Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2010 January 14; 114(1): 317–326. doi:10.1021/jp9062669.

Understanding Electrocatalytic Activity Enhancement of Bimetallic Particles to Ethanol Electro-oxidation: (1) Water Adsorption and Decomposition on Pt_nM ($n=2,3$ and 9 ; $M=Pt, Ru, Sn$)

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Abstract

The fundamental assumption of the bi-functional mechanism for PtSn alloy to catalyze ethanol electro-oxidation reaction (EER) is that Sn facilitates water dissociation and EER occurs over Pt site of the PtSn alloy. To clarify this assumption and achieve a good understanding about the EER, H_2O adsorption and dissociation over bimetallic clusters PtM ($M=Pt, Sn, Ru, Rh, Pd, Cu$ and Re) are systematically investigated in the present work. To discuss a variety of effects, Pt_nM ($n=2$, and 3 ; $M=Pt, Sn$ and Ru), one-layer Pt_6M ($M=Pt, Sn$ and Ru), and two-layer $(Pt_6M)Pt_3$ ($M=Pt, Sn, Ru, Rh, Pd, Cu$ and Re) clusters are used to model the PtM bimetallic catalysts. Water exhibits atop adsorption on Pt and Ru sites of the optimized clusters Pt_nM ($n=2$, and 3 ; $M=Pt$ and Ru), yet bridge adsorption on Sn sites of Pt_2Sn as well as distorted tetrahedral Pt_3Sn . However, in the cases of one-layer Pt_6M and two-layer Pt_9M cluster models water preferentially binds to all of investigated central atom M of surface layer in atop configuration with the dipole moment of water almost parallel to the cluster surface. Water adsorption on the Sn site of Pt_nSn ($n=2$ and 3) is weaker than those on the Pt site of Pt_n ($n=3$ and 4) and the Ru site of Pt_nRu ($n=2$ and 3), while water adsorptions on the central Sn atom of Pt_6Sn and Pt_9Sn are enhanced so significantly that they are even stronger than those on the central Pt and Ru atoms of Pt_nM ($n=6$ and 9 ; $M=Pt$ and Ru). For all of the three cluster models, energy barrier (E_a) for the dissociation of adsorbed water over Sn is lower than over Ru and Pt atoms (e.g., E_a : 0.78 vs 0.96 and 1.07 eV for Pt_9M), which also remains as external electric fields were added. It is interesting to note that the dissociation energy on Sn site is also the lowest (E_{diss} : 0.44 vs 0.61 and 0.67 eV). The results show that from both kinetic and thermodynamic viewpoints Sn is more active to water decomposition than pure Pt and the PtRu alloy, which well supports the assumption of the bi-functional mechanism that Sn site accelerates the dissociation of H_2O . The extended investigation for water behavior on the $(Pt_6M)Pt_3$ ($M=Pt, Sn, Ru, Rh, Pd, Cu$ and Re) clusters indicate that the kinetic activity for water dissociation increases in the sequence of $Cu < Pd < Rh < Pt < Ru < Sn < Re$.

1. Introduction

A direct ethanol proton exchange membrane fuel cell (PEMFC) offers a promising alternative power source because of its superiority to the most studied H_2 - O_2 PEMFC in a few aspects. As a liquid fuel, it firstly avoids storage issue associated with H_2 gas fuel cell. Direct ethanol fuel cells also provide attractive mass energy density (8.1kW·h/kg for ethanol vs. 0.42 kW·h/kg for H_2 1.5 wt% storage).¹ In addition, ethanol is a renewable fuel since it can be produced in a great quantity from biomass and it is much less toxic than methanol as well. However, the

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complete oxidation of ethanol to H_2O and CO_2 is much more difficult than those of H_2 as well as methanol because of C-C bond in ethanol. Much effort has been put into searching for efficient electrocatalysts for ethanol electro-oxidation reaction (EER) and considerable progress has also been made.^{1–6} Pt was recognized to be the most active catalyst for the EER, however it is readily poisoned by adsorbed CO species and is hard to provoke C-C bond breaking for complete oxidation of ethanol. PtSn/C has been recently demonstrated the ability to enhance the electrocatalytic activity of Pt towards the EER with respect to increasing current density as well as to lowering the onset potential of ethanol oxidation by approximately 0.2V compared to Pt alone.^{1, 3, 7, 8}

The mechanism of ethanol electro-oxidation on PtSn was widely interpreted with bifunctional mechanism and ligand effect,^{9, 10} where dissociative adsorption of ethanol occurs only on platinum sites and tin primarily promotes adsorption and dissociation of water to form OH oxidizing intermediates from ethanol.⁴ Other researchers suggested rather similar mechanisms for the EER.^{2, 3, 8, 11} Although some interesting assumptions have been made, several essential issues still remain uncertain. For example, although Sn and Ru have similar activity for water dissociative adsorption, PtRu does not show as active as PtSn to the EER. Thus, Sn must have another effect besides ligand effect and enhancing H_2O dissociation because otherwise Ru should display almost the same activity as Sn for the EER.⁴

To well understand electrocatalytic enhancement of PtSn for the EER and eventually design more efficient catalysts for the EER, it is essential to investigate adsorption and dissociation of both water and ethanol over Pt-based bimetallic particles at molecular level. The fundamental assumption of the bi-functional mechanism for PtSn alloy to catalyze EER is that Sn facilitates the dissociation of H_2O . Although water adsorption as well as decomposition have been previously investigated on Pt, Au, Ag, Pd, Cu and other transition metal surfaces as well as Pt-based alloys,^{12–17} except for Ishikawa et al's¹⁵ density functional study (DFT) on water behavior over PtSn alloy no other report has been available to the best of our knowledge. In addition, the energy barrier for homolytic H_2O dissociation over PtSn was estimated with the empirical UBI-QEP equation instead of *ab initio* transition state location.¹⁵ Thus, to clarify the bi-functional assumption of PtSn more actively catalyze the EER, it is essential to investigate water adsorption over PtSn with *ab initio* DFT method. To be consistent with the present study in terms of primarily theoretical treatment and then make a meaningful comparison on water adsorption and dissociation over Pt and other bimetallic clusters PtM (M=Ru, Rh, Pd, Cu and Re) are systematically explored. It is expected that a careful comparison on water adsorption behavior over such clusters will provide a meaningful understanding for the mechanism by which Sn enhances the electrocatalytic activity of Pt towards the EER.

2. Methodology and Bimetallic Models

LANL2DZ type of effective core potential (ECP) and the corresponding double- ζ basis set were employed for all the involved metal atoms, while the basis sets for H and O are 6–311++G(d,p). In the LANL2DZ ECP scheme valence electron shells for ground state of Pt, Sn, Ru, Rh, Pd, Cu, and Re are $5s^25p^65d^96s^1$, $5s^25p^2$, $4s^24p^24d^65s^2$, $4s^24p^64d^75s^2$, $4s^24p^64d^85s^2$, $3s^23p^63d^{10}4s^1$, and $5s^25p^65d^56s^2$, respectively. The geometric structure of clusters Pt_nM ($n=2$ and 3; M=Pt, Sn and Ru) and water adsorption complexes with a variety of electronic structures are fully optimized with B3PW91 density functional theory as implemented in Gaussian03 Rev.D02.¹⁸ The transition states (TS) for dissociations of the adsorbed water were directly searched for by either the transit-guided quasi-Newton (STQN) method or the eigenvector following with the Berny algorithm. A frequency analysis 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.

