

# Reactive Molecular Dynamics Simulation of Hydrogen/Oxygen Adsorption and Dissociation on Pd/TiO<sub>2</sub>

Qian Mao <sup>1</sup>, K. H. Luo<sup>\*, 1, 2</sup>

<sup>1</sup> Center for Combustion Energy, Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China

<sup>2</sup> Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

## 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 TiO<sub>2</sub> 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 H<sub>2</sub> and O<sub>2</sub> reactions at the atomic scales.

## 1. Introduction

Hydrogen is regarded as the cleanest fuel with zero CO<sub>2</sub> 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/TiO<sub>2</sub>) 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 H<sub>2</sub>/O<sub>2</sub> 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/TiO<sub>2</sub>. In their simulation, through calculation, they directly connected the O<sub>2</sub> molecules at the interface and CO molecules on the Au surface. Groß [11] also did AIMD simulations to investigate the hot dynamics of H<sub>2</sub> 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 H<sub>2</sub> and O<sub>2</sub> on the TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 O<sub>2</sub>, 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

\* Corresponding author: K.Luo@ucl.ac.uk

Proceedings of the European Combustion Meeting 2015

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 (QE<sub>q</sub>) 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> (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 TiO<sub>2</sub> surface and the behavior of H<sub>2</sub> and O<sub>2</sub> on them. In the present simulation, the dynamic processes of H<sub>2</sub>/O<sub>2</sub> adsorption, diffusion and dissociation on the TiO<sub>2</sub> 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/TiO<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub> firstly undergo energy minimization with a steepest descent algorithm, separately. Upon dynamics simulations, the system of Pd/TiO<sub>2</sub> 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 H<sub>2</sub> and O<sub>2</sub> molecules are added in the vacuum above the Pd/TiO<sub>2</sub>. 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/TiO<sub>2</sub> catalyst by Li et al. [4], the controlled lattice of TiO<sub>2</sub> is anatase (101). Therefore in the present simulation, the TiO<sub>2</sub> 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 TiO<sub>2</sub>. 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 Pd<sub>43</sub>) 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 Pd<sub>43</sub> cluster supported on the anatase (101) slab is situated ~ 2 Å away from TiO<sub>2</sub> surface and in the center region of the x-y plane. The vacuum region in the z direction above the TiO<sub>2</sub> surface is 80 Å, which is filled by 10 molecules of H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> / O<sub>2</sub> (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 H<sub>2</sub> on Pd/TiO<sub>2</sub> Surface

The adsorption and dissociation of H<sub>2</sub> molecules on the catalyst are the initial step of the reaction. Here we run simulations of pure H<sub>2</sub> molecules in the Pd/TiO<sub>2</sub> system at T = 373 K, 573K and 873 K in the canonical ensemble (NVT). The initial pressure is about 3 atm with 10 H<sub>2</sub> molecules in the gas phase to investigate the influence of temperature on the H<sub>2</sub> behavior. The temperatures and pressure are within the experiment setting [5-8]. The initial positions and orientations of H<sub>2</sub> molecules are chosen randomly, and the velocities are in the Boltzmann distribution of the target temperature. From the trajectory of H<sub>2</sub> molecules, we find that not all collisions of H<sub>2</sub> with Pd cluster or TiO<sub>2</sub> 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 H<sub>2</sub> molecules adsorb on the TiO<sub>2</sub> surface, but no dissociation of H<sub>2</sub> is found. At T = 573 K, the adsorbed H<sub>2</sub> molecules all appear on the TiO<sub>2</sub> surface but the number of the adsorbed molecules is smaller than that of T = 373 K. Moreover, the H<sub>2</sub> molecules diffuse on the TiO<sub>2</sub> surface and then dissociate at the Pd/TiO<sub>2</sub> interface. The detailed behaviors of H<sub>2</sub> molecules in the Pd/TiO<sub>2</sub> system at 873K are shown in Figure 1. With higher temperature, H<sub>2</sub> molecules take two dissociation paths. Some H<sub>2</sub> 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 H<sub>2</sub> molecules may have higher kinetic energy which leads to a higher percentage of effective collision with the Pd surface. However, most of the H<sub>2</sub> molecules firstly adsorb on the TiO<sub>2</sub> slab. Then they diffuse on the surface of Pd cluster.

