

Reactive Molecular Dynamics Simulation of Hydrogen/Oxygen Adsorption and Dissociation on Pd/TiO₂

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Abstract

Dynamic processes of adsorption and dissociation of hydrogen and oxygen are of theoretical and practical importance in the field of combustion and energy. In the present study, reactive molecular dynamics (RMD) is employed to simulate the relevant phenomena associated with adsorption and dissociation of hydrogen and oxygen under the influence of TiO₂ supported Pd catalyst. A comprehensive parametric study has been conducted by varying key parameters such as the temperature. The MD results show qualitative agreement with experimental results while revealing the detailed dynamic catalytic process of H₂ and O₂ reactions at the atomic scales.

1. Introduction

Hydrogen is regarded as the cleanest fuel with zero CO₂ emissions. Meanwhile the hydrogen or hydrogen rich fuels are a promising option for the high energy-density devices. Potential applications include micro-combustors and internal combustion engines [1, 2]. For micro-combustors, the surface-to-volume ratio is very high so the heat loss rate is quite large and flame quenching (via the quenching of radicals on the wall) is much more frequent. Both the ignition and flame stabilization are difficult to achieve under such circumstances. Typically, catalysts are required for low-temperature oxidation and combustion as they can lower the activation energy, reduce the ignition temperature as well as the emission of pollutants. Hence, combustion process in microreactors and especially nanoreactors may benefit from the catalyst-assisted reactions. For example, the titania-supported palladium (Pd/TiO₂) nanoparticles have been widely used as the catalyst in the low-temperature methane catalytic oxidation reactions [3, 4]. Both experiments and numerical simulations have been attempted to reveal the mechanism of the catalytic combustion process of H₂/O₂ on the surface of palladium (Pd), platinum (Pt) and some other transition metals [5-7].

The heterogeneous catalytic reaction process can be divided into the following five steps [8]. The gas phase reactants firstly diffuse and collide with the surface of the catalysts. Some may be reflected back into the gas phase, while others adsorb on the surface. It can also be divided into physical adsorption and chemical adsorption process. The former means that the adsorption will not lead to the bond-breaking of the reactants, so the adsorbate may diffuse back into the gas phase. With the chemical adsorption, the reactant molecules subsequently dissociate to form the respective molecule-catalyst complexes. After that the reaction may be between either two adsorbed molecules or an adsorbed molecule and a molecule in the gas phase. Finally, the products formed are then desorbed from the surface and diffuse back into the gas phase. Among them, the dissociative adsorption

of molecules is a crucial reaction step in most catalytic processes at surfaces [9]. The traditional experiments [5, 8] focus on the ignition temperatures and the activation energy for catalytic reactions. Numerical CFD methods [6,7] have applied a 2-D elliptic fluid mechanical model with multicomponent transport and elementary hetero/homogeneous reaction schemes to predict the ignition distance, ignition temperature and so on; Wang [10] has applied the ab initio molecular dynamics simulation to investigate the catalytic mechanism of CO oxidation on Au/TiO₂. In their simulation, through calculation, they directly connected the O₂ molecules at the interface and CO molecules on the Au surface. Groß [11] also did AIMD simulations to investigate the hot dynamics of H₂ after dissociative adsorption on Pd (100). He found that the energy dissipation to the substrate will determine the mean distance of the two H atoms after adsorption.

However, little work has been reported on the dynamic adsorption and dissociation processes of H₂ and O₂ on the TiO₂ supported Pd nanoparticle catalyst. In the present study, reactive molecular dynamics (RMD) is employed to simulate the adsorption and dissociation of hydrogen and oxygen on the TiO₂ supported Pd catalyst. By utilizing the ReaxFF potential rather than any classic intermolecular potential, we can accurately simulate the reactive processes. The temperature influence on the adsorption and the dissociation sites is investigated. Moreover, the subsequent reaction of the dissociated radicals of O₂, which was reported in [4], is studied in detail.

