Article

Theoretical Study of an almost Barrier-Free Water Dissociation on a Platinum (111) Surface Alloyed with Ruthenium and Molybdenum

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ABSTRACT: A theoretical study based on density functional theory for H_2O dissociation on the metal surface of Pt(111) alloyed simultaneously with Ru and Mo was performed. The determination of the minimum energy path using the climbing image nudged elastic band (CI-NEB) method shows that the dissociation reaction of H_2O with this catalyst requires almost no energy cost. This dissociation reaction is not only kinetically favored but also almost thermodynamically neutral and somewhat exothermic. The electronic structure analysis showed that much more charge was released in Mo and was used to bind the adsorbed hydroxyl (OH_{ad}). Further analyses of the density of states (DOS) showed that the large number of orbitals that overlap when OH binds to Mo are responsible for the stabilization of the OH-surface bond. The stability of the OH_{ad} fragment on the surface is believed to be a descriptor for the dissociation of H_2O with an almost spontaneous process.
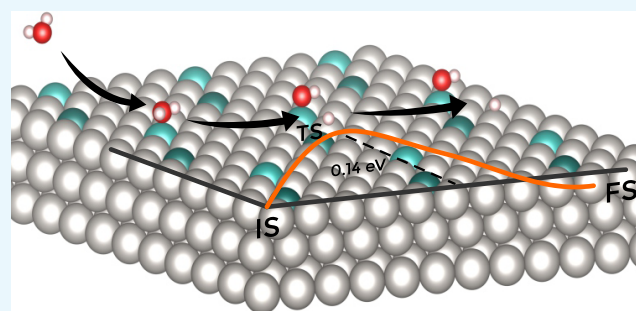
1. INTRODUCTION

The dissociation of water (H_2O) molecules into hydrogen (H) and hydroxyl (OH) is one of the most important things in chemical reactions in connection with industrial processes and has been discussed for eight decades.[1] This work was done to provide evidence of experiments to measure the dissociation energy of $H_2O \rightarrow H + OH$ that were previously developed photochemically[2] or using the explosion method.[3] Using their own unique method, Lewis and von Elbe predicted the activation energy required to dissociate the water molecule. In addition to technological advancements in recent years, the dissociation of water molecules catalyzed by metal surfaces can also be found in energy-supply technologies of nuclear reactors[4] or fuel cells.[5] Studies of the interaction of water molecules with group 4 metal oxides to understand hydrolysis reactions have become a trend for physicists and chemists.[6−9] The important result of this interaction is that the dissociation of H_2O is still relatively easier than the process of the formation of hydrogen (H_2) and oxygen (O_2) molecules.[9] However, the dissociation of H_2O to H and OH is still an important step in the water gas shift (WGS) reaction.[10,11] Our main emphasis is the interest to study the reaction mechanism of H_2O dissociation on the metal surface. A well-known example of the dissociation of $H_2O_{ad} \rightarrow H_{ad} + OH_{ad}$ on the metal surface is an intermediate step in the Langmuir−Hinshelwood (LH) process of the CO oxidation reaction.[12] The subscript "ad" indicates that the species are in the absorbed phase.

When discussing the dissociation of H_2O with respect to the CO oxidation reaction, one might consider modifying a platinum-based (Pt) catalyst to optimize the electrooxidation process that researchers have long adopted. One of the efforts that has been made for several decades is to add other metals to Pt catalysts. Some metals that are still used to alloy Pt are ruthenium (Ru),[13,14] molybdenum (Mo)[14,15] as well as both Ru and Mo simultaneously.[15,16] It has been shown that these metals improve CO tolerance when reacting to catalysts. Existing explanations in the literature for the use of Pt(111)-substituted Ru and Mo catalysts come from experimental studies. We have not yet found a theoretical explanation or density functional theory (DFT) studies for the advantages of the system. In particular, there is no detailed explanation for each specific intermediate step, such as water dissociation on the metal catalyst of alloyed Pt(111). This explanation is very important to clarify the details of the mechanisms that take place during the overall reaction. This paper aims to explain the details of energetics and reaction mechanisms of H_2O dissociation on the Ru- and Mo-alloyed Pt(111) surface based on density functional theory.