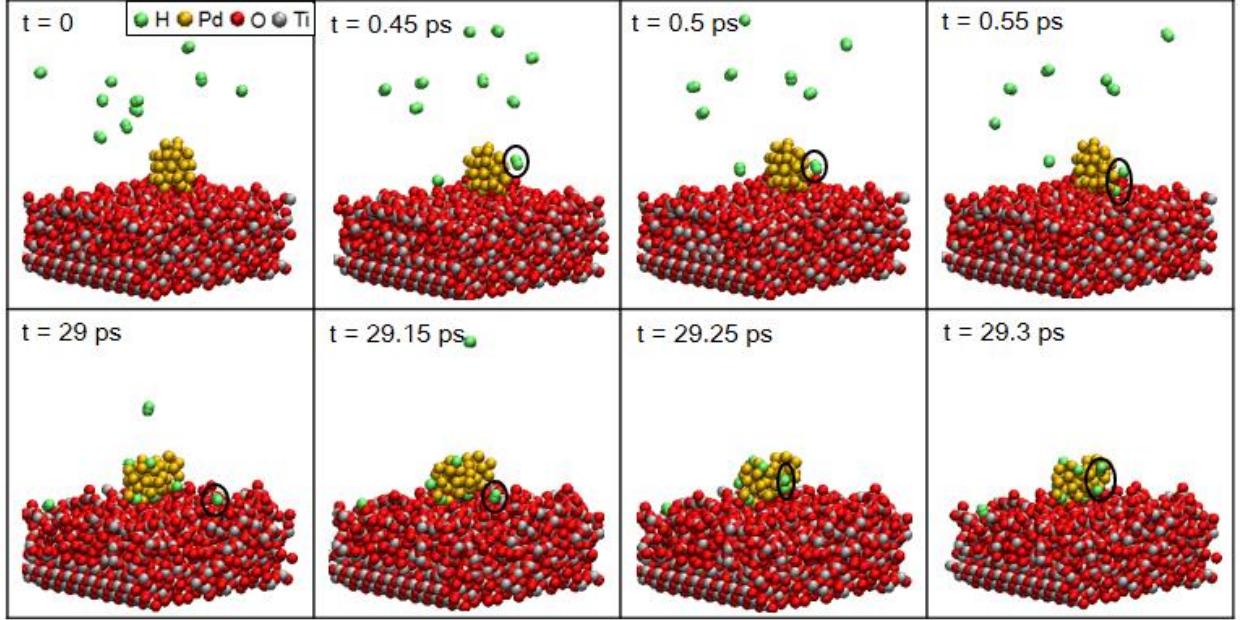


Figure 1. Snapshots of H<sub>2</sub> molecules dissociate on the surface of Pd cluster ( $t = 0.45\text{--}0.55\text{ ps}$ ) and at the interface of Pd cluster and TiO<sub>2</sub> slab ( $t = 29\text{--}29.3\text{ ps}$ ) at 873K. The exact H<sub>2</sub> molecules are highlighted in black circles.

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

The trajectories of H<sub>2</sub> molecules illustrate that H<sub>2</sub> molecules diffuse on the surface of TiO<sub>2</sub> to the interface of Pd/TiO<sub>2</sub> and dissociate at the interface, which is consistent with what we have observed in Figure 1.

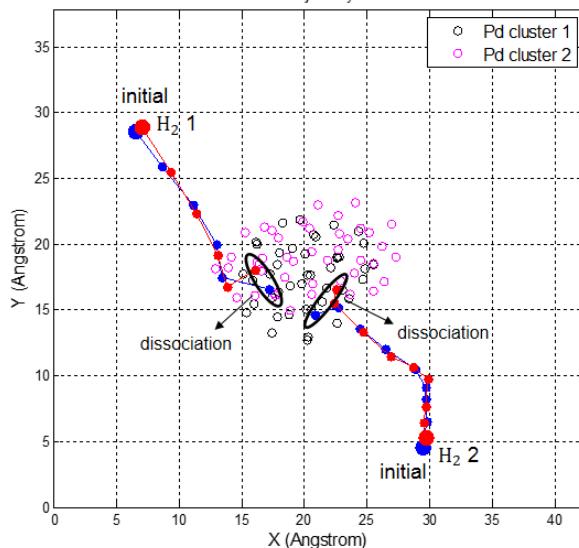


Figure 2. Diffusion trajectories of two H<sub>2</sub> molecules (denoted as H<sub>2</sub> 1 and H<sub>2</sub> 2) on the TiO<sub>2</sub> slab after adsorption and dissociation at the Pd/TiO<sub>2</sub> interface at 873 K. The X and Y coordinates are in the same sizes with the TiO<sub>2</sub> slab, the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