2. Computational Details

2.1 ReaxFF MD Simulation

The state-of-the-art ab initio quantum chemical methods (QC), which calculate electron behavior and are accessible to describe chemical reactions, generally are expensive and limited to small systems, with spatial and temporal scales on the order of tens of atoms and picoseconds, respectively [12]. Though classical molecular dynamics (MD) simulations are able to

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describe systems with hundreds of thousands of atoms using empirical force fields with rigid connectivity, they are not capable of describing chemical reactions [13]. The ReaxFF reactive force field method has been developed by van Duin et al. [14, 15, 16] to bridge the gap between the quantum chemical methods (QC) and the classical molecular dynamics (MD) simulations. A bond order / bond-energy relationship and a charge equilibrium scheme (QEq) are employed to calculate the charge and atomic polarization properties to update the bond-order information directly from instantaneous interatomic distances. The parameters in the force field are developed based on fitting ab initio quantum mechanics results, therefore providing an accurate description of bond breaking, bond formation and charge transfer. It has already been used to investigate the various reaction intermediates as well as for reactants and products, especially for the combustion processes of hydrocarbon and the pyrolysis of coal.

The ReaxFF reactive force field of Ti/O/Pd/H was trained by Addou & Senftle et al. [17] to study the hydrogen transfer between the TiO₂ surface and Pd clusters of varying size. The force field parameters are fitted to a set of Density Function Theory (DFT) results of the adsorption energies of hydrogen and Pd single atoms and clusters on the TiO₂ (011)-2×1 surface. Meanwhile the simulation results with the ReaxFF reactive force field are in good agreement with the STM experimental data, which implies the ReaxFF is well suited to investigating the interaction between Pd and TiO₂ surface and the behavior of H₂ and O₂ on them. In the present simulation, the dynamic processes of H₂/O₂ adsorption, diffusion and dissociation on the TiO₂ anatase (101) supported Pd nanocluster are investigated with the large-scale atomic/molecular massively parallel simulator (LAMMPS) package [18]. The ReaxFF force field is employed as an external library to the LAMMPS. MD calculations with a ReaxFF reactive force field are capable of simulating larger systems with longer time scales than quantum mechanism methods. The dynamics of Newton's equations of motion are integrated using the Velocity-Verlet algorithm using a time step of 0.25 fs. Before the MD simulations, the Pd/TiO₂, H₂ and O₂ firstly undergo energy minimization with a steepest descent algorithm, separately. Upon dynamics simulations, the system of Pd/TiO₂ is equilibrated at 373K, 573K and 873K using the canonical ensemble (NVT) for 100ps, which is enough to reach temperature equilibrium. The Nose-Hoover chain thermostat is applied for temperature control [19]. After that the H₂ and O₂ molecules are added in the vacuum above the Pd/TiO₂. Then the processes of the adsorption, diffusion and dissociation are simulated in the canonical ensemble (NVT) for 200ps.

2.2 Model Construction

For the flame-made Pd/TiO₂ catalyst by Li et al. [4], the controlled lattice of TiO₂ is anatase (101). Therefore in the present simulation, the TiO₂ anatase (101) surface is modeled by a periodic anatase (101) slab with (10 × 10)

unit cells in the x and y directions parallel to the surface that contains eleven layers of TiO₂. In the simulation, we keep the uppermost six layer free to move while the five bottom layers are kept fixed at the bulk geometry. A Pd cluster of 43 atoms (denoted as Pd₄₃) is obtained by cutting from the fcc bulk Pd. Its diameter is about 1nm, which is within the size of clusters in experiments of fuel cell catalysis application (i.e., 1-5 nm) [20, 21]. The initial structure of the Pd₄₃ cluster supported on the anatase (101) slab is situated ~ 2 Å away from TiO₂ surface and in the center region of the x-y plane. The vacuum region in the z direction above the TiO₂ surface is 80 Å, which is filled by 10 molecules of H₂, O₂ and H₂ / O₂ (1:1 ratio), separately. Periodic boundary conditions are applied in the x and y directions and a fixed wall is positioned in the top of the z direction to reflect gas molecules.