2. COMPUTATIONAL DETAILS

We adopt the surface model of Pt−Ru−Mo in our latest work[17] to study the dissociation of water. Indeed, this research is a continuation of efforts to understand in detail the electrochemical reactions on metal surfaces in relation to hydrous molecules. Since previous work has shown that, of the surface models introduced, a water monomer interacts preferentially with Pt(111)−Ru−Mo, we now study the behavior of this surface in catalyzing the water monomer. This paper specifically discusses the effect of the substitution of Pt atoms on the Pt(111) surface by Ru and Mo atoms simultaneously in catalyzing the dissociation of water molecules. In the experiments, the concentration of the Ru and Mo atoms that are substituted on the Pt surface is kept small.[16,18] This situation is modeled by a metal surface made up of three-layer slabs with 16 atoms in each layer, resulting in a process of 1/16 ML H_2O coverage on the surface. This three-layer surface model has been tested to match the condition of the actual surface, taking into account the minimum formation energy, surface segregation of additional metals, and bulk representation of the bottom layer. The vacuum between the slabs is set at ~15 Å to ignore the interaction between the substrates and the adsorbates in the next cell.

Periodic density functional theory was used through Vienna Ab initio Simulation Package (VASP)[19,20] to calculate the total energy. Projector augmented wave (PAW) formulation[21] was used to treat the rapid oscillation of valence wave functions as they approach ion cores. Moreover, in this work, we applied the generalized gradient approximation (GGA) with Perdew−Wang (PW91) exchange−correlation functionals[22,23] and a cutoff energy of 400 eV. The dissociation process of a water molecule catalyzed by the surface of the Pt−Ru−Mo alloy was simulated by atomic relaxation. This convergence criterion for ion relaxation is considered to be fulfilled if the change in eigenvalue in adjacent iterations is less than 10^{-4} eV. For the calculation of the Brillouin zone integral, we use a $5 \times 5 \times 1$ k-point grid from the Monkhorst and Pack platform[24] with a Methfessel−Paxton smear[25] of 0.2 eV. In addition, to describe the H_2O dissociation on the Pt−Ru−Mo(111) surface, we used the climbing image nudged elastic band (CI-NEB)[26,27] to determine the minimum energy paths and transition states. In this case, the transition states (TSs) are confirmed using vibrational frequency analysis. Calculations of the vibrational frequency itself are performed using the finite difference method. Furthermore, the adsorption energy was calculated using the formula $E_{ads} = E_{tot} - E_{adsorbates} - E_{surfaces}$, where E_{tot} represents the total energy of the entire system, $E_{adsorbates}$ denotes the total energy of the adsorbates, and $E_{surfaces}$ is the total energy of the surface system. When calculating the adsorption energy, we took into account the zero point energy (ZPE) corrections. The activation energy (E_a) is then calculated from the difference between the total energy of transition states (E_{TS}) and the initial states (E_{IS}) as $E_a = E_{TS} - E_{IS}$, while reaction energy (E_r) is defined as $E_r = E_{FS} - E_{IS}$. Likewise, the charge distribution difference $\Delta\rho(\vec{r})$ is defined as $\Delta\rho(\vec{r}) = \rho_{OH+H/surf}(\vec{r}) - (\rho_{OH+H}(\vec{r}) + \rho_{surf}(\vec{r}))$, where $\rho_{OH+H/surf}(\vec{r})$ is the charge density of the adsorbate on the surface, $\rho_{OH+H}(\vec{r})$ represents the charge density of the adsorbate, and $\Delta\rho_{surf}(\vec{r})$ is the charge density of the related surface.

