Formation of water at a Pt(111) surface: A study using reactive force fields (ReaxFF)

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ABSTRACT

In this paper, we report preliminary studies of formation of water from molecular oxygen and hydrogen. Using a series of atomistic simulations carried at finite temperature, we describe the dynamics of water formation at a Pt catalyst using a new reactive ReaxFF potential. By performing a series of studies, we obtain statistically meaningful trajectories to extract rate constants of water formation. This allows an estimate for the activation energy during water formation, which is found to be in reasonable agreement with the activation barrier calculated by restraint driven molecular dynamics simulation of water formation at the Pt surface.

INTRODUCTION

Water is one of the most important substances on earth, as it plays a very important role in many biological systems. However, the chemical complexities of modelling the properties of water in particular during formation of water have so far not been accessible to molecular dynamics simulations at large time and length scales necessary to describe the dynamics of realistic systems. This is because so far, atomistic modeling of chemical reactions has been limited to a few hundred atoms and very short time scales, since only DFT methods could be used to describe the correct quantum mechanical effects. Such techniques have been used to describe the processes associated with water formation and reactions at metal surfaces (see, for instance [1, 2]).



Figure 1: Schematic view of the simulation condition (a) and snapshot at the beginning of a dynamical calculation (b). A mixture of H_2 and O_2 molecules in stochiometric ratio embedded in a finite volume serves as a starting point.



Figure 2: Part of the QM based training set used to develop the reactive force field for the O/H-Pt system. The force field is still under development, and for the simulations reported in this paper we have used a preliminary version of this force field (QM data by Jacab and Goddard [3])

From numerous experimental studies, it is well-known that Pt plays an important role as catalyst in the process of water formation based on molecular oxygen and hydrogen. However, to our knowledge, no direct atomistic simulation has been performed to show the effect of catalysts at finite temperature. To fill this gap, we have carried out finite temperature atomistic studies of water formation at Pt surfaces using a new first principles based reactive force field (ReaxFF) capable of describing the complex chemistry of water formation at Pt surfaces.

Here we demonstrate that ReaxFF is a useful concept to bridge the gap between purely quantum mechanical approaches (e.g. DFT) to more macroscopic descriptions of atomic interactions (e.g. non-reactive force fields such as TIP or SSD). In contrast to purely quantum mechanical methods suitable for dynamical calculations (e.g. CPMD), ReaxFF can be used to model the dynamical trajectory of thousands of atoms over a time span of several nanoseconds.

To elucidate the dynamical, finite temperature mechanism of water formation at a Pt(111) surface, we perform a series of ReaxFF molecular dynamics (MD) simulations at different temperatures. In agreement with experimental observations, we find that water formation without the Pt catalyst leads to highly explosive reactions. In contrast, presence of the Pt catalyst yields better controlled reaction conditions and much higher reaction rates. Results of our calculations clearly demonstrate the catalytic effect to enhance chemical reactions. Further, by performing a series of calculations with distinct starting configurations, we obtain statistically meaningful trajectories that allow us extracting the rate constants of water formation as a function of temperature. These numerical results enable us to estimate the activation energy of water formation. We find reasonable agreement of the resulting activation barrier compared with

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Figure 3: Water concentration as a function of simulation time, comparing a system with Pt catalyst and without. This result clearly indicates the effect of the catalyst in greatly enhancing the reaction rate. Furthermore, the presence of the Pt catalyst also leads to more controlled reaction conditions, as observed in experiment.

quantum mechanical and experimental data. Similar computational approaches as the one described in this paper could be applied to other systems and may help to understand fundamental processes at reactive gas-solid interfaces.

One of the first molecular dynamics simulations have been focused on modeling the properties of water, at that time with much simplified interatomic potentials [4, 5]. Popular classical, nonreactive models for water include the TIP3/4P, SPC, SPC/E, BF & ST2 potentials.(for an overview of various classical water models, please see [6, 7]). We focus on the following questions:

- Can ReaxFF model the finite temperature dynamics of chemical reactions, in particular solidgas phase interface reactions?
- Can we estimate the activation barriers from the dynamical runs, and does it agree with QM and experimental results?
- Can we demonstrate the effect of catalysts based on first principle modeling?