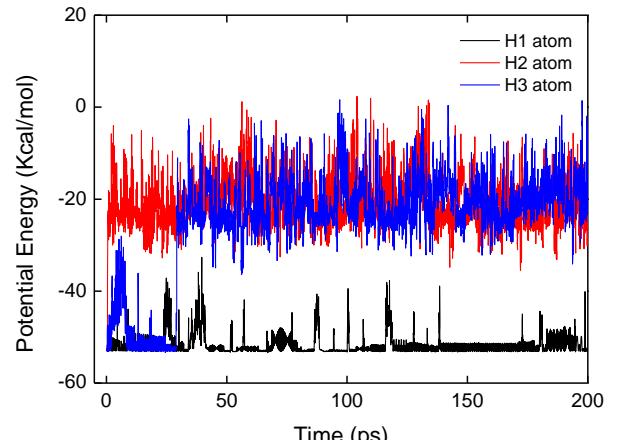


Figure 3. Potential energy of H atoms during the simulation of 200 ps at 873K. The black line is the potential energy of H in a H<sub>2</sub> molecule. The red line and blue line are the potential energy of H atom before and after dissociation from a H<sub>2</sub> on the Pd surface and at the interface of Pd/TiO<sub>2</sub>, separately.

Potential energy of H atoms in the simulation of T = 873K is tracked in Figure 3. Here we choose three H atoms of different H<sub>2</sub> molecules. The value of the black line is nearly constant in the whole simulation with only several weak fluctuations, which presents the H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. In both cases, after the dissociation, the potential energy rises sharply from about -52.5 Kcal/mol to -22 Kcal/mol,

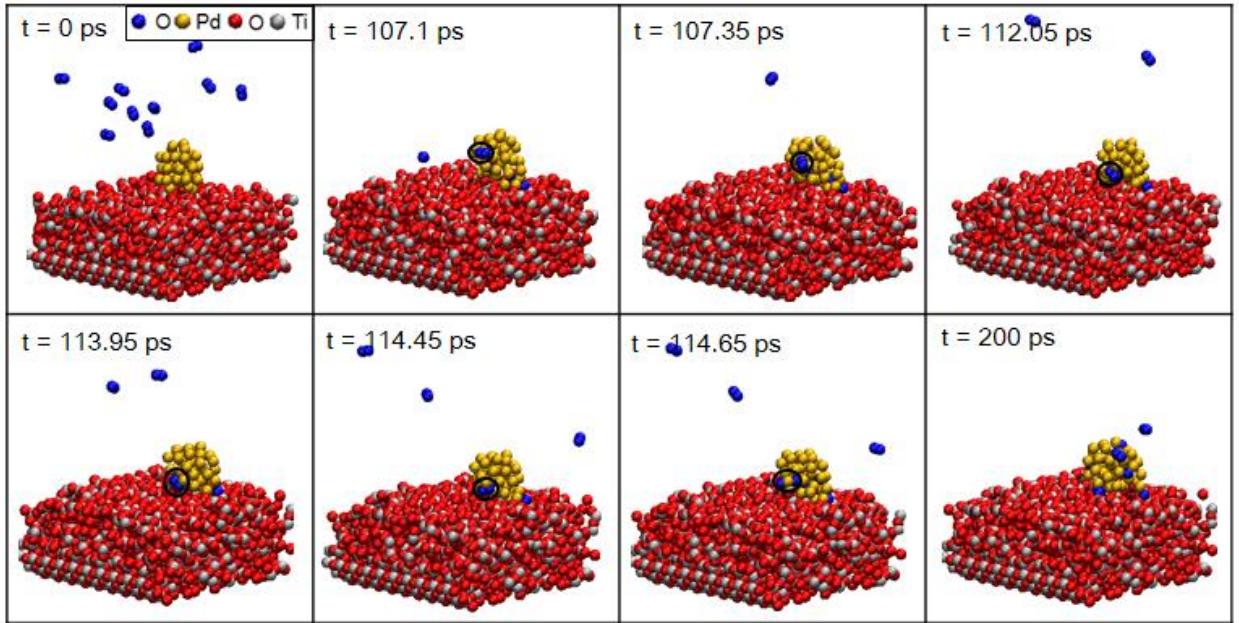


Figure 4. Snapshots of  $O_2$  molecules adsorb and diffuse on the surface of Pd cluster and dissociate at the interface of Pd cluster and  $TiO_2$  slab ( $t = 107.1$ - $114.65$  ps) at 873 K. The exact  $O_2$  molecules are highlighted in black circles.