3. Result and Discussion

3.1 Molecular Adsorption and Dissociation of H₂ on Pd/TiO₂ Surface

The adsorption and dissociation of H₂ molecules on the catalyst are the initial step of the reaction. Here we run simulations of pure H₂ molecules in the Pd/TiO₂ system at T = 373 K, 573K and 873 K in the canonical ensemble (NVT). The initial pressure is about 3 atm with 10 H₂ molecules in the gas phase to investigate the influence of temperature on the H₂ behavior. The temperatures and pressure are within the experiment setting [5-8]. The initial positions and orientations of H₂ molecules are chosen randomly, and the velocities are in the Boltzmann distribution of the target temperature. From the trajectory of H₂ molecules, we find that not all collisions of H₂ with Pd cluster or TiO₂ slab are efficient, most may reflect back into the gas phase. Some of the physical adsorption may also take desorption from the catalyst surface. At T = 373 K, in the 200 ps simulation period, we find nearly all the H₂ molecules adsorb on the TiO₂ surface, but no dissociation of H₂ is found. At T = 573 K, the adsorbed H₂ molecules all appear on the TiO₂ surface but the number of the adsorbed molecules is smaller than that of T = 373 K. Moreover, the H₂ molecules diffuse on the TiO₂ surface and then dissociate at the Pd/TiO₂ interface. The detailed behaviors of H₂ molecules in the Pd/TiO₂ system at 873K are shown in Figure 1. With higher temperature, H₂ molecules take two dissociation paths. Some H₂ molecules may directly collide and diffuse on the surface of Pd cluster, subsequently dissociate on the Pd surface, as shown from t = 0.45 - 0.55 ps in Figure 1. This process does not happen in the low temperature cases. This is mainly because with higher temperature, the H₂ molecules may have higher kinetic energy which leads to a higher percentage of effective collision with the Pd surface. However, most of the H₂ molecules firstly adsorb on the TiO₂ slab. Then they diffuse on the surface of Pd cluster.

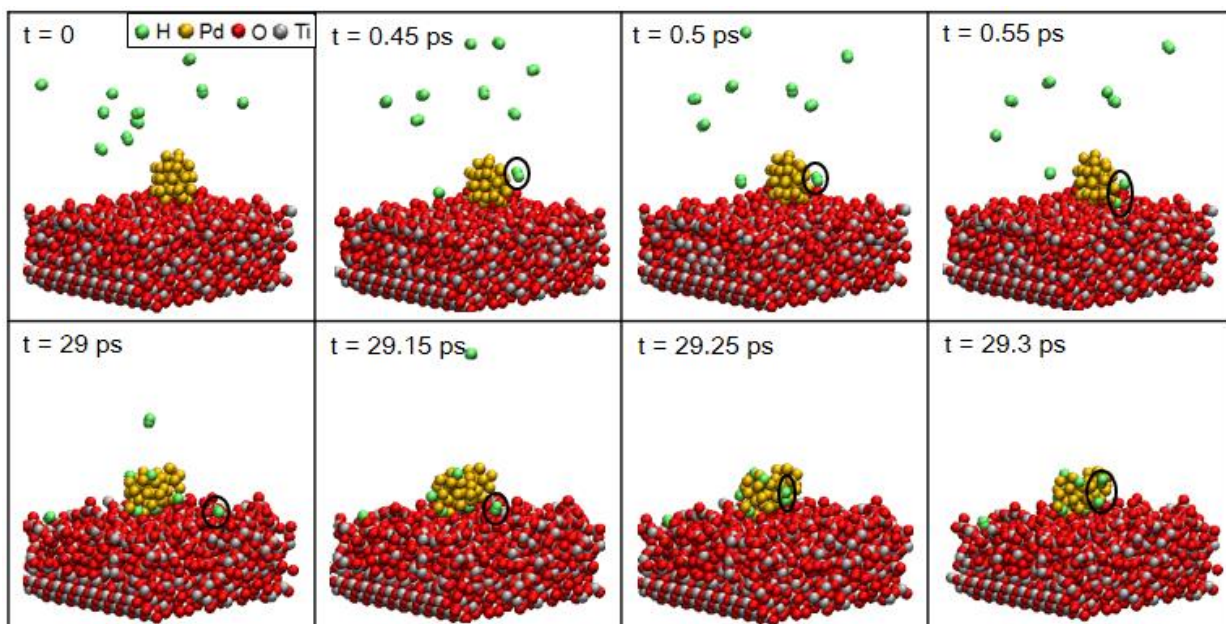


Figure 1. Snapshots of H_2 molecules dissociate on the surface of Pd cluster ($t = 0.45\text{-}0.55$ ps) and at the interface of Pd cluster and TiO_2 slab ($t = 29\text{-}29.3$ ps) at 873K. The exact H_2 molecules are highlighted in black circles.