To discuss the decomposition of H₂O over nano-scale particle catalysts that usually have a well defined fcc surface, the one layer extend cluster model Pt₆M as well as the two layer model (Pt₆M)Pt₃ have also been applied, which will be described in detail in the next section. Constraint optimization was employed for H₂O adsorption on the surface models with the fixed cluster. The frequency analysis usually presents a few small imaginary frequencies due to the fixed cluster structure, while for the relevant TS structures of adsorbed water dissociation there is a unique significant imaginary frequency that can be assigned to OH breaking.

The geometric structures for Pt_nM as well as adsorptions of H₂O on Pt_nM were optimized for a variety of electronic states, and their relative energies are illustrated in Figure 1, which shows that physisorption of water on the optimized Pt_nM (n=2–3, M=Pt, Sn and Ru) does not alter stability trend of electronic states, while the complexes of water-Pt_nM (n=6 and 9) usually have the different ground states than the cluster. Water adsorption energies (E_{ads}) are defined as $E_{\text{ads}} = E(\text{H}_2\text{O-Pt}_n\text{M in ground state}) - [E(\text{H}_2\text{O}) + E(\text{Pt}_n\text{M in ground state})]$, the difference between energy of the adsorption complex and the energy summation of the cluster at ground state and water. The higher negative E_{ads} indicates the stronger adsorption between water and the cluster.

To discuss electric field effects on energetic of H₂O decomposition over Pt_nM clusters, a finite external electric field was added to water-Pt_nM (n=6 and 9) systems on the basis of the optimized potential profile without electric fields. The cluster was placed in the xy plane, and the z axis passes through the central M atom with positive in H₂O side. The three electric field intensities were selected in z component, −0.001, +0.001, and +0.01 au (1 au=5.14×10⁹ V/cm).

3. Results

3. 1. H₂O adsorption over Pt_nM clusters (n=2–5; M=Pt, Sn, Ru)

Pt₃ and Pt₄—The ground state of Pt₃ is a singlet state with an average binding energy (E_b) per atom of 1.87 eV. E_b was calculated with Eq. (1), where E_i and E_{cluster} represent the electronic energies for a single atom and cluster, respectively, and n is the number of atoms of a cluster.

$$E_b = (\sum_i E_i - E_{\text{cluster}}) / n \quad (1)$$

Three sorts of adsorptions for water on Pt₃ were located as shown in Figure 2. In the first one (2a) water is atop adsorbed on Pt₃ via the oxygen with Pt-O distance of 2.233 Å and adsorption energy of −0.79 eV. The dipole moment of H₂O is coplanar with the Pt₃ cluster in 2a. In the adsorption configurations 2b and 2c, H₂O sits above the Pt₃ plane while OH pointing towards Pt-Pt bridge and Pt atom, respectively, with almost the same adsorption energy of −0.22 eV. The two latter adsorptions (2b and 2c) are much less stable than the former configuration by 0.57 eV.

Exemplified by Parreira et al. and references therein,¹⁴ Pt₄ is one of the most widely investigated metal clusters. Consistent with the previous results,^{13, 14, 19} the current full optimization shows that the ground state of Pt₄ is a triplet distorted tetrahedral with an average binding energy of 2.17 eV/atom, in which one Pt-Pt length, 2.744 Å, is longer than the rest by approximately 0.12–0.13 Å (2.744 vs 2.611, 2.609, 2.610, 2.598, and 2.608 Å). Another widely reported geometry of Pt₄, rhombus (quintet S=2 for the ground state) is presented to be less stable than the distorted triplet tetrahedral Pt₄ by 0.56 eV. Different from the result of constraint optimization,²⁰ this full optimization presents that the ground state of rhombic Pt₄ is a nonplanar V-shaped quintet. For the adsorption of H₂O on the distorted tetrahedral Pt₄ a

configuration similar to 2a of Pt₃ was located with a slightly longer Pt-O distance (2.237 vs 2.233 Å), yet the adsorption energy is lower than on Pt₃ by 0.16 eV (E_{ads} : -0.63 eV vs. -0.79 eV). The Pt-Pt bond directly absorbing H₂O was stretched to 2.809 Å. The adsorption energy on Pt₄ agrees well with the previously reported theoretical results in the range of -0.56 and -0.62 eV,¹⁴ and the ZPE corrected E_{ads} (-0.54 eV) is overestimated as compared with an experimental result of -0.42 eV. In both cases, Pt₃ and Pt₄, water adsorption induces electron transfer (ET) from water to the clusters, resulting in +0.26 e and +0.22 e charge for water in Pt₃-H₂O and Pt₄-H₂O complexes, respectively. This basically agrees with the Jacob's result of 0.28 e electron transfer from water to Pt₃₅.²² The electron transfer from water to the clusters implies that the interaction may occur on the HOMO of H₂O and frontier empty or singly occupied orbitals of the clusters.

Pt₂Sn and Pt₃Sn—Both distorted tetrahedral and the V-shaped Pt₃Sn were located, and the former is more stable than the latter by 0.24 eV. As compared with Pt₃ and Pt₄, as alloyed with Sn the average binding energies of Pt₂Sn and distorted tetrahedral Pt₃Sn are dramatically increased to 2.46 and 2.61 eV from 1.87 and 2.17 eV, respectively. Because of its lower ionization potential than Pt (7.3 vs 9.0 eV), electron transfer from Sn to Pt results in positive charges of +0.62 e (Pt₂Sn) and +0.67 e (Pt₃Sn) in Sn. The electron transfer may be responsible for the enhanced stability of clusters, Pt₂Sn and Pt₃Sn. The charge distributions for Pt₃ and Pt₂Sn are illustrated in Figure 3 with top and/or side views of electron density superimposed by electrostatic potential. In Pt₂Sn and Pt₃Sn clusters, Sn atom depletes electron density (blue), resulting in a hole, while Pt atoms increase electron density.

Apparently there will be more adsorption sites on the alloys than on Pt clusters. A variety of potential adsorptions were considered, including atop (Pt and Sn), bridge (Pt-Pt and Pt-Sn) as well as hollow (Pt-Pt-Pt and Pt-Pt-Sn) adsorption sites via both head (O and H) and bond (O-H) approaches. However, full optimizations only turned out two major adsorption configurations for Pt₂Sn, atop one at Pt (2d) and bridge one at Sn-Pt (2e). For example, O head approach at Pt and Pt-Sn bridge result in 2d, while O head approach at Sn and Pt-Pt-Sn face, H head approach at Pt-Sn bridge, and O-H bond approach at Sn-Pt bridge converge to configuration 2e. Although electron density around Pt is higher in Pt₂Sn than in Pt₃, the adsorption pattern in 2d, both the Pt-O distance (2.221 Å) and the adsorption energy (E_{ads} = -0.79 eV) are rather similar to Pt₃ as H₂O adsorbs on the Pt site of Pt₂Sn cluster. This similarity indicates that the supposed ligand effect on H₂O adsorption on Pt sites is not remarkable in the case of Pt₂Sn. In configuration 2e, the distances of Sn-O (2.531 Å) and Pt-H (2.535 Å) are relatively long, and consequently the adsorption on the Sn site is weaker than on the Pt site (E_{ads} = -0.52 eV).

The atop adsorption at Pt site (2f) of Pt₃Sn is enhanced as compared with the case of Pt₄ (E_{ads} : -0.80 vs -0.63 eV), which may be due to the charge transfer from Sn to Pt. The ligand effect is higher than Pt₂Sn. The corresponding electron transfer from H₂O to Pt₃Sn is also larger than in the case of Pt₄ (0.24 vs 0.22 e). Adsorption pattern of water on the Sn site of distorted tetrahedral Pt₃Sn (2g) is the same as that in Pt₂Sn, yet is further weakened with SnO distance of 2.84 Å and only -0.20 eV of adsorption energy. Opposite to the distorted tetrahedral Pt₃Sn, water adsorption on the Sn site of the V-shaped Pt₃Sn generates atop configuration (2h) with Sn-O distance of 2.48 Å and considerable adsorption energy of -0.53 eV. Although V-shaped Pt₃Sn is less stable than the distorted tetrahedral one, the adsorption complex on the Sn site of the former is more stable than that of the latter by 0.09 eV. This shows that the atop adsorption on the Sn site of the V-shaped Pt₃Sn stabilizes the complex.

