-p) lies below the reactants by 0.49 eV. The low energy processes, the adsorption and dehydrogenation reactions, are also expected to occur spontaneously.

The hydroxyl of CH₃CH₂OH can be adsorbed on both the Pt and Sn sites of Pt₃Sn readily. The adsorption complexes, Pt₃Sn-b and Pt₃Sn-c, are formed by the O atom approaching Pt and Sn atoms, respectively, with the O-Pt(Sn) distance of 2.189 (2.689) Å. From Figure 3, the adsorption energies of Pt₃Sn-b and Pt₃Sn-c are almost the same, -0.84 and -0.85 eV. Compared with Pt alone, the stronger binding on the Pt site of PtSn indicates that the

adsorption of hydroxyl on the Pt is also enhanced by the alloying of Sn. However, on the other hand, one can see that the transition states of the dehydrogenation processes of the adsorption complexes are above the reactants by 0.39 and 0.28 eV for Pt₃Sn-b-ts and Pt₃Sn-c-ts, respectively, resulting in the reaction barriers greater than 1.1 eV, which are considerably higher than that for the process through C-H_α cleavage on the Pt site of PtSn. Thus, the contribution of the Pt₃Sn-b and Pt₃Sn-c to the dehydrogenation may be negligible compared to Pt₃Sn-a. The alloying of Sn does not alter the favorable pathway, and the lowest energy pathway for the EER on PtSn is the C-H_α cleavage on the Pt site.

Pt₃Re + CH₃CH₂OH

The energy profile of the Pt₃Re + CH₃CH₂OH reaction system is displayed in Figure 4. Similar to PtRu, the α-hydrogen of CH₃CH₂OH can also be adsorbed on both Pt and Re sites to form complexes, Pt₃Re-a and Pt₃Re-b, respectively. For Pt₃Re-a, the adsorption energy is −0.35 eV and its dehydrogenation transition state, Pt₃Re-a-ts, has lower energy than the reactants by 0.19 eV. The small barrier of 0.16 eV, indicates that the dehydrogenation can also occur readily as in the above three PtM systems. However, the adsorption/dehydrogenation process of the α-hydrogen on Re site appears to be a higher energetic process. The adsorption energy of the complex, Pt₃Re-b, is only −0.12 eV and its dehydrogenation transition states, Pt₃Re-b1-ts (atop) and Pt₃Re-b2-ts (bridge), are 0.34 and 0.37 eV in energy over the reactants, respectively. Compared with the adsorption/dehydrogenation process of the α-hydrogen on the Pt site, the dehydrogenation of the α-hydrogen over the Re site can be negligible.

The adsorption energies of the hydroxyl adsorbed on Re and Pt sites are −0.83 and −0.71 eV, respectively, forming the complexes Pt₃Re-d and Pt₃Re-c. The two dehydrogenation channels via atop (Re) and bridge (Pt-Re) were located for Pt₃Re-d. The atop transition state, Pt₃Re-d1-ts, has the energy of 0.16 eV relative to the reactants and the barrier is approximately 1.00 eV. However, the transition state Pt₃Re-d2-ts, a four membered ring transition state for the bridge path has rather low energy of −0.58 eV relative to the reactants and the barrier is only 0.25 eV, which is rather similar to that of the α-hydrogen cleavage on the Pt site. The close energy barriers indicate that the two paths are quite competitive. Similar to the hydroxyl adsorption on Pt site of other PtM, the dehydrogenation of Pt₃Re-c is very difficult to take place because of its high dehydrogenation barrier of 1.16 eV.

Pt₃Rh + CH₃CH₂OH

Similar to the case of Pt₃Sn, the α-hydrogen adsorption complex on Rh site of Pt₃Rh cannot be located with the B3PW1 method, as shown in Figure 5A. For the complex (Pt₃Rh-a) due to the adsorption of α-hydrogen on the Pt site, the adsorption energy is −0.29 eV, and the dehydrogenation barrier is only 0.15 eV. The adsorption energies of hydroxyl on the Rh and Pt sites of PtRh are −0.53 eV and −0.60 eV, weaker than that on Pt₄. The dehydrogenation from the hydroxyl adsorption complexes again needs to overcome the high barriers of 1.08 eV through all of the transition states, Pt₃Rh-b1-ts, Pt₃Rh-b2-ts and Pt₃Rh-c-ts. Thus, the adsorption/dehydrogenation reaction of CH₃CH₂OH on Pt₃Rh via the α-hydrogen adsorption on Pt atom and then dehydrogenation via Pt₃Rh-a-ts is still a favorable path.