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.

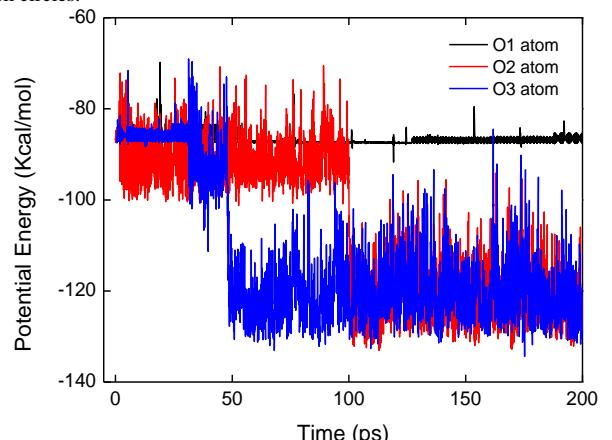


Figure 5. Potential energy of O atoms during the simulation of 200 ps at 873K. The black line is the potential energy of O in an  $O_2$  molecule. The red line and blue lines are the potential energy of O atoms before and after dissociation in the simulation.

### 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.

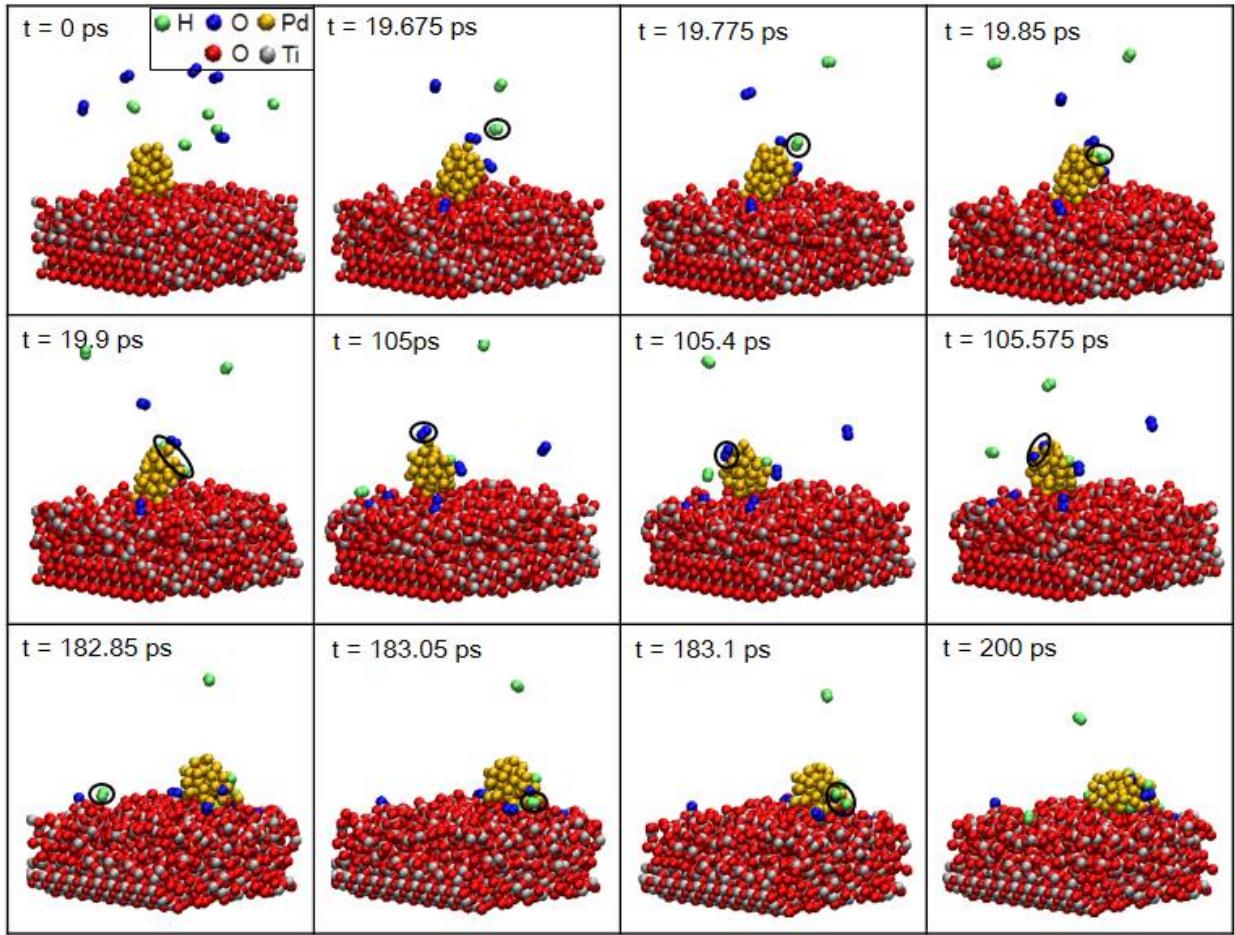


Figure 6. Snapshots of  $\text{H}_2$  and  $\text{O}_2$  molecules adsorb, diffuse and dissociate on the surface of Pd cluster ( $t = 19.675\text{-}19.9 \text{ ps}$  and  $t = 105\text{-}105.575 \text{ ps}$ ).  $\text{H}_2$  adsorbs and diffuses on the  $\text{TiO}_2$  slab and dissociate at the interface of Pd cluster and  $\text{TiO}_2$  slab ( $t = 182.85\text{-}183.1 \text{ ps}$ ) at 873 K. The exact molecules are highlighted in black circles.

However, at  $T = 873\text{K}$ ,  $\text{H}_2$  molecules not only dissociate at the interface of the Pd cluster and  $\text{TiO}_2$  but also on the surface of Pd after directly colliding with the Pd cluster. The detailed processes of  $\text{H}_2$  dissociation are shown in Figure 6, at  $t = 19.675\text{-}19.9 \text{ ps}$  and  $t = 182.85\text{-}183.1 \text{ ps}$ . For the dynamic process of  $\text{O}_2$  dissociation, we find two  $\text{O}_2$  molecules adsorb on the  $\text{TiO}_2$  slab and dissociate on the slab surface without moving to the interface. This mainly results from the O vacancy on the

$\text{TiO}_2$  slab. In our simulation, the surface layer of  $\text{TiO}_2$  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  $\text{H}_2\text{O}$  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  $\text{PdO}_x$ . 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  $\text{PdO}_x$  is an important intermediate in the catalytic combustion of  $\text{H}_2$ . Similar results have been found in the catalytic reaction of  $\text{CH}_4$  in Pd/ $\text{TiO}_2$  system [4].