3. RESULTS AND DISCUSSION

Screening for the most preferred sites for the interaction of H_2O molecules and OH + H fractions with the Pt−Ru−Mo surface was carefully performed. In our proposed surface model, a water molecule on the PtRuMo surface absorbed at the top of the Mo atom.[13,17] Since the adsorption of H_2O molecules over Pt(111)−Ru−Mo is strongest compared to other alloy models, this interaction is dissociative according to the predictions of Hammer and Nørskov.[28] The results of our simulation for modeling the H_2O dissociation on the PRM surface are described as follows. The energy profile for the H_2O dissociation is then shown in Figure 1. IS, TS, and FS
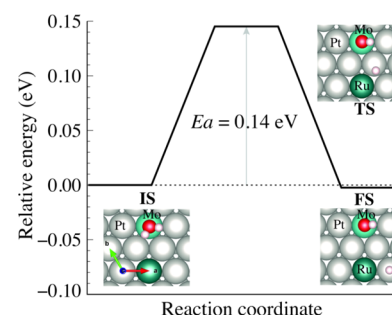

Figure 1. Energy barrier for the dissociation of the water monomer to form OH_{ads} and H_{ads} on the Pt−Ru−Mo surface. The inset images are the geometric structures of the initial, transition, and end states.

denote the initial state, transition state, and final state of the water dissociation reaction, respectively. The associated adsorption energies for IS, TS, and FS of the water dissociation reaction are 1.50, 7.38, and 6.79 eV, respectively. The geometrical structure of these states appears in the insertion of the respective relative energy of Figure 1. It can be seen from Figure 1 that the dissociation of water is activated at a barrier of 0.14 eV. It is much lower than that of pure Pt(111), Pt(111)−Ru, and Pt(111)−Mo surfaces. Our calculation of the water dissociation on pure Pt(111) showed that a barrier of 0.64 eV is required. We compare the result with the case of the Pt(111) surface as we can compare it with other DFT calculations. Our result for the activation energy of H_2O dissociation on Pt(111) agrees well with Kauppinen et al.[10] and Wang and Hammer.[29] On the Pt(111) surface, H_2O dissociation is an endothermic reaction with an energy of 0.52 eV. It also agrees perfectly with other DFT calculations[8] and experiments.[30] A further comparison with other surface models, as described in our previous work,[17] showed that Pt(111) substituted with Ru and Mo at the same time is the lowest barrier to H_2O dissociation. Alloying Pt(111) with only Ru atoms reduces the activation energy to 0.56 eV, and the reaction is endothermic at 0.36 eV. If we compare it with the case of a monomer water dissociation barrier on the Ru cluster,[31] it has a very similar value of activation energy, which is 0.01 eV lower according to our calculation. The combination of Pt(111)−Mo surfaces causes the activation of H_2O_{ad} to OH_{ad} and H_{ad} with an energy consumption of 0.20 eV, and the reaction energy is 0.08 endothermically. We can see here that of the proposed models, the Pt−Ru−Mo surface gives the lowest energy barrier for H_2O dissociation. In general, our proposed models for alloying Pt with a small amount of transition-metal catalyst, the combination of Ru and Mo, are the best candidates for H_2O decomposition. As seen in Figure 1, the dissociation reaction between the reactant and product is
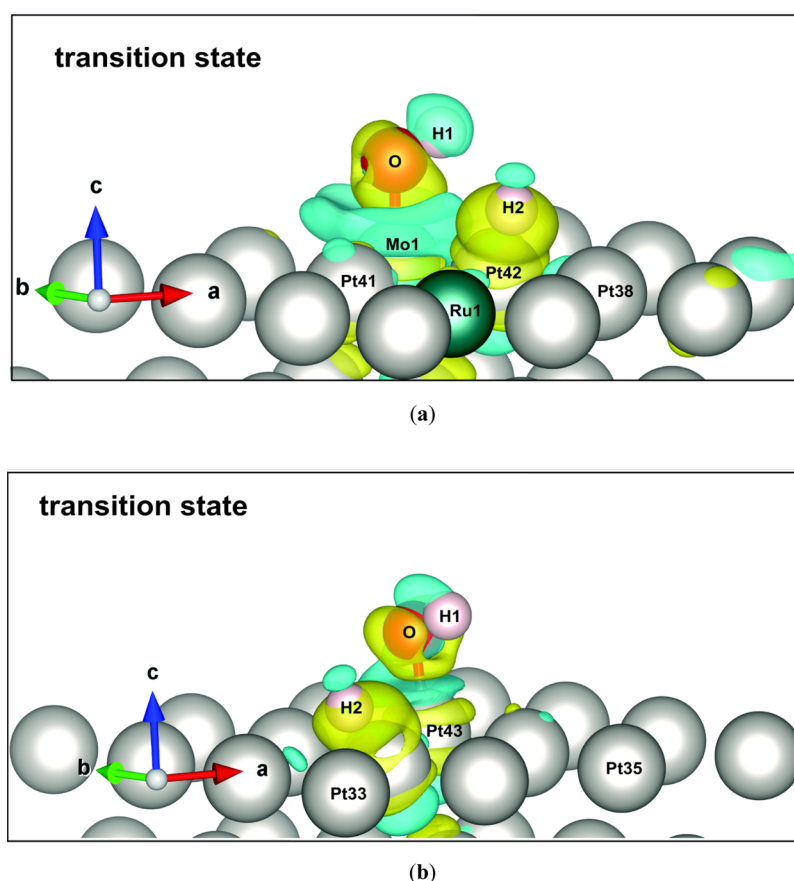
Figure 2. Charge density difference distributions of the transition states of the dissociation of the water monomer on (a) Pt−Ru−Mo and (b) Pt surfaces.