Pt₃Pd + CH₃CH₂OH

Figure 5B exhibits the potential energy profiles of CH₃CH₂OH on Pt₃Pd. Similar to Pt₃Re and Pt₃Ru, ethanol can be adsorbed on the Pt and Pd sites via α-hydrogen atom and hydroxyl group. For the α-hydrogen adsorptions on the Pt and Pd sites of PtPd, the adsorption energies are −0.37 eV and −0.18 eV for the complexes Pt₃Pd-a and Pt₃Pd-b, respectively. The dehydrogenation barrier from Pt₃Pd-a is only 0.08 eV, while the barrier for the Pt₃Pd-b dehydrogenation is high to 0.65 eV. Although the adsorption energies for the

hydroxyl complexes (Pt₃Pd-c and Pt₃Pd-d) are again higher than those of both Pt₃Pd-a and Pt₃Pd-b, the hydroxyl adsorption processes have too high dehydrogenation barriers to overcome.

According to above discussions, for the bimetallics Pt₃M (M=Sn, Rh, and Pd) one can see that the dominant reaction pathways for the initial dehydrogenation of ethanol are predicted to be α -hydrogen pathways on the Pt site rather than the hydroxyl process. However, for Pt₃Ru the α -hydrogen dehydrogenations on Ru and Pt sites have almost the same adsorption energy and barrier, yet less favorable than on Pt alone. The dehydrogenation of hydroxyl on Re site of Pt₃Re has only a slight higher barrier than the α -hydrogen on Pt site of Pt₃Re (0.25 vs. 0.16 eV). Thus, the two paths may be competitive in the Pt₃Re catalyzed reaction.

Ligand effect of alloyed atoms

As discussed above, the alloyed atoms M of PtM may affect properties of the adsorption and dehydrogenation of α -hydrogen and hydroxyl on Pt, which are summarized in Figure 6. It can be seen that from Figure 6A, compared with Pt₄, the alloying of Sn enhances the adsorption on Pt site of Pt₃Sn for both the α -H and hydroxyl of ethanol, which favors dehydrogenation rate. The adsorption of the α -H on the Sn site of Pt₃Sn is unstable, and the adsorption of the hydroxyl group on the Sn site of Pt₃Sn is similar to that on the Pt site. Re alloying slightly enhances the adsorption of the hydroxyl on the Pt site, but it does not favor the adsorption of the α -H. Ru and Rh decrease both adsorptions on the Pt site of PtRu/Rh; however, alloying of Pd does not affect the adsorptions on the Pt site of PtPd.

According to Figure 6B, for all of the investigated metals the dehydrogenation barriers for the α -H adsorption complex (bottom) are much lower than those for the hydroxyl adsorption complexes (top). For the kinetically favorable path, as compared with Pt₄ only Pd has a similar barrier, and others have higher barrier than Pt₄. The effect of metal alloying in Pt will be further thoroughly explored with a larger cluster model.

The above adsorption and dehydrogenation mechanisms of ethanol on the surface of Pt-based alloy can be represented by the reaction scheme:

E is ethanol and -M- is the surface of the alloy, while A- and H- are the decomposition products of ethanol. On the basis of the steady state approximation, the overall rate constant for the generation of the adsorbed product can be expressed as

$$k = \frac{k_2 k_1}{k_{-1} + k_2} = \frac{K k_2}{1 + k_2/k_{-1}} \quad (1)$$

where k_1 and k_{-1} are the adsorption and desorption reaction rate constants, and k_2 is the reaction rate constant for the decomposition, and $K (= k_1/k_{-1})$ is the adsorption equilibrium constant. For the α -H dehydrogenation path since k_2 is much higher than k_{-1} , then the entire rate can be approximated as $k = K k_{-1}$. Because it is difficult to calculate k_1 and k_{-1} , we can use the adsorption equilibrium constant K to approximately represent the reaction

processing. The adsorption equilibrium constants (K) can be calculated by statistical thermodynamical partition functions of Pt_3M , $\text{CH}_3\text{CH}_2\text{OH}$ and adsorption complex:

$$K = \frac{Q_{\text{complex}}}{Q_{\text{Pt}_3\text{M}} Q_{\text{C}_2\text{H}_5\text{OH}}} \exp\left(-\frac{E_{\text{ads}}}{RT}\right) \quad (2)$$