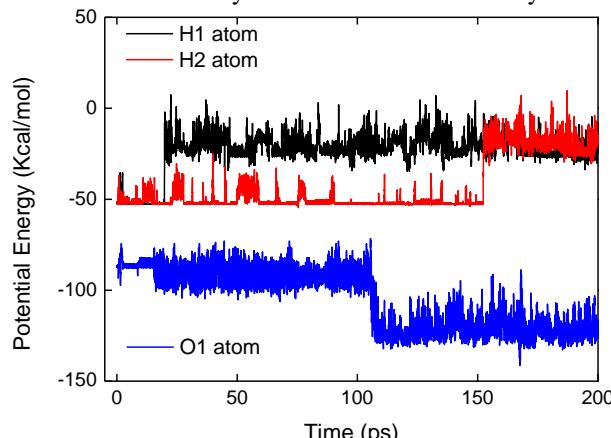


Figure 7. Potential energy of H and O atoms during the simulation of 200 ps at 873K. The black line and the red line are the potential energy of H atoms before and after dissociation from an  $\text{H}_2$  molecule. The blue line is the potential energy of O atoms before and after dissociation in the simulation.

#### 4. Conclusion

This research expands our understanding of the adsorption, diffusion and dissociation process of  $\text{H}_2$  and

$O_2$  on the  $TiO_2$  supported Pd catalyst. From the ReaxFF MD simulation, we find the adsorption and dissociation processes of  $H_2$  and  $O_2$  are different from each other but both strongly dependent on temperature. At low temperature of 373K, nearly all the  $H_2$  molecules adsorb on the surface of  $TiO_2$ , while only two  $O_2$  molecules absorb on the Pd surface. At this temperature, no  $H_2$  or  $O_2$  dissociation is observed in the simulation period of 200 ps. At 573K,  $H_2$  molecules are more likely to adsorb on the surface of  $TiO_2$ , which diffuse to and dissociate at the interface of Pd/ $TiO_2$ . On the contrary, although  $O_2$  molecules also adsorb on the Pd surface, no molecular dissociation is found in our simulation, indicating that the dissociation of  $O_2$  molecule are more difficult than that of  $H_2$  molecules. When the temperature reaches 873K, we find both  $H_2$  and  $O_2$  dissociate. Some  $H_2$  molecules with high kinetic energy may directly dissociate after effective collisions on the surface of Pd, while other  $H_2$  molecules firstly adsorb on the surface of the  $TiO_2$  slab, diffuse to the interface of Pd/ $TiO_2$  and dissociate there. The dissociated H free radicals subsequently diffuse on the surface of the Pd cluster. However, the  $O_2$  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/ $TiO_2$  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  $H_2$ .