The diffusion and dissociation trajectories of H_2 molecules on the TiO_2 anatase (1 0 1) surface are present in Figure 2 from the projection of x and y axes. The initial sites of two H_2 molecules are indicated by the bigger filled circles whereas the open circles denote positions of

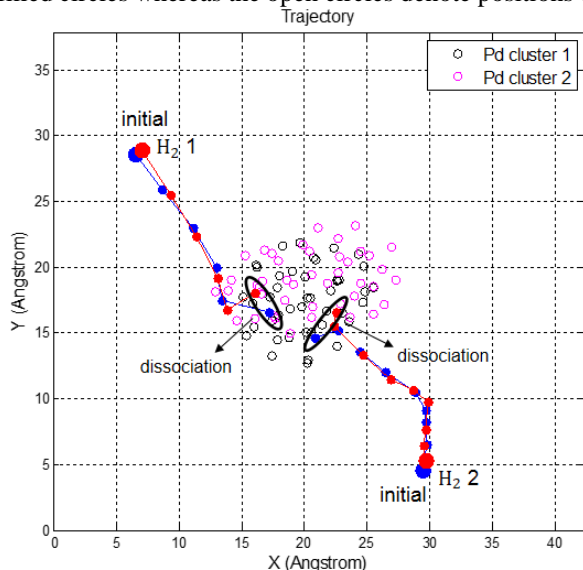


Figure 2. Diffusion trajectories of two H_2 molecules (denoted as H_2 1 and H_2 2) on the TiO_2 slab after adsorption and dissociation at the Pd/ TiO_2 interface at 873 K. The X and Y coordinates are in the same sizes with the TiO_2 slab, the atoms in Pd cluster are shown in black and magenta hollow circles and placed in the center of the TiO_2 slab. The black hollow circles located at the dissociation moment of H_2 1 and the magenta ones are for H_2 2. Two H atoms in a H_2 molecule are colored in red and blue and the initial sites are shown with bigger atom size. Pd atoms at the moments of H_2 dissociations. The black ones correspond to H_2 1, which dissociates at about 6 ps, and the magenta ones are to H_2 2, at about 30 ps. From Figure 2 we may easily find the structure of the Pd cluster deforms and atoms in the cluster will slightly diffuse on the TiO_2 slab during the H_2 dissociation and H diffusion.

The trajectories of H_2 molecules illustrate that H_2 molecules diffuse on the surface of TiO_2 to the interface of Pd/ TiO_2 and dissociate at the interface, which is consistent with what we have observed in Figure 1.

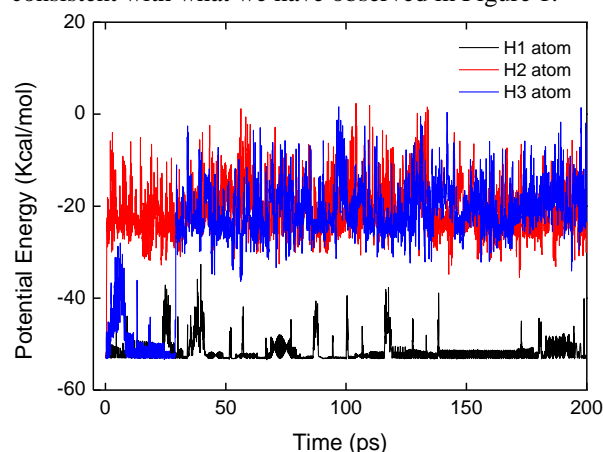


Figure 3. Potential energy of H atoms during the simulation of 200 ps at 873K. The black line is the potential energy of H in a H_2 molecule. The red line and blue line are the potential energy of H atom before and after dissociation from a H_2 on the Pd surface and at the interface of Pd/ TiO_2 , separately.