Pt₂Ru and Pt₃Ru—The ionization potential of Ru is also lower than that of Pt (7.4 vs. 9.0), as demonstrated by Figure 3 and the data in Table 1 charge was therefore transferred to Pt. The electron densities on the Ru of Pt₂Ru and Pt₃Ru (shown in dark blue) are lower than those on

the Pt atoms (light blue). The nonplanar rhombic V-shaped Pt₃Sn (total spin S=3 for the ground state) is slightly more stable by 0.08 eV than the distorted tetrahedral one (S=2 for the ground state). Similar to the cases of Pt₃ and Pt₄, the adsorption of H₂O on the Ru sites of Pt₂Ru and Pt₃Ru tends to be atop (2i and 2j), rather than the bridge as in the cases of Pt₂Sn and distorted tetrahedral Pt₃Sn. Ru-O distances in Pt₂Ru and V-shaped Pt₃Ru (distorted tetrahedral Pt₃Ru) are 2.330 and 2.325 (2.295) Å, respectively, which are only approximately 0.1 Å longer than Pt-O in Pt₃ and Pt₄. Consequently, although the adsorptions with respective adsorption energy of -0.78 and -0.56 eV are only slightly weaker than on Pt₃ and Pt₄ (E_{ads} : -0.80 and -0.63 eV), they are much stronger than the adsorptions on Sn sites of Pt₂Sn and distorted tetrahedral Pt₃Sn (E_{ads} : -0.52 and -0.20 eV).

In spite of electron density enhancement on the Pt atoms of Pt₃Sn as well as Pt₃Ru, water adsorption on the Pt site of Pt₃Ru is even weaker than that on the Pt of Pt₄ (E_{ads} : -0.59 vs -0.63 eV), rather than increase as in the case of Pt₃Sn.

Pt₅, Pt₆, Pt₄Sn, and Pt₅Sn—Trigonal bipyramidal and prism structures are located for Pt₅ and Pt₆ with spin multiplicity of 5 and 3 for ground states, respectively. When alloying with Sn, average bond lengths of Pt₄Sn and Pt₅Sn are also prolonged to some extent, while the average binding energies per atom are greater than those of Pt₅ and Pt₆ (2.71 and 2.85 eV vs. 2.31 and 2.45 eV) as in the cases of Pt₂Sn and Pt₃Sn clusters. In spite of much effort, only bridge adsorptions on the Sn sites of Pt₄Sn, and Pt₅Sn have been located, and they are rather weak with respective adsorption energies of -0.37 and -0.12 eV and SnO bond lengths of 2.552 and 2.654 Å.

The above results for H₂O adsorption on PtM bimetallic clusters indicate that for the edge atoms water has the strongest adsorption on Pt atoms, and water adsorption on Ru is slightly weaker than on the Pt atoms. The H₂O adsorptions on Pt and Ru have the similar pattern, i.e., atop adsorption. However, when Sn alloying Pt clusters, except for the V-shaped Pt₃Sn cluster Sn usually has rather low tendency to adsorb water molecules and water takes bridge adsorption via OH bond along Sn-Pt. In the above clusters Pt_nSn (n=2–5), Sn always sits on the vertices. It seems that the adsorption of water on Sn vertex tends to be bridge adsorption and is much weaker than the atop adsorptions on Pt and Ru vertexes.

3. 2 H₂O adsorption over Pt_nM clusters (6 and 9; M=Pt, Sn, Ru)

To model sub-nano particle surface and discuss water behavior over alloy surface, Pt_nM (n=6 and 9; M=Pt, Sn and Ru) with given distances are chosen. According to Table 1, as compared with Pt cluster the bond lengths of the bimetallic Pt_nSn are extended for both Pt-Sn and Pt-Pt to some extent, which qualitatively agree with the empirical equation for nearest neighbor distances R of PtM bimetallic cluster,¹⁵ $R = (R_M/R_{\text{Pt}})^{1/3} \times 2.77$ Å, where R_M and R_{Pt} are atomic radii for the alloyed metal M and Pt, respectively. Therefore, the nearest distance in the following PtM bimetallic cluster will be estimated by the empirical formula. As stated in Ref.¹⁵, we also agreed that the cluster models are unable to simulate bulk surface properties because of its limited size and undercoordinated metal atoms. However, the model may be suitable for simulating the properties of nano-scale particle catalysts, e.g., Pt-Sn (Ru) alloy nanoparticles with a fcc surface.^{15,29}

Pt₇ is one layer model consisting of a hexagon of 6 Pt atoms surrounding a central Pt atom; while in the Pt₆M bimetallic alloy the central atom will be replaced by alloyed atoms such as Sn and Ru. To eliminate the edge effect, a two layer cluster, (Pt₆M)Pt₃, with 7 atoms (Pt₆M) on the surface layer and 3 Pt atoms on the second layer, has also been used to model Pt-M alloy surface, as employed by Ishikawa et al.¹⁵

Pt₇-H₂O—Water adsorptions on both central and peripheral Pt atoms of Pt₇ are explored. The adsorption on the peripheral Pt is slightly stronger than on the central Pt (E_{ads} : -0.46 vs -0.43 eV), and the weaker adsorption on the central Pt accompanies a slight larger Pt-O distance by 0.01 Å (Pt-O: 2.347 vs 2.331 Å). Both adsorptions take atop configuration (Figures 4a and 4b) with O-Pt-Pt angle in a range of 85 – 95° and water almost parallel to Pt(111) surface. The binding energy of H₂O on the central Pt is well within the literature reported result for Pt(111) surface with a variety of theoretical methods and models, -0.27 eV,²³ -0.29 eV,²⁴ -0.33 eV,²⁵ -0.42 eV,¹⁵ and -0.56 eV.¹⁴

Pt₆Sn-H₂O and Pt₆Ru-H₂O—The nearest neighbor distance in the one layer Pt₆Sn adopt the experimental value, 2.83 Å.¹⁵ Starting with atop (Sn), bridge (Sn-Pt), as well as hollow (Sn-Pt-Pt) adsorptions via O head approach at and water parallel to Pt₆Sn surface, only atop adsorption was located. The adsorption in the central Sn becomes remarkably strong with adsorption energy of -1.30 eV and Sn-O distance of 2.305 Å. To investigate the edge effect of Sn on water adsorption, one peripheral Pt atom in Pt₇ was also replaced by Sn. Water adsorption on the peripheral Sn ($E_{\text{ads}} = -0.61$ eV; Sn-O: 2.417 Å; Sn-H: 2.73 and 2.79 Å) is turned out to be much weaker than that on the central Sn atom, yet much stronger than the bridge adsorptions on Sn sites of the above optimized smaller clusters Pt_nSn ($n=2$ – 5). Despite different favorable adsorption patterns of H₂O on Sn and Ru sites of clusters Pt_nM ($n=2$ – 3), as shown in Figures 4c and 4d, primarily the adsorptions on central and outside Sn of the Pt₆Sn surface are atop, where oxygen sits approximately right above Sn with O-Sn-Pt in the range of 82 – 97° and water is roughly parallel to the Pt₆Sn (111) surface.