almost thermoneutral or slightly exothermic on this Pt−Ru−Mo surface as well. This means that among the Pt-based catalyst models that we have introduced, water dissociation is thermodynamically favorable only on the Pt−Ru−Mo surface. From this result, it is therefore interesting to further discuss the unique behavior of the Pt(111)−Ru−Mo catalyst in terms of the electronic structure of the interactions that occur during this dissociation process.

First, we discuss the charge density analysis in this electronic structure. What is important in this dissociation process is the transition state. At the transition state, the OH_{ad} site retains its original location, indicating that the top of Mo is the most preferred site for both H_2O molecules and OH fractions. The dissociation of a H_2O monomer on Pt(111)−Ru−Mo occurs by stretching a H atom until the energy passes the transition state and then continuously moving further to a final state in which the H_2O is completely broken. Figure 2 shows the charge distribution of the H_2O dissociation in the transition state for the case of the Pt−Ru−Mo catalyst (a) compared to that of the pure Pt catalyst (b). The yellow regions indicate the accumulation of charge, while the blue areas indicate electron depletion. In Figure 2a, it can be seen that the blue area around the Mo atom, the place where the direct interaction between the surface and the OH fragment occurs, is large enough. On the other hand, Figure 2b shows that only a small portion of the blue region appears over the Pt atom that is in contact with OH. This shows that there is a charge redistribution in TS, with the reduced charge in Mo being greater than the Pt atom on the pure Pt surface when interacting with the OH fraction.

Bader's charge analysis also supports this interpretation by showing the result that 0.37 electrons were lost from the Mo atom of the Pt(111)−Ru−Mo surface in transition states. However, the Pt atom of the pure Pt(111) surface is only deficient by 0.02 electrons upon interaction with the adsorbate. The same feature observed in Figure 2a,b is the charge accumulation over the O atom and the depletion region around the H atom of OH that are bound to the surface. This indicates the polarity between O and H of adsorbed hydroxyl groups formed by the dissociation of the water monomer. Bader's charge analysis shows that the same electron density is redistributed into the H atom of adsorbed hydroxyl group on both surfaces; this suggests that the polarity of OH does not significantly affect the dissociation process of water. Therefore, the factor to be discussed, since it is believed to affect the activation energy and reaction energy of dissociation of the water monomer, is the depletion area on the Mo atom, which is larger than the Pt atom.