Potential energy of H atoms in the simulation of $T = 873\text{K}$ is tracked in Figure 3. Here we choose three H atoms of different H_2 molecules. The value of the black line is nearly constant in the whole simulation with only several weak fluctuations, which presents the H_2 adsorption on the surface. However, it does not dissociate in the whole simulation period. For the red line and the blue line, they are the potential energy of atoms in the H_2 molecules discussed in Figure 1. The red line represents the H atom dissociated directly after colliding on the surface of Pd. And the blue one is for the H atom dissociates at the interface of Pd/ TiO_2 . In both cases, after the dissociation, the potential energy rises sharply from about -52.5 Kcal/mol to -22 Kcal/mol,

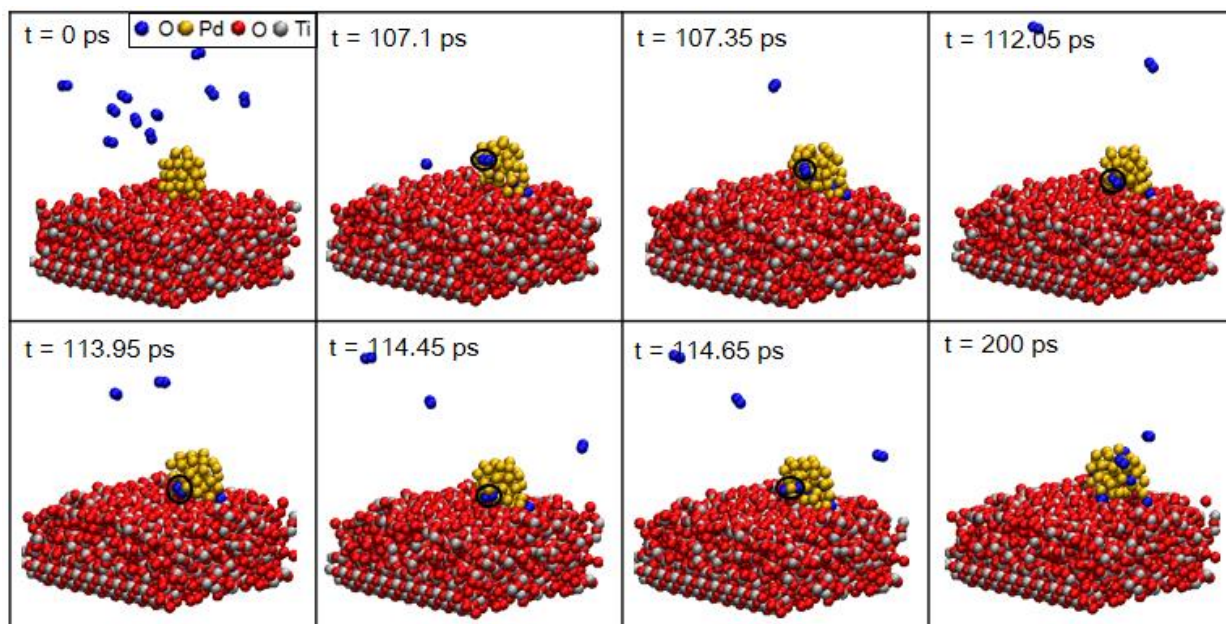


Figure 4. Snapshots of O_2 molecules adsorb and diffuse on the surface of Pd cluster and dissociate at the interface of Pd cluster and TiO_2 slab ($t = 107.1-114.65$ ps) at 873 K. The exact O_2 molecules are highlighted in black circles.

which indicates the H atoms has become a free radical. Then the dissociated H atoms will diffuse on the surface of the Pd cluster seen from Figure 1.