The nearest neighbor distance in the one layer Pt₆Ru was 2.74 Å, estimated by the above mentioned empirical formula. Adsorption on the central Ru (4e) is slightly weaker than on Sn (E_{ads} : -1.25 vs -1.30 eV) yet much stronger than that on the central Pt of Pt₇ (E_{ads} : -1.25 vs -0.43 eV). According to Table 3, water adsorption on one-layer Pt₆M cluster induces more electron transfer than on Pt_nM ($n=2$ and 3).

Pt₁₀-H₂O—To address the 3-dimensional structure effect, the second layer with 3 Pt atoms was added in (111) pattern. For the two-layer cluster Pt₁₀, the adsorption strength on the peripheral Pt atom is similar to that of one-layer Pt₇ (E_{ads} : -0.48 vs -0.46 eV); however, in spite of similar atop adsorption pattern and slightly longer Pt-O distance (2.367 vs 2.347 Å) the adsorption on the central Pt of Pt₁₀ is much weaker than that of Pt₇ (E_{ad} : -0.26 vs. -0.43 eV). The predicted binding energy of H₂O on the central Pt atom of Pt₁₀ in this work, -0.26 eV, is rather close to the plane-wave periodic DFT calculations of monomer water on Pt(111) surface, -0.29 eV,²⁴ and -0.33 eV.²⁵ Although the same cluster model, two-layer Pt₁₀, has been employed by Ishikawa et al.¹⁵ and the present investigation, the present adsorption is weaker than that predicted with the ADF method there (-0.26 vs -0.46 eV).

Pt₉Sn-H₂O—As the surface of Pt₁₀ was alloyed with Sn in the center, similar to the cases of Pt₆Sn and Pt₇ the adsorption enhancement still remains due to alloying Sn. The water adsorption energy on central Sn of Pt₉Sn is much stronger than that on central Pt of Pt₁₀ (E_{ads} : -0.80 vs. -0.26 eV). Compared with the adsorption on Pt₆Sn, the introduction of the second layer in Pt₉Sn weakens water atop adsorption on the Sn site (E_{ads} : -0.80 vs -1.30 eV). The result is significantly stronger than the unique available reference to our knowledge for H₂O adsorption on Sn site (-0.80 vs -0.39 eV¹⁵). Atop adsorption on the peripheral Sn (Figure 4g) was also located ($E_{\text{ads}} = -0.32$ eV, Sn-O = 2.579 Å) and is significant weaker than the atop adsorption on the central Sn, which has the same trend as the one-layer Sn alloying cluster Pt₆Sn, yet opposite to the central and peripheral Pt atoms of Pt₁₀.

Pt₉Ru-H₂O—Likewise, water adsorption on the central Ru site of the Pt₉Ru surface also presents atop configuration with adsorption energy of -0.39 eV and Ru-O distance of 2.425 Å.

It is interesting to note that water adsorption strength has the same trend as the above one-layer models as compared with Pt and Sn alloying surfaces, i.e., the adsorption on Ru atop site is also in-between those on Sn of Pt₉Sn ($E_{\text{ads}} = -0.80 \text{ eV}$, Sn-O = 2.085 Å) and on Pt of Pt₁₀ ($E_{\text{ads}} = -0.26 \text{ eV}$, Pt-O = 2.367 Å). I acknowledge that the absolute energetic data for individual Pt_nM cluster may not be accurate, but the comparative study on the base of the bimetallic cluster still well fulfils the present objective. No matter how large the theoretical model is, the critical issue is whether the applied model provides consistent result and could provide new insight into the objective. As shown by Table 4, three distinct models ranging from 3 to 10 atoms and one to two-layers qualitatively show the same trend that Sn has lowest E_{a} for water decomposition, closely followed by Ru, and Pt with the greatest E_{a} . Quantitatively, the relative ΔE_{a} of PtSn, PtRu and Pt is also comparable for the three models. The consistent trend provides a theoretical evidence for the fact that Sn is more active to water decomposition than Ru and Pt.

Pt₉Cu, Pt₉Rh, Pt₉Pd, and Pt₉Re—The above two-layer model (Pt₆M)Pt₃ was also extended to alloying Cu, Rh, Pd, and Re, all of which have lower first IP than Pt. Therefore, electron transfer should occur from the central atoms to the surrounding Pt atoms. The total spin (S) of the ground state is 3/2, 1/2, 1, and 5/2 for bimetallic PtCu, PtRh, PtPd, and PtRe, respectively. In all of the cases, H₂O preferentially binds to the central atom M in atop configuration with the dipole moment of water almost parallel to the cluster surface. The binding energy of H₂O on Re site of Pt₉Re (Figure 4h) is stronger than that on Sn site of Pt₉Sn (E_{ads} , -1.13 vs -0.80 eV), while all of others are weaker. In addition, E_{ad} on Re in this work is the same as the reported value by Ishikawa et al.¹⁵ The current adsorption energy on Cu site of Pt₉Cu (E_{ads} , -0.52 eV) is close to Ishikawa's result (E_{ads} , -0.66 eV), but that on Rh is much weaker than that predicted by Ishikawa et al. (E_{ad} , -0.45 vs -0.81 eV). The binding energy on Pd site (-0.37 eV) is comparable to that on Pd(111) (-0.33 eV).²⁵ Water adsorption strength on the central M of Pt₉M decrease in the sequence, Re (-1.25 eV) > Sn (-0.80 eV) > Cu (-0.52 eV) > Rh (-0.45) > Ru (-0.39) > Pd (-0.37 eV) > Pt (-0.26 eV). The adsorption strength seems to have a weak correlation with the valence d orbital vacancy of ground state M. For instance the high vacant d shell of Re and Sn (5d⁵6s² and 5s²5p²5d⁰) accompany strong water adsorption, on the other hand water adsorption on the low vacancy of Pd and Pt (4d¹⁰ and 5d⁹6s¹) are weak.

3. 3 Decomposition of Adsorbed Water

To investigate effects of alloyed metals on the dissociation of H₂O over metal clusters, the transition states (TS) for dissociations of the adsorbed water were directly searched for with either the transit-guided quasi-Newton (STQN) method or the eigenvector following with the Berny algorithm. The characteristic parameters of the relevant TS, such as the imaginary frequency, the distance between O and metal atom $R(\text{O-M})$, the angle of H-O-H, and the distance between O and leaving H, are summarized in Tables 2 and 3. In these TS, in spite of incomplete broken, one O-H bond has already been considerably extended to 1.54–1.73 Å from shorter than 1.0 Å. The O-H extension was accompanied by approximately 0.3 Å compression of $R(\text{O-M})$ as compared to the adsorption complexes. To get insights on whether the alloyed metals can catalyze H₂O dissociation, it is essential to compare kinetics (activation energy, E_{a}) and thermodynamics (dissociation energy, ΔE_{diss}) for the dissociation of adsorbed water, which are also listed in Tables 2 and 3.

The decomposition of adsorbed water over the clusters Pt₃, Pt₂Sn and Pt₂Ru, was found to have two pathways: atop and bridge decomposition (shown in Figure 5). For Pt₃, atop decomposition has lower energy barrier than the bridge one (activation energy E_{a} : 1.14 eV vs. 1.49 eV); while for the adsorbed water on Sn and Ru sites of Pt₂M the energy barriers for bridge decompositions along Sn-Pt or Ru-Pt are lower than the atop ones (0.61 vs 2.47 eV for Sn;

0.63 vs. 1.19 eV for Ru). It is apparent that the driven force for the adsorbed water decomposition is co-adsorptions of OH and H radicals on metal surface. The different TS patterns may be due to the fact that Pt has stronger binding to H than Ru and Sn (binding energies: -3.43 vs -2.77 and -2.55 eV at B3PW91 level).