From the depletion zone shown in Figure 2, we still cannot confirm where the electrons went. To support this analysis, the charge profile and partial density of states (PDOS) of the dissociation process in TS are presented. Figure 3 shows the charge density profile and the PDOS of the orbitals involved in bond formation between OH and the substrate. It turns out that the loss of electrons from Mo is probably used to bind to the OH group that remains absorbed at the top of the Mo. A careful study of the Bader analysis shows that the Pt atoms surrounding the Mo atom change slightly when they interact with the adsorbate. The contribution of the Mo atom is 5 times
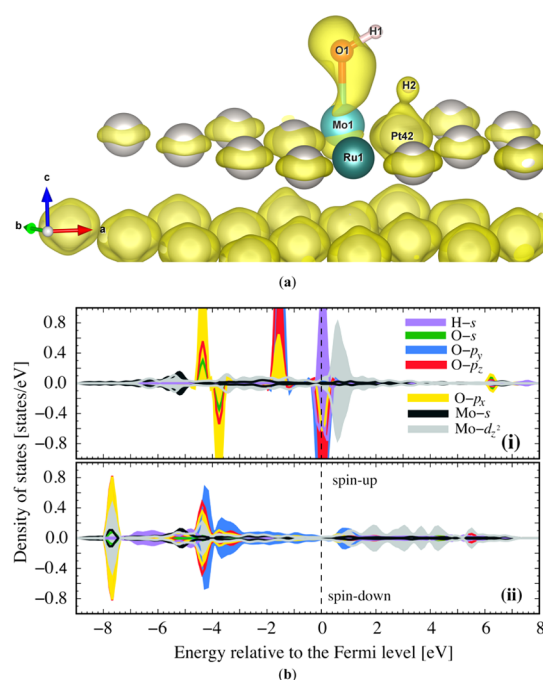
Figure 3. Plot of (a) partial charge density in the energy range of −4.8 to −4.0 eV of the transition states of the water monomer dissociation on the Pt−Ru−Mo surface and (b) associated partial density of states of separated H-s; hydroxyl's O-s, O-p_y, O-p_z, and O-p_x; and Mo-s and Mo-d_{zz} of the surface. The notations (i) and (ii) represent the system before and after the interaction.

greater than the largest contribution of the nearest Pt atom. The Mo on the Pt(111)−Ru−Mo surface stabilizes OH more strongly than on the pure Pt surface. This is supported by our calculation of the vibrational frequency of 642 cm^{-1} of the Mo−O stretching mode. This value is much greater than the vibrational frequency of the Pt−O stretching, which is only 514 cm^{-1}. In a further discussion with other prepared surface models, the vibrational frequencies in the stretching mode for Mo−O and Ru−O on Pt(111)−Mo and Pt(111)−Ru were 560 and 544 cm^{-1}, respectively. Compared with the IS of adsorption of water monomer on Pt(111) and Pt(111)−Ru−Mo surfaces, it is calculated that both give a higher vibrational frequency of the surface−O stretching mode. For initial state, the Mo−O stretching mode was 324 cm^{-1}, while the Pt−O vibration in the same mode was 189 cm^{-1}.[17] Visual observation of the geometrical structure of the bond length between O and the atomic surface also shows that Mo−O is shorter than Pt−O. It is noted that in TS, the bond length of Mo−O is 1.89Å, while that of Pt−O is 1.99 Å. Again, the Mo−O bond length is the shortest distance compared to the pure Pt and Pt−Ru surface models, which are not discussed in this article. Based on the data of the vibrational frequency and the surface−O bond length at TS, it can be seen that OH is most strongly adsorbed on the Mo of Pt(111)−Ru−Mo among other models. Unfortunately, in this case, there are no direct comparative data on the surface model, which is exactly identical to Pt(111)−Ru−Mo in terms of bonding with OH. An important piece of information is that OH is strongly bound to the MoS$_2$ surface.[32] The stability of OH when it binds to the surface could be related to the low activation barrier in the separation of the H fraction from adsorbed OH in the H$_2$O monomer dissociation process. During the dissociation process of the H$_2$O monomer in TS, the stable