3.2 Molecular Adsorption and Dissociation of Oxygen on TiO_2/Pd Surface

The dynamic processes of O_2 adsorption and dissociation on the catalyst are also investigated. O_2 molecules are colored in blue. The initial setting is the same as that of H_2 in Section 3.1, with 10 O_2 molecules in the gas phase. The simulations last for 200 ps for $T = 373$ K, 573 K and 873 K, separately. At 373 K, we find most of the O_2 molecules are in the gas phase. Only two O_2 molecules adsorb on the surface of the Pd cluster directly. At 573 K, more O_2 molecules appear on the surface of the Pd cluster. However, there is still no dissociation at this temperature. Then at $T = 873$ K, we find the O_2 molecules adsorb both on the surface of the Pd cluster and TiO_2 slab. Meanwhile dissociation takes place. Clearly, Figure 4 demonstrates the dissociation process of O_2 molecule after adsorption on the Pd cluster from $t = 107.1$ to 114.65 ps. The O_2 molecule has the tendency to diffuse on the surface of the Pd cluster and dissociate at the interface of Pd/ TiO_2 . Different from the H_2 molecules, though O_2 molecules also adsorb on the surface of the TiO_2 slab, they trend to dissociate directly on the TiO_2 surface, without moving to the interface.

In order to quantify the potential energy of H atoms during the simulation process, we plot the potential energy of the O atoms in different molecules. The black line is nearly constant in the simulation, which means the O_2 that the O atom belongs to does not dissociate in the whole simulation. However, the red and blue lines are for the dissociated O atoms, with a sharp drop of potential energy after the dissociation, contrary to the potential energy trajectory of H_2 dissociation. Therefore, it illustrates that the dissociated O atoms are more likely to form a more stable compound with Pd atoms instead of being a free radical.

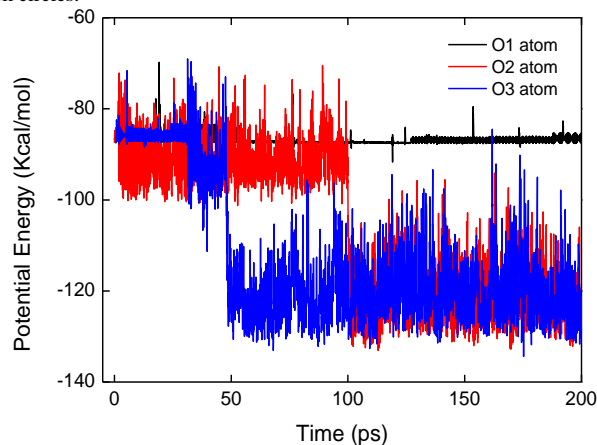


Figure 5. Potential energy of O atoms during the simulation of 200 ps at 873K. The black line is the potential energy of O in an O_2 molecule. The red line and blue lines are the potential energy of O atoms before and after dissociation in the simulation.

3.3 Molecular Adsorption and Dissociation of H_2/O_2 on TiO_2/Pd Surface

The above two sections are about the adsorption and dissociation of pure hydrogen and oxygen molecules, respectively, on the Pd/ TiO_2 system. Here we fill the vacuum region with 5 O_2 molecules and 5 H_2 molecules. The initial gas phase pressure is the same as that of the pure O_2 and H_2 cases. As mentioned before, at $T = 373$ K, we have not found any H_2 or O_2 dissociation on the surface of the Pd cluster or at the interface. Therefore, for the mixed gas case, we run simulations at $T = 573$ K and $T = 873$ K in the canonical ensemble. The initial positions and orientations of H_2 and O_2 molecules are chosen randomly, and the velocities are also in the Boltzmann distribution of 573K and 873 K. At $T = 573$ K, we find the H_2 adsorption and dissociation processes are much like that of the pure H_2 case. H_2 molecules diffuse on the surface of TiO_2 slab and dissociate at the interface of Pd/ TiO_2 . While O_2 molecules are more stable, though absorbed on the surface of the Pd cluster, they do not dissociate in our simulation period.