The potential energy profiles for the more favorable pathway (atop path for Pt, and bridge one for Sn and Ru) of water decomposition over Pt_2M (M=Pt, Sn and Ru) are displayed in Figure 6. A comparison on E_a indicates that the decompositions of H_2O over Sn and Ru sites are kinetically more favorable than Pt site (E_a : 0.61, 0.63 vs. 1.14 eV). The dissociation energy (E_{diss}) for adsorbed water to co-adsorbed H and OH on Sn is comparable to that on Pt (0.35 vs. 0.34 eV), while is less favorable than that on Ru (0.35 vs. -0.21 eV).

Water decomposition on Pt_4 via atop TS has also lower barrier than via bridge path (E_a : 0.95 vs 1.30 eV). The TS are searched for as water was adsorbed on both tetrahedral and V-shaped clusters of Pt_3M (Sn and Ru). According to Table 2, the decomposition energy barrier via bridge path for the adsorbed water on V-shaped clusters is 0.74 and 0.72 eV for Pt_3Sn and Pt_3Ru , respectively. They are again rather lower than the barrier for the water decomposition over Pt_4 (E_a : 0.74, 0.72 vs 0.95 eV).

For the adsorbed water on the central metal of Pt_6M (111) surfaces (M=Pt, Sn and Ru), dissociation kinetics and thermodynamics agree well with the trends for the optimized Pt_2M . According to Table 3, dissociation energy barrier for the adsorbed water over Sn is slightly lower than over Ru but remarkably lower than over the central Pt (E_a : 0.60 vs 0.67 and 1.14 eV). In spite of dramatically smaller than in the gas phase (5.26 eV), for all of three cases dissociation energies of adsorbed water on Pt_6M (111) are still positive (0.50, 0.32 and 0.90 eV). Dissociated OH and H groups are atop adsorbed on M and Pt with O-M distances 0.1 Å less than corresponding transition states. In the case of Pt_6M , all of the TS were turned out to have a major imaginary frequency characterizing OH breaking of the adsorbed water. However, besides the major imaginary there are a few small imaginary frequencies that merely belong to vibrational modes of the Pt_6M cluster and are very similar to those for $\text{Pt}_6\text{Sn-H}_2\text{O}$ adsorption complex. For example, in the case of Pt_6Sn the imaginary frequency for the TS of adsorbed water dissociation is 425 cm^{-1} and a few others are 151, 50 and 25 cm^{-1} , whose corresponding vibrational modes in $\text{Pt}_6\text{Sn-H}_2\text{O}$ are 163, 67 and 33 cm^{-1} .

For the extended two-layer (111) surfaces Pt_9M (M=Pt, Sn, Ru, Cu, Rh, Pd, and Re), the adsorbed water on the central M of the top layer exhibits atop configuration. The transition states of adsorbed water on Pt and Ru are later as compared those of Pt_6M , which was evidenced by longer O-H distances. Consequently, the corresponding imaginary frequencies of the TS are smaller. For Sn, the characteristics of the TS are very comparable to one-layer Pt_6Sn . E_a for the central Pt atom of Pt_{10} is slightly lower than that of Pt_7 (1.07 vs 1.14 eV), while the barriers for Sn and Ru are increased to different magnitude due to the second layer effect (0.78 vs 0.60 eV for Sn; 0.96 vs 0.67 eV for Ru). According to Table 3 and Figure 7, the energy barriers for Pt_9M (M=Pt, Sn, and Ru) have the same trend as the above one-layer model Pt_6Sn and small optimized clusters Pt_nM . Once again the adsorbed water on Sn shows the lowest dissociation energy barrier, followed by Ru and Pt (E_a : 0.79 vs 0.96 and 1.07 eV). It is interesting to note that the dissociation energy on Sn site is also the lowest (E_{diss} : 0.44 vs 0.61 and 0.67 eV). This implies that from both kinetic and thermodynamic viewpoints Sn is the most active to water decomposition among the pure Pt and two PtM (M=Sn and Ru) alloys, which well supports the assumption of the bi-functional mechanism that Sn site accelerates the dissociation of H_2O .

The present E_a for water decomposition on Pt_{10} (1.07 eV) is slightly higher than the reported values with a variety of theoretical methods and models, such as 1.02 eV with ADF code and

two-layer Pt₁₀ cluster,¹⁵ 0.68–0.88 eV on Pt(111) with plane-wave periodic DFT (RPBE or PW91) and ultrasoft pseudopotential (USPP) implemented on VASP, DACAPO or CASTEP.^{25–27} The E_a on Sn (0.79 eV) is lower by 0.13 eV than that (0.92 eV) calculated with the two-layer Pt₉Sn model and ADF code,¹⁵ while others are systematically higher by 0.05–0.54 eV than those from Ishikawa et al. (E_a : 0.71 vs 0.66 eV for Re; 0.96 vs 0.84 eV for Ru; 1.81 vs 1.38 eV for Cu; 1.18 vs 1.00 eV for Rh). The E_a on Pt₉Pd (1.36 eV) is rather comparable to literature data on Pd(111), e.g., 1.12 eV,¹⁷ 1.09²⁸, and 1.05 eV.²⁵ Water dissociation kinetic activity increases in the sequence of Cu < Pd < Rh < Pt < Ru < Sn < Re. In spite of different, the sequence is somewhat relevant to water adsorption strength order, Pt < Pd < Ru < Rh < Cu < Sn < Re. Taking Pt as a reference, the plot of relative E_a against relative E_{diss} for water dissociation over the investigated transition metals M (Pd, Ru, Rh, Cu, Sn, and Re) is illustrated in Figure 8. According to the plot, the bimetallic alloys PtM (M=Re, Sn and Ru) are more active to water dissociation both kinetically and thermodynamically, while the bimetallic alloying with Cu, Pd and Rh are less active than Pt from both aspects.

To discuss external electric field (EF) effects on water decomposition over Pt_nM (n=6 and 9; M=Pt, Sn, and Ru), external electric fields were applied to the adsorbed water in the z direction perpendicular to the top surface (xy plane) of the clusters Pt_nM. The energy barriers E_a and dissociation energies E_{diss} after applying external electric field are summarized in Table 5. Electric field effect on water decomposition over Pt₇ is opposite to those over Pt₆Sn and Pt₆Ru. E_a for adsorbed water over the former in the applied electric fields is considerably increased as compared to non-electric field (1.14 eV), and such a variation does not change much with the strength (E_a =1.40 eV at EF=0.001 au vs. 1.42 eV at EF=0.01 au) as well as with the direction (1.40 eV at EF=0.001 au vs. 1.41 eV at EF=-0.001 au). However, E_a for water decomposition over the bimetallic clusters Pt₆M (M=Sn and Ru) are in general decreased. For the decomposition over Sn site of Pt₆Sn, upon the applied fields E_a is much lower by 23–52% than that without EF. E_a over Ru site of Pt₆Ru is weakly affected by external electric fields, with a slight decrease in positive fields while little increase in negative field. It is interesting to notice that in the external electric fields PtSn still exhibits the most active kinetically to water decomposition among the three clusters. Electric fields were also extended to the two layer model Pt₉M. For all of the three Pt₉M (M=Pt, Sn and Ru) E_a was increased after applying electric fields. Under the given electric field PtSn again has the lowest energy barrier for adsorbed water to decompose.