bond between Mo and O is visualized by a charge profile that mainly accumulates around the O atom, as shown in Figure 3a. This is probably due to the higher electronegativity of O than that of Mo. The electronegativity difference between O and Mo is the largest compared to the electronegativity difference between O−Ru and O−Pt. This can also influence the behavior of Ru on Pt(111)−Ru and Pt(111)−Ru−Mo surfaces. From the Bader analysis, we found that Ru in Pt(111)−Ru−Mo acts as an electron donor in the transition states (TS) in contrast to Ru in Pt(111)−Ru, which accepts electrons. The proportion of electrons released from Ru in Pt(111)−Ru−Mo is 8 times the charge that Ru receives in Pt(111)−Ru. Compared to the Mo atom in the Pt(111)−Mo alloy, the Ru atom in Pt(111)−Ru−Mo also donates a 1.5 times higher charge than the Mo atom in Pt(111)−Mo. Based on these data, we propose that electron donation from the Ru in Pt(111)−Ru−Mo also affects the stabilization of OH and pushes the residual H to separate completely upon H$_2$O dissociation. Then, from the ionicity perspective of the H$_2$O dissociation on the Pt(111)−Ru−Mo surface, we observe that the most ionic character is shown in the transition states (TS). In this TS, the hydroxyl group bonded to the Pt(111)−Ru−Mo surface, which begins to separate from the hydrogen atom, receives the highest charge compared to other surface models. This is probably due to the contribution of the Ru atom, which also releases the most charge compared to the alloyed metals on other surfaces. Moreover, the bond between OH and Mo can be further explained by DOS analysis. In Figure 3b, it is clear that the strong bond between Mo and O is mediated naturally by the nucleophilic OH and the electrophilic Mo. The peaks of the filled and empty orbitals of each representative atom are close together and both orbitals have a high probability of overlapping. The overlap of the orbitals of the OH adsorbed on the surface can be seen in Figure 3b(ii). As seen in Figure 3b(ii), the separated H atom does not overlap with the orbitals of OH$_{ad}$ after the interaction. This shows that the interaction between separated H and OH in the TS is now very weak. Thus, we can conclude that the more the overlap, the higher the mixing. Hence, the interaction that is formed should be stronger. On further consideration, it appears that the location of the mixed orbitals that are formed is relatively close to the Fermi level for both bonding and antibonding states. This also implies that the OH adsorbed system is still reactive so that complete dissociation is more easily facilitated.

4. CONCLUSIONS

In the present work, we report the results of the first-principles calculation for the dissociation of H$_2$O on the Pt−Ru−Mo surface. The calculation of the transition states with the CI-NEB method led to the conclusion that this catalyst model facilitates the H$_2$O cleavage with almost no barrier. By adding the combination of these two metals to the Pt catalyst, the reaction could also be almost thermoneutral with a tendency to exotherm. From an energetic point of view, it is observed that the dissociation reaction mechanism took place through the elongation of the H atom until finally H$_2$O is completely broken. The low barrier to this dissociation process of the H$_2$O monomer is most likely related to the strength of the surface-OH bonds. A detailed analysis of the electronic structure shows that Mo donates a lot of electrons to form strong bonds. Apart from that, due to the different electronegativities with Pt and Mo, Ru also donates more electrons in this surface system.

In addition, the large number of overlapping orbitals in the TS and the position of the overlapping orbitals near the Fermi level are believed to be indicative of the catalyst reactivity causing a low activation barrier. Therefore, the results may be a consideration in the choice of a platinum-based catalyst for H_2O separation reactions in view of atomic composition.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00389.

Atomic coordinates in a unit cell and related data; adsorption energy of associated adsorbate(s) in the initial, transition, and final states; and activation energy of H_2O dissociation for the following surface models: Pt(111)−Ru−Mo (Figure S1), Pt(111)−Mo (Figure S2), Pt(111)−Ru (Figure S3), and Pt(111) (Figure S4) (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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