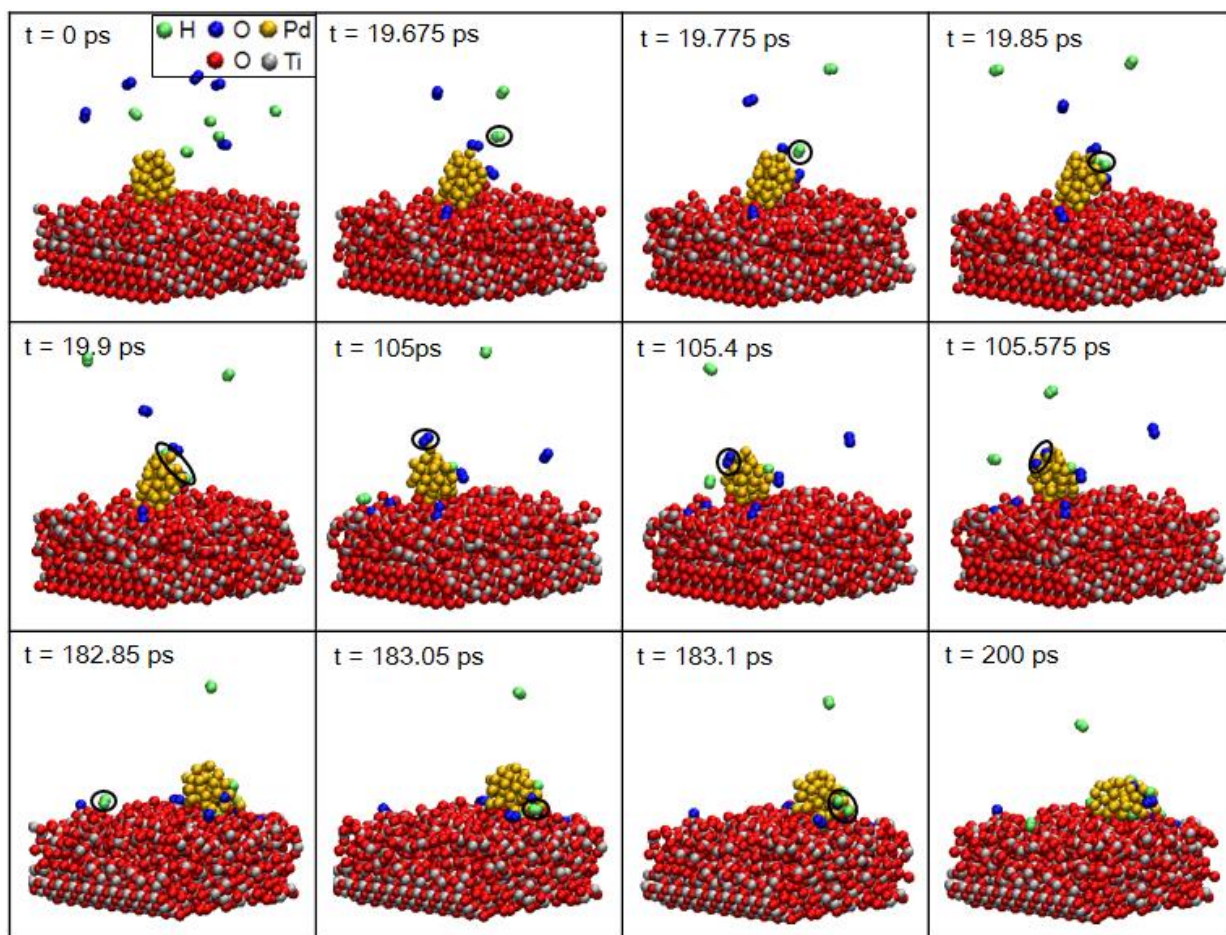


Figure 6. Snapshots of H_2 and O_2 molecules adsorb, diffuse and dissociate on the surface of Pd cluster ($t = 19.675$ - 19.9 ps and $t = 105$ - 105.575 ps). H_2 adsorbs and diffuses on the TiO_2 slab and dissociate at the interface of Pd cluster and TiO_2 slab ($t = 182.85$ - 183.1 ps) at 873 K. The exact molecules are highlighted in black circles.