4. Conclusion

To gain a better understanding about the EER, H₂O adsorption and dissociation over bimetallic clusters PtM (M=Pt, Sn, Ru, Rh, Pd, Cu and Re) are systematically investigated in the absence of electrolyte that would be there in an electrochemical environment. Pt_nM (n=2, and 3; M=Pt, Sn and Ru), one-layer Pt₆M (M=Pt, Sn and Ru), and two-layer (Pt₆M)Pt₃ (M=Pt, Sn, Ru, Rh, Pd, Cu and Re) clusters are used to model the PtM bimetallic nano-particle catalysts. Although the cluster models are unable to simulate bulk surface properties, they are suitable for simulating the properties of nano-scale particle catalysts. Moreover, since the major objective of the present investigation is to compare the catalytic activity of various PtM bimetallic nanoparticles, the trial error due to the cluster model and omission of solvent environment may be limited to some degree. Water exhibits atop adsorption on Pt and Ru sites of the optimized clusters Pt_nM (n=2, and 3; M=Pt and Ru), yet bridge adsorption on Sn sites of Pt₂Sn as well as distorted tetrahedral Pt₃Sn. However, in the cases of one-layer Pt₆M and two-layer Pt₉M cluster models water preferentially binds to all of investigated central atom M of surface layer in atop configuration with the dipole moment of water almost parallel to the cluster surface. Water adsorption on the Sn site of Pt_nSn (n=2 and 3) is weaker than those on the Pt site of Pt_n (n=3 and 4) and the Ru site of Pt_nRu (n=2 and 3), while water adsorptions on the central Sn atom of Pt₆Sn and Pt₉Sn are enhanced so significantly that they are stronger than those on the

central Pt and Ru atoms of Pt_nM ($n=6$ and 9 ; $\text{M}=\text{Pt}$ and Ru). For all of the three cluster models, energy barrier (E_a) for the dissociation of adsorbed water over Sn is lower than over Ru and Pt atoms (e.g., E_a : 0.78 vs 0.96 and 1.07 eV for Pt_9M), which also remains as external electric fields were added. It is interesting to note that the dissociation energy on Sn site is also the lowest (E_{diss} : 0.44 vs 0.61 and 0.67 eV). The results show that from both kinetic and thermodynamic viewpoints Sn is more active to water decomposition than pure Pt and two PtRu alloy, which well supports the assumption of the bi-functional mechanism that Sn site accelerates the dissociation of H_2O . The extended investigation for water behavior on the $(\text{Pt}_6\text{M})\text{Pt}_3$ ($\text{M}=\text{Pt}$, Sn, Ru, Rh, Pd, Cu and Re) clusters indicate that the kinetic activity for water dissociation increases in the sequence of $\text{Cu} < \text{Pd} < \text{Rh} < \text{Pt} < \text{Ru} < \text{Sn} < \text{Re}$.

Acknowledgments

This research is supported by the American Chemical Society Petroleum Research Fund (47286-GB5). The effort to the project in terms of scholarly development was also partially supported by MBRS/SCORE research continuance award (SC3GM082324) from the National Institute of General Medical Sciences of NIH. Natalie Redmon and Jessica Holiday's involvement are supported by the NSF HBCU-UP program at Albany State University.

References

1. Vigier F, Coutanceau C, Perrard A, Belgsir EM, Lamy C. Development of anode catalysts for a direct ethanol fuel cell. *J Appl Electrochem* 2004;34(4):439–446.
2. Song S, Tsiakaras P. Recent progress in direct ethanol proton exchange membrane fuel cells (DE-PEMFCs). *Appl Catal B: Environ* 2006;63(3–4):187–193.
3. Jiang L, Sun G, Sun S, Liu J, Tang S, Li H, Zhou B, Xin Q. Structure and chemical composition of supported Pt-Sn electrocatalysts for ethanol oxidation. *Electrochim Acta* 2005;50(20):5384–5389.
4. Vigier F, Coutanceau C, Hahn F, Belgsir EM, Lamy C. On the mechanism of ethanol electro-oxidation on Pt and PtSn catalysts: electrochemical and in situ IR reflectance spectroscopy studies. *J Electroanal Chem* 2004;563(1):81–89.
5. Mann J, Yao N, Bocarsly AB. Characterization and Analysis of New Catalysts for a Direct Ethanol Fuel Cell. *Langmuir* 2006;26(25):10432–10436. [PubMed: 17129012]
6. Rousseau S, Coutanceau C, Lamy C, Leger JM. Direct ethanol fuel cell (DEFC): Electric performances and reaction products distribution under operating conditions with different platinum-based anodes. *J Power Sources* 2006;158:18–24.
7. Lamy C, Rousseau S, Belgsir EM, Coutanceau C, Leger JM. Recent progress in the direct ethanol fuel cell: development of new platinum-tin electrocatalysts. *Electrochim Acta* 2004;49:3901–3908.
8. Song SQ, Zhou WJ, Zhou ZH, Jiang LH, Sun GQ, Xin Q, Leontidis V, Kontou S, Tsiakaras P. Direct ethanol PEM fuel cells: The case of platinum based anodes. *Int J Hydrogen Energy* 2005;30:995–1001.
9. Watanabe M, Motoo S. Electrocatalysis by Ad-atoms. *J Electroanal Chem* 1975;60:275–283.
10. Iwasita T, Pastor E. A DEMS and FTIR spectroscopic investigation of adsorbed ethanol on polycrystalline platinum. *Electrochim Acta* 1994;39:531.
11. Lux KWC, Elton J. Lanthanide-platinum intermetallic compounds as anode electrocatalysts for direct ethanol PEM fuel cells. II. Performance of LnPt_2 ($\text{Ln} = \text{Ce}$, Pr) nanopowders in an operating PEM fuel cell. *J Electrochem Soc* 2006;153(6):A1139–A1147.
12. Balbuena PB, Altomare D, Vadlamani N, Bingi S, Agapito LA, Seminario JM. Adsorption of O, OH, and H_2O on Pt-Based Bimetallic Clusters Alloyed with Co, Cr, and Ni. *J Phys Chem A* 2004;108:6378–6384.
13. Wang YX, Balbuena PB. Potential Energy Surface Profile of the Oxygen Reduction Reaction on a Pt Cluster: Adsorption and Decomposition of OOH and H_2O_2 . *J Chem Theory Comput* 2005;1:935–943.
14. Parreira RLT, Caramori GF, Galembeck SE, Huguenin F. The Nature of the Interactions between Pt_4 Cluster and the Adsorbates $\cdot\text{H}$, $\cdot\text{OH}$, and H_2O . *J Phys Chem A* 2008;112(46):11731–11743. [PubMed: 18942818]