### Acknowledgement

Sincere thanks are due to Prof. A. C. van Duin for providing the ReaxFF Force Field for the Ti/Pd/O/H system. Support from the Major Project of the National Science Foundation of China (Grant No. 51390493) is gratefully acknowledged. The simulations were partly performed on the Tsinghua High-Performance Parallel Computer supported by the Tsinghua National Laboratory for Information Science and Technology and partly on ARCHER funded under the EPSRC project “UK Consortium on Mesoscale Engineering Sciences (UKCOMES)” (Grant No. EP/L00030X/1).

### Reference

- [1] G. A. Boyarko, C. J. Sung, S. J. Schneider, Proceedings of the Combustion Institute, 30 (2) (2005) 2481-2488.
- [2] P.L. Mills, D.J. Quiram, J. F. Ryley, Chemical Engineering Science, 62(24) (2007) 6992-7010.
- [3] N. M. Kinnunen, J. T Hirvi, M. Suvanto, T. A. Pakkanen, The Journal of Physical Chemistry C, 115(39) (2011) 19197-19202.
- [4] F. Niu, S. Li, Y. Zong, Q. Yao, Journal of Physical Chemistry C, 118(33) (2014) 19165-19171.
- [5] J. Warnatz, M.D. Allendorf, R. J. Kee, M. E. Coltrin, Combustion and Flame, 96(4) (1994) 393-406.
- [6] P. A. Bui, D. G. Vlachos, P.R. Westmoreland, Symposium (International) on Combustion, 26(1) (1996) 1763-1770.
- [7] C. Appel, J. Mantzaras, R. Schaeren, R. Bombach, A. Inauen, B. Kaepeli, A. Stampanoni, Combustion and Flame, 128(4) (2002) 340-368.
- [8] T. Zhang, D. Zhu, N. Yao, F. Qi, C. K. Law, Proceedings of the Combustion Institute, 33(2) (2011) 1819-1825.
- [9] A. Groß, A. Dianat, Physical review letters, 98(20) (2007) 206107.
- [10] Y. G. Wang, Y. Yoon, V. A. Glezakou, J. Li, R. Rousseau, Journal of the American Chemical Society, 135(29) (2013) 10673-10683.
- [11] A. Groß, Physical review letters, 103(24) (2009) 246101.
- [12] C. J. Cramer, Essentials of computational chemistry: theories and models, John Wiley & Sons, (2013)
- [13] D. Frenkel, B. Smit, Understanding molecular simulation: from algorithms to applications (Vol.1). Academic press, (2001)
- [14] A. C. van Duin, S. Dasgupta, F. Lorant, W. Goddard, Journal of Physical Chemistry A, 105(41) (2001) 9396–9409.
- [15] Q. Zhang, T. Cagin, A. C. van Duin, W. A. Goddard, Y. Qi, L. G. Hector. Physics Letters B, 69 (2004) 045423.
- [16] K. D. Nielson, A. C. van Duin, J. Oxgaard, W. Q. Deng, W. A. Goddard, Journal of Physical Chemistry A, 109(3) (2005) 493-499.
- [17] R. Addou, T. P. Senftle, N. O'Connor, M. J. Janik, A. C. van Duin, M. Batzill, ACS nano. 8(6) (2014) 6321–6333.
- [18] S. Plimpton, J. Comput. Phys. 117 (1) (1995) 1–19.
- [19] G. J. Martyna, M. L. Klein, M. Tuckerman, Journal of Chemical Physics, 97(1992) 2635 –2643.
- [20] K. Lee, J. Zhang, H. Wang, D. P. Wilkinson, Journal of Applied Electrochemistry, 36 (2006) 507–522.
- [21] I. Kvande, S. T. Briskeby, M. Tsyplkin, N. Hammer, M. Rønning, S. Sunde, D. Chen, R. Tunold, Topics in Catalysis, 45 (2007) 81–85.