However, at $T = 873$ K, H_2 molecules not only dissociate at the interface of the Pd cluster and TiO_2 but also on the surface of Pd after directly colliding with the Pd cluster. The detailed processes of H_2 dissociation are shown in Figure 6, at $t = 19.675$ - 19.9 ps and $t = 182.85$ - 183.1 ps. For the dynamic process of O_2 dissociation, we find two O_2 molecules adsorb on the TiO_2 slab and dissociate on the slab surface without moving to the interface. This mainly results from the O vacancy on the

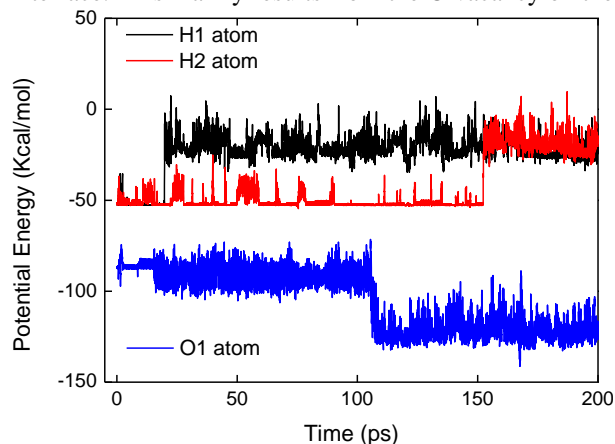


Figure 7. Potential energy of H and O atoms during the simulation of 200 ps at 873K. The black line and the red line are the potential energy of H atoms before and after dissociation from an H_2 molecule. The blue line is the potential energy of O atoms before and after dissociation in the simulation.

TiO_2 slab. In our simulation, the surface layer of TiO_2 is not fixed, which means they will vibrate at the equilibrium and the vibration will become more violent with the increase of temperature. Therefore it will lead to the formation of O vacancy. Though the dissociated H and O atoms are diffusing on the surface of the Pd cluster, we have not found the formation of H_2O molecules.

To further check the potential energy of H atoms and O atoms, we plot the potential energy of the H and O atoms of the molecules which are highlighted in Figure 7. The value of potential energy before and after dissociation of H and O atoms are much the same as that in Figure 3 and Figure 5. This indicates that the existence of O radical may not influence the potential energy of H radical. Hence the possible reason for the change of potential energy of O atom is that before the formation of OH radical with H free radicals, the O radical directly reacts with Pd atoms and form the PdO_x . Meanwhile the bond energy of Pd-O is about 125 kcal/mol, which is much the same as the potential energy of O after dissociation as shown in Figure 7. This implies that PdO_x is an important intermediate in the catalytic combustion of H_2 . Similar results have been found in the catalytic reaction of CH_4 in Pd/ TiO_2 system [4].

4. Conclusion

This research expands our understanding of the adsorption, diffusion and dissociation process of H_2 and

O₂ on the TiO₂ supported Pd catalyst. From the ReaxFF MD simulation, we find the adsorption and dissociation processes of H₂ and O₂ are different from each other but both strongly dependent on temperature. At low temperature of 373K, nearly all the H₂ molecules adsorb on the surface of TiO₂, while only two O₂ molecules adsorb on the Pd surface. At this temperature, no H₂ or O₂ dissociation is observed in the simulation period of 200 ps. At 573K, H₂ molecules are more likely to adsorb on the surface of TiO₂, which diffuse to and dissociate at the interface of Pd/TiO₂. On the contrary, although O₂ molecules also adsorb on the Pd surface, no molecular dissociation is found in our simulation, indicating that the dissociation of O₂ molecule are more difficult than that of H₂ molecules. When the temperature reaches 873K, we find both H₂ and O₂ dissociate. Some H₂ molecules with high kinetic energy may directly dissociate after effective collisions on the surface of Pd, while other H₂ molecules firstly adsorb on the surface of the TiO₂ slab, diffuse to the interface of Pd/TiO₂ and dissociate there. The dissociated H free radicals subsequently diffuse on the surface of the Pd cluster. However, the O₂ molecules have the tendency to adsorb on the Pd surface and some with higher kinetic energy dissociate directly after collision on the Pd surface, and others may diffuse to the interface of Pd/TiO₂ and dissociate there. The dissociated O radicals are observed to react directly with Pd other than recombine with H radicals due to the larger Pd-O bond energy compared with O-O and O-H band energy, implying that PdO_x is an important intermediate in the catalytic combustion of H₂.

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