15. Ishikawa Y, Liao MS, Cabrera CR. Energetics of H₂O dissociation and COads+OHads reaction on a series of Pt-M mixed metal clusters. A relativistic density-functional study. *Surf Sci* 2002;513:98–110.
16. Ishikawa Y, Diaz-Morales RR, Perez A, Vilkas MJ, Cabrera CR. A density-functional study of the energetics of H₂O dissociation on bimetallic Pt/Ru nanoclusters. *Chem Phys Lett* 2005;411(4–6): 404–410.
17. Wang GC, Tao SX, Bu XH. A systematic theoretical study of water dissociation on clean and oxygen-preadsorbed transition metals. *J Catal* 2006;244:10–16.
18. Frisch, MJ.; Trucks, GW.; Schlegel, HB.; Scuseria, GE.; Robb, MA.; Cheeseman, JR.; Montgomery, JA.; Vreven, T.; Kudin, KN.; Burant, JC.; Millam, JM.; Iyengar, SS.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, GA.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, JE.; Hratchian, HP.; Cross, JB.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, RE.; Yazyev, O.; Austin, AJ.; Cammi, R.; Pomelli, C.; Ochterski, JW.; Ayala, PY.; Morokuma, K.; Voth, GA.; Salvador, P.; Dannenberg, JJ.; Zakrzewski, VG.; Dapprich, S.; Daniels, AD.; Strain, MC.; Farkas, O.; Malick, DK.; Rabuck, AD.; Raghavachari, K.; Foresman, JB.; Ortiz, JV.; Cui, Q.; Baboul, AG.; Clifford, S.; Cioslowski, J.; Stefanov, BB.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, RL.; Fox, DJ.; Keith, T.; Al-Laham, MA.; Peng, CY.; Nanayakkara, A.; Challacombe, M.; Gill, PMW.; Johnson, B.; Chen, W.; Wong, MW.; Gonzalez, C.; Pople, JA. Gaussian 03, Rev. D.02. Gaussian, Inc; Pittsburgh PA: 2003.
19. Li T, Balbuena Perla B. Computational Studies of the Interactions of Oxygen with Platinum Clusters. *J Phys Chem B* 2001;105:9943–42.
20. Kumar TJD, Zhou C, Cheng H, Forrey RC, Balakrishnan N. Effect of Co doping on catalytic activity of small Pt clusters. *J Chem Phys* 2008;128(12):124704/1–11. [PubMed: 18376957]
21. Sexton BA, Hughes AE. A comparison of weak molecular adsorption of organic molecules on clean copper and platinum surfaces. *Surf Sci* 1984;140:227–48.
22. Jacob T. The mechanism of forming H₂O from H₂ and O₂ over a Pt catalyst via direct oxygen reduction. *Fuel Cells* 2006;6:159–181.
23. Kandoi SGAA, Grabow LC, Dumesic JA, Mavrikakis M. Why Au and Cu are more selective than Pt for preferential oxidation of CO at low temperature. *Catal Lett* 2004;93:93–100.
24. Meng S, Wang EG, Gao S. Water adsorption on metal surfaces. A general picture from density functional theory studies. *Phys Rev B* 2004;69(19):195404/1–195404/13.
25. Phatak AA, Delgass WN, Ribeiro FH, Schneider WF. Density Functional Theory Comparison of Water Dissociation Steps on Cu, Au, Ni, Pd, and Pt. *J Phys Chem C* 2009;113(17):7269–7276.
26. Michaelides A, Hu P. Catalytic Water Formation on Platinum: A First-Principles Study. *J Am Chem Soc* 2001;123(18):4235–4242. [PubMed: 11457189]
27. Grabo LC, Gokhale AA, Evans ST, Dumesic JA, Mavrikakis M. Mechanism of the Water Gas Shift Reaction on Pt: First Principles, Experiments, and Microkinetic Modeling. *J Phys Chem C* 2008;112(12):4608–4617.
28. Cao Y, Chen ZX. Theoretical studies on the adsorption and decomposition of H₂O on Pd(1 1 1) surface. *Surf Sci* 2006;(19):4572–4583.
29. Hoster H, Iwasita T, Baumgartner H, Vielstich W. Pt Ru model catalysts for anodic methanol oxidation: Influence of structure and composition on the reactivity. *Phys Chem Chem Phys* 2001;3:337.

Figure 1.

The relative energy for clusters and water adsorption complexes. The asterisk refers to water adsorption site; and black (-), red(-), blue (-), and green (-) lines represent the electronic states with total spin S of 0, 1, 2, and 3, respectively.

Figure 2.

H₂O adsorption configuration on the cluster Pt_nM. a, atop on Pt of Pt₃; b- H bridge along Pt-Pt of Pt₃; c-H atop on Pt of Pt₃; d-atop on Pt of Pt₂Sn; e- OH bridge along Sn-Pt of Pt₂Sn; f- atop on Pt of Pt₃Sn; g- OH bridge along Sn-Pt of Pt₃Sn; h- atop on Sn of V-shaped Pt₃Sn; i- atop on Ru of Pt₂Ru; j- atop on Ru of Pt₃Ru

Figure 3.

The electron density isosurface superimposed with electrostatic potential. The values in parenthesis refer to the isovalue.

Figure 4. Water atop adsorption on M site of Pt₆M and Pt₉Sn. In each panel the first one is side view and the second top view.

Figure 5.
The transition states for the bridge (left) and atop (right) decomposition pathways over the Sn site of Pt_2Sn .

Figure 6. Potential energy profile for water adsorption and dissociation on the M site of Pt_2M (M=Pt, Ru and Sn).

Figure 7. Potential energy profile for water adsorption and dissociation on the M site of Pt_nM ($n=6$ and 9 ; $M=Pt, Ru$ and Sn). The solid and dotted lines link the species from water adsorption and dissociation on Pt_6M and Pt_9M , respectively.

Figure 8.

The plot of the relative dissociation energy against the relative energy barrier for water dissociation over the M site of Pt_9M .

Table 1

The characteristics of ground state Pt_nM ($n=2-5$) cluster. 2S+1: Spin Multiplicity; q/e : Mulliken Charge Carried by M; $R/\text{\AA}$: Average Distance of the nearest neighbors Pt-Pt and Pt-M; E_b/eV : Average Binding Energy per Atom.

cluster	2S+1	q	R	E_b	HOMO	LUMO
H ₂ O	1				-0.32143	-0.01172
Pt ₃	1		2.499	1.87	-0.2158	-0.1470
Pt ₂ Sn	1	0.62	2.531	2.46	-0.2120	-0.1262
Pt ₂ Ru	5	0.56	2.510	1.91	-0.1903	-0.1152
Pt ₄	3		2.630	2.17	-0.1849	-0.1258
Pt ₃ Sn	3	0.68	2.636	2.61	-0.1912	-0.1442
Pt ₃ Ru	5	0.47	2.628	2.20	-0.1744	-0.1059
Pt ₄ *	5		2.557	2.03	-0.2156	-0.1708
Pt ₃ Sn*	1	0.68	2.590	2.55	-0.2117	-0.1422
Pt ₃ Ru*	7	0.79	2.544	2.22	-0.2047	-0.1411
Pt ₅	5		2.647	2.31	-0.2037	-0.1443
Pt ₄ Sn	3	0.78	2.676	2.71	-0.2073	-0.1425

* V-shaped cluster

Table 2

Water adsorption and decomposition over **M** site of Pt_nM (n=2 and 3; M=Pt, Sn and Ru) E_{ads} (eV): adsorption energy on M site; $R(\text{O-M}/\text{\AA})$: distance between H₂O oxygen and M; q (e): charge carried by adsorbed water; ν (cm⁻¹) and E_a (eV): imaginary frequency and activation energy for the transition state of adsorbed water decomposition; E_{diss} (eV): dissociation energy for the adsorbed water. The favorable E_a for the given adsorption were marked in red.