Here, Q_{complex} , $Q_{\text{Pt}_3\text{M}}$ and $Q_{\text{C}_2\text{H}_5\text{OH}}$ are partition functions, for which the translation and rotation partition functions of both Pt_3M and adsorption complex are excluded because of their solid characteristic; E_{ads} is adsorption energy, T is temperature; R is gas constant. As shown by Figure 6(C), the adsorption equilibrium constant of the Pt_3Sn system is greater than those of others by over one order of magnitude. This means that tin exhibits positive ligand effect and is the most favorable ligand atoms for the adsorption and dehydrogenation reactions of the Pt based alloy to ethanol. This interprets why the PtSn is the most active to the oxidation of ethanol.

Molecular orbital analysis

In order to analyze the interaction of ethanol molecule with the bimetallic catalysts, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are drawn in Figure 7 with Mulliken atomic charges. It is known that the hydroxyl of ethanol binds to Pt through the lone electron pair of the oxygen. Figure 7 reveals that HOMO's phase of ethanol matches well with the LUMO of all of investigated Pt_3M ($\text{M}=\text{Pt}$, Ru , Sn , Re , Rh , Pd). Thus, the hydroxyl of ethanol has stable adsorptions on all of the investigated metallic sites. The unstable adsorptions for the α -hydrogen of ethanol on the sites of Sn of Pt_3Sn and Rh site of Pt_3Rh can also be revealed from the HOMO plots. Although the HOMOs have considerable distribution adjacent to Pt sites, Ru of Pt_3Ru , Re of Pt_3Re , and Pd of Pt_3Pd , minor electron density on the Sn and Rh sites is found. Thus, the α -hydrogen adsorption complexes were not located on the Sn site of PtSn and Rh site of PtRh .

Figure 8 shows the frontier molecular orbital energy levels of ethanol and Pt_3M ($\text{M}=\text{Pt}$, Ru , Sn , Re , Rh , Pd). It can be seen that, because the bimetallic models have very close HOMOs and LUMOs energies, they should have similar interactions with ethanol to form adsorption complexes. However, the best interaction may happen between ethanol and Pt_3Sn since the energy differences of $E(\text{LUMO}, \text{Pt}_3\text{Sn})-E(\text{HOMO}, \text{ethanol})$ and $E(\text{LUMO}, \text{ethanol})-E(\text{HOMO}, \text{Pt}_3\text{Sn})$ are the smallest.

4. Conclusion

With DFT theory, the adsorption and dehydrogenation of ethanol over bimetallic clusters, Pt_3M ($\text{M} = \text{Pt}$, Ru , Sn , Re , Rh , and Pd), initiated by α -hydrogen and hydroxyl adsorptions have been extensively investigated. The adsorptions of ethanol on Pt and M sites of some PtM via the α -hydrogen were well established. Although the α -hydrogen adsorption on Pt site is weaker than the hydroxyl, the potential energy profiles show that the dehydrogenation via the α -hydrogen path has much lower energy barrier than that via the hydroxyl path. Generally for the α -hydrogen path the adsorption is a rate-determining-step because of rather low energy barrier for the α -hydrogen adsorption complex (thermodynamically control), while the hydroxyl path is determined by its dehydrogenation step (kinetically control). Among all of the alloyed metal only Sn enhances the rate constant of the dehydrogenation via the α -hydrogen path on the Pt site of Pt_3Sn as compared with Pt alone, which interprets why the PtSn is the most active to the oxidation of ethanol.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Potential energy profile for the adsorption and dehydrogenation of $\text{CH}_3\text{CH}_2\text{OH}$ on Pt_4 , with B3PW91 including ZPE. The red line refers to the α -H pathway.

Figure 2. Potential energy profile for the adsorption and dehydrogenation of $\text{CH}_3\text{CH}_2\text{OH}$ on Pt_3Ru , with B3PW91 including ZPE. The red lines refer to the α -H pathways on both Pt and Ru sites.

Figure 3. Potential energy profile for the adsorption and dehydrogenation of $\text{CH}_3\text{CH}_2\text{OH}$ on Pt_3Sn , with B3PW91 including ZPE. The red line refers to the α -H pathway on the Pt site.