We proceed as follows. After describing the atomistic modeling procedure, we present a set of results of various dynamical runs. We calculate the water production rate as a function of temperature, and use this information to extract parameters for an Arrhenius equation describing the effective water production rate at a coarse-grain, continuum scale. We conclude with a discussion and outlook to future research.

ATOMISTIC MODELING PROCEDURE

All simulations reported in this paper are carried out in a NVT ensemble, with controlled temperature and constant volume [8]. The time step chosen is $\Delta t=0.25$ fs, and we use a Velocity Verlet algorithm for dynamical integration and a Berendsen thermostat. After setting up an initial structure according to desired partial pressure of H₂ and O₂, we relax the system using a minimizer, and then start finite temperature NVT dynamics. For the first few picoseconds we equilibrate the system with nonreactive force field to avoid any chemical reactions. We then use



Figure 4: Number of water molecules as a function of simulation time, for different temperatures. We find that the higher the temperature, the higher the production rate of water molecules.

a variety of initial conditions to obtain statically relevant runs. For each temperature and pressure we perform 10 runs of the system. The simulation geometry is shown in Figure 1.

We use the reactive ReaxFF force field developed by Duin and coworkers [9, 10] adapted to a training set that includes QM data of dissociation and chemisorption of H and O atoms on Pt surfaces and clusters [3] (see Fig. 2 for an example).

MODELING RESULTS

First we address the question wether the catalyst has major impact on the water formation rate, as known from experiment. Figure 3 shows the water concentration as a function of simulation time, comparing a system with Pt catalyst and without. This results clearly shows the dramatic effect of the presence of the Pt catalyst in (i) increasing the water production rate, and (ii) leading to more continuous, less explosive water production.

Figure 4 depicts the number of water molecules as a function of simulation time, for different temperatures. We find that the higher the temperature, the higher the production rate of water molecules. The rates depend on concentration, and we observe that the higher the concentration, the higher the water formation rates. It is critical that the simulations are carried out in the right MD window, with sufficiently high temperature and pressure to observe the formation of water molecules at the MD time scale of a few nanoseconds.

Figure 5 shows the results of the water production rates at different temperatures. This measurement of rates allows to plot the data in an Arrhenius plot (log of reaction rate). We fit a linear curve to the data to obtain the prefactors and the activation barrier from the dynamical runs. The activation barrier is determined to be around 12 kcal/mol. This is in reaonable agreement with restrained reactive calculations (see Figure 2).



Figure 5: Simulations at different temperatures and measurement of rates allows to plot the data in an Arrhenius plot (log of reaction rate). We fit linear curve to the data to obtain prefactors and activation barrier. The activation barrier is determined to be around 12 kcal/mol. This is in good agreement with restrained reactive calculations (see Figure 2).

DISCUSSION AND CONCLUSION

We have successfully carried out dynamical calculations of water formation at a Pt surface. Even though we used a preliminary version of a new reactive force field, the results are encouraging. We summarize the main observations and results:

- We observe that water formation rates are dependent on temperature.
- We could link atomistic simulation to "continuum description" and extract barriers and prefactors.
- The reaction barriers from dynamical runs in good agreement with the prediction by restraint MD simulation with ReaxFF.
- Using MD simulations, we have shown clear catalyst effect (first time by pure MD simulation of this process).

The main result is that ReaxFF can be successfully applied to model chemical solid-gas-phase reactions and can reproduce predictions by quantum mechanics and experimental results. Future studies could be used to apply our technique to other systems and predict the changes in dynamics of water production rates. This can be used to design optimal surface to enhance reactivity, or to test functionalization of surfaces. A schematic of such a calculation is shown in Figure 6.

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Figure 6: Our technique can also be used to study change in dynamics at defects (e.g. due to surface steps). Such studies may eventually lead to re-designed and improved surfaces for optimal catalytic properties, and could play a critical role as one of tomorrow's engineering tools.

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