Adsorption Complex				Dissociation H ₂ O [*] →H [*] +HO [*]							
H ₂ O+ Pt _n M→H ₂ O-Pt _n M				Transition State				Energetic Data			
Pt _n M	2S+1	R(O-M)	E _{ads}	q	ν	R(O-M)	R(O-H)	HOH	E _a	E _{diss}	
Pt ₃ [*]	1	2.233	−0.79 (−0.69)	0.26	Atop	983	2.089	1.511	110	1.14(0.98)	0.34(0.23)
					Bridge	698	2.075	1.577	105	1.49(1.27)	0.22(0.10)
Pt ₂ [*] Sn	1	2.221	−0.79(−0.69)	0.21	Atop	957	2.089	1.514	105	1.05(0.90)	0.55(0.41)
					Bridge	531	2.168	1.738	102		
Pt ₂ Sn [*]	1	2.531	−0.52(−0.43)	0.21	Atop	1350	2.123	1.503	132	2.47(2.26)	0.82(0.69)
					Bridge	495	2.146	1.467	116	0.61(0.45)	0.35(0.21)
Pt ₂ [*] Ru	5	2.240	−0.80(−0.71)	0.17	Atop	1009	2.093	1.465	107	0.92(0.76)	0.23(0.11)
Pt ₂ Ru [*]	5	2.330	−0.78(−0.72)	0.09	Atop	1093	2.071	1.468		1.19(1.05)	0.35(0.23)
					Bridge	502	2.108	1.450	107	0.63(0.48)	−0.21(−0.33)
Pt ₄ [*]	3	2.237	−0.63 (−0.54)	0.22	Atop	1072	2.104	1.441	105	0.95(0.78)	0.03(−0.06)
					Bridge	400	2.089	1.601	106	1.30(1.11)	−0.03(−0.12)
Pt ₃ [*] Sn ^a	3	2.230	−0.80(−0.70)	0.24	Atop	870	2.089	1.587	101	1.42(1.25)	0.91(0.79)
					Bridge	510	2.085	1.593	105	1.30(1.12)	0.30(0.17)
Pt ₃ Sn ^{*a}	3	2.838	−0.20		Atop	1318	2.143	1.528		2.36	
Pt ₃ Sn ^{*b}	1	2.477	−0.53(−0.44)	0.26	Bridge	270	2.103	1.607	107	0.74(0.60)	0.64(0.48)
	5	2.253	−0.59(−0.49)	0.19	Atop	959	2.105	1.525	103	1.11(0.95)	0.08(−0.02)
Pt ₃ Ru ^{*a}	5	2.295	−0.56(−0.48)	0.08	Bridge	465	2.092	1.612	105	1.35(1.14)	−0.11(−0.22)
					Atop	1133	2.092	1.396	97	0.92(0.74)	−0.21(−0.37)
Pt ₃ Ru ^{*b}	7	2.325	−0.64(−0.57)	0.10	Bridge	445	2.104	1.481	103	0.53(0.35)	−0.55(−0.69)
					Bridge	675	2.105	1.471	107	0.72(0.56)	

Adsorption Complex				Dissociation $\text{H}_2\text{O}^* \rightarrow \text{H}^* + \text{HO}^*$				Energetic Data			
$\text{H}_2\text{O} + \text{Pt}_n\text{M} \rightarrow \text{H}_2\text{O-Pt}_n\text{M}$				Transition State							
Pt_nM	2S+1	$R(\text{O-M})$	E_{ads}	q	v	$R(\text{O-M})$	$R(\text{O-H})$	HOH	E_a	E_{diss}	
Pt_5^*	5	2.261	-0.62								
Pt_4Sn^*	3	2.552	-0.37								
Pt_5Sn^*	5	2.654	-0.12								

$E_{\text{ad}} = E(\text{Pt}_n\text{M-H}_2\text{O}) - E(\text{Pt}_n\text{M}) - E(\text{H}_2\text{O}); E_{\text{a}} = E(\text{TS}) - E(\text{Pt}_n\text{M-H}_2\text{O}); E_{\text{diss}} = E(\text{Pt}_n\text{M-OH+H}) - E(\text{Pt}_n\text{M-H}_2\text{O});$

^{*} Adsorption site;

^a and ^b refer to distorted tetrahedral and V-shaped Pt_3M clusters, respectively.

Table 3

Water adsorption and decomposition over **M** site of Pt_nM (n=6 and 9; M=Pt, Sn, Ru, etc.) E_{ads} (eV): adsorption energy on M site; $R(\text{O-M}/\text{\AA})$: distance between H₂O oxygen and M; q (e): charge carried by adsorbed water; ν (cm⁻¹) and E_a (eV): imaginary frequency and activation energy for the transition state of adsorbed water decomposition; E_{diss} (eV): dissociation energy for the adsorbed water

		Adsorption Complex**									Dissociation H ₂ O [*] →H [*] +HO [*]			
		Transition State					Energetic Data							
		2S+1	R(O-M)	E _{ads}	q	ν	R(O-M)	R(O-H)	E _a	E _{diss}				
H ₂ O														
	Pt ₇ _a	5	2.347	-0.43(-0.34)	0.44	844	2.044	1.512	1.14 (0.98)	5.26				
	Pt ₇ _b	3	2.332	-0.46(-0.36)	0.33					0.90				
	Pt ₆ Sn*_a	3	2.305	-1.30(-1.19)	0.37	425	2.083	1.529	0.60(0.45)	0.50(0.37)				
	Pt ₆ Sn*_b	3	2.417	-0.61(-0.53)										
	Pt ₆ Ru*_a	7	2.116	-1.25(-1.12)	0.51	880	1.973	1.431	0.67(0.50)	0.32(0.18)				
	Pt ₁₀ _a	3	2.367	-0.26(-0.14)	0.32	226	2.062	1.726	1.07(0.93)	0.67				
	Pt ₁₀ _b	3	2.255	-0.48(-0.35)	0.16	1085	2.095	1.480	1.19(1.03)					
	Pt ₆ Sn*_a	3	2.402	-0.80(-0.72)	0.33	412	2.085	1.539	0.78(0.64)	0.41(0.28)				
	Pt ₆ Sn*_b	5	2.579	-0.32										
	Pt ₉ Ru*	7	2.425	-0.39(-0.28)	0.39	522	2.048	1.554	0.96(0.81)	0.61(0.50)				
	Pt ₉ Rh*	2	2.200	-0.45	0.53	346	2.017	1.660	1.18(1.02)	0.87				
	Pt ₉ Pd*	3	2.364	-0.37	0.38	308	2.027	1.848	1.36	1.20				
	Pt ₉ Re*	4	2.192	-1.25	0.42	1127	2.042	1.378	0.71	-0.43				
	Pt ₉ Cu*	4	2.414	-0.52	0.47	616	1.949	2.146	1.81(1.60)	1.60				

* adsorption site;

** Pt₁₀M*_a and Pt₁₀M*_b stand for adsorptions on the central and peripheral M atoms, respectively.

Table 4Variation of Activation Energy of water decomposition on Pt_nM

	M	Ea/eV	Δ Ea/eV
Pt ₂ M	Sn	0.61	0.0
	Ru	0.63	0.03
	Pt	1.14	0.53
Pt ₆ M	Sn	0.60	0.0
	Ru	0.67	0.07
	Pt	1.14	0.54
Pt ₆ M	Sn	0.78	0.0
	Ru	0.96	0.18
	Pt	1.07	0.29

Table 5Electric Field Effects on Water Decomposition over **M** site of Pt_nM ($n=6$ and 9 ; $\text{M}=\text{Pt}$, Sn , and Ru).

Electric Field/a.u	Pt₇	
	E_{ap}/eV	E_{dis}/eV
0	1.14	0.90
0.001	1.40	0.88
0.01	1.42	0.65
-0.001	1.41	1.03
Pt₆Sn		
0	0.60	0.50
0.001	0.46	0.38
0.01	0.38	0.19
-0.001	0.29	0.21
Pt₆Ru		
0	0.67	0.32
0.001	0.66	0.29
0.01	0.51	0.08
-0.001	0.69	0.34
Pt₁₀		
0	1.07	0.67
0.001	1.20	0.77
0.01	1.21	1.02
Pt₉Sn		
0	0.78	0.41
0.001	0.99	
0.01	1.06	0.99
Pt₉Ru		
0	0.96	0.61
0.001	0.99	0.61

	Pt_7	
	E_f/eV	E_{dis}/eV
Electric Field/a.u		
0.01	1.22	1.34