Figure 4. Potential energy profile for the adsorption and dehydrogenation of $\text{CH}_3\text{CH}_2\text{OH}$ on Pt_3Re , with B3PW91 including ZPE. The top red line refers to the α -H pathway on the Pt site, while the bottom one to the hydroxyl pathway on Re site.

Figure 5. Potential energy profile for the adsorption and dehydrogenation CH₃CH₂OH on Pt₃Rh (A), and Pt₃Pd (B) with B3PW91 including ZPE.

Figure 6.

Ligand effects on the adsorption and dehydrogenation of C_2H_5OH on the bimetallic clusters, Pt_3M (M=Pt, Ru, Sn, Re, Rh, Pd). (A) adsorption energies; (B) dehydrogenation barriers; and (C) adsorption equilibrium constants.

Figure 7. Frontier molecular orbitals and Mulliken atomic charges of CH₃CH₂OH and Pt₃M (M=Pt, Ru, Sn, Re, Rh, Pd)

Figure 8.
Energies of HOMOs and LUMOs of CH₃CH₂OH and Pt₃M (M=Pt, Ru, Sn, Re, Rh, Pd)

Table 1

Adsorption energy (E_{ads}), dissociation energy (E_{diss}), energy barrier (E_a), and imaginary frequency (ν/cm^{-1}) of transition state for all reaction channels of $\text{C}_2\text{H}_5\text{OH} + \text{Pt}_3\text{M}$ ($\text{M}=\text{Pt}, \text{Ru}, \text{Sn}, \text{Re}, \text{Rh}, \text{Pd}$). (energy unit: eV)

Reaction	E_{ads}/eV	E_a/eV	$E_{\text{diss}}/\text{eV}$	ν/cm^{-1}
$\text{Pt}_4 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_4\text{-a-p}$	-0.37	0.02	-1.19	605
$\text{Pt}_4 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_4\text{-b1-p}$	-0.66	1.07	-0.87	376
$\text{Pt}_4 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_4\text{-b2-p}$	-0.66	0.82	-0.65	1118
$\text{Pt}_3\text{Ru} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Ru-a-p}$	-0.28	0.12	-0.75	658
$\text{Pt}_3\text{Ru} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Ru-b-p}$	-0.29	0.15	-0.75	646
$\text{Pt}_3\text{Ru} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Ru-c-p}$	-0.61	1.03	-0.27	1028
$\text{Pt}_3\text{Ru} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Ru-d-p}$	-0.59	0.79	-1.00	1187
$\text{Pt}_3\text{Sn} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Sn-a-p}$	-0.44	0.14	-0.49	610
$\text{Pt}_3\text{Sn} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Sn-b-p}$	-0.84	1.23	-0.58	925
$\text{Pt}_3\text{Sn} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Sn-c-p}$	-0.85	1.13	-0.74	466
$\text{Pt}_3\text{Re} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Re-a-p}$	-0.35	0.16	-0.57	662
$\text{Pt}_3\text{Re} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Re-b1-P}$	-0.12	0.46	-0.56	711
$\text{Pt}_3\text{Re} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Re-b2-P}$	-0.12	0.49	-1.12	1014
$\text{Pt}_3\text{Re} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Re-d1-P}$	-0.83	0.99	-1.13	855
$\text{Pt}_3\text{Re} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Re-d2-P}$	-0.83	0.25	-1.90	1208
$\text{Pt}_3\text{Re} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Re-e-P}$	-0.72	1.15	-0.54	1020
$\text{Pt}_3\text{Rh} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Rh-a-P}$	-0.29	0.15	-0.58	660
$\text{Pt}_3\text{Rh} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Rh-b-P}$	-0.53	1.08	-0.24	1040
$\text{Pt}_3\text{Rh} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Rh-c-P}$	-0.53	1.08	-0.28	460
$\text{Pt}_3\text{Rh} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Rh-d-P}$	-0.60	1.04	-0.50	1004
$\text{Pt}_3\text{Pd} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Pd-a-P}$	-0.37	0.06	-0.96	621
$\text{Pt}_3\text{Pd} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Pd-b-P}$	-0.18	0.66	-0.30	743
$\text{Pt}_3\text{Pd} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Pd-c-P}$	-0.67	0.85	-0.50	1055
$\text{Pt}_3\text{Pd} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Pd-d1-P}$	-0.48	1.10	0.15	185
$\text{Pt}_3\text{Pd} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pt}_3\text{Pd-d2-P}$	-0.48	1.49	0.60	873