Computational Chemistry Modelling of the Oxidation of Highly Oriented Pyrolitic Graphite (HOPG)

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1 Introduction

The flow over hypersonic vehicles is characterized by extreme conditions with shock layer temperatures reaching 10000 K and heat fluxes as high as 5 kW/cm². Thermal protection systems (TPS) consisting of carbon-based surface-ablating materials are effective structures that enable much of the heat flux to be carried away from the vehicle by the ablatin material.

At these high temperatures, dissociated oxygen atoms (O) strike the TPS surface leading to several possible gas-surface chemical reactions. Specifically, the oxygen atom could chemically bond to the surface, it could recombine with another adsorbed oxygen and leave the surface as a molecular (O₂), or the impinging atom could ‘oxidize’ the carbon surface resulting in products such as CO and CO₂ leaving the surface and being injected into the boundary layer. Such oxidation reactions result in the recession of the surface (surface ablation). Currently, much uncertainty exists in both the dominant reactions themselves as well as the rates of these reactions. The mechanisms and rates are required as input into state-of-the-art CFD simulations of hypersonic flows. Experimental determination of the chemical mechanisms themselves under extreme hypersonic conditions is difficult and often they must be inferred from macroscopic observations such as heat flux and surface recession measurements. However, as the field of computational chemistry continues to advance in step with advances in computational power, fundamental chemical studies may be able to provide insight into the chemical mechanisms and associated rates for such surface ablation processes.

The goal of this work is to develop finite rate models through large scale Molecular Dynamics (MD) simulations using the ReaxFF force field. Our current effort is to validate our ReaxFF simulations with existing data available from molecular beam experiments. In this work, we simulate the collision of hyperthermal (5eV) O atoms with Highly Oriented Pyrolitic Graphite (HOPG) and compare our results to the molecular beam experiments performed by Minton and co-workers.

2 Molecular Dynamics Simulations

In contrast to previous computational chemistry work in this area where isolated single-collision events are studied on graphite sheets (one atomic layer), we simulate sequential gas-surface collisions on multi-layered graphite (representing HOPG) with large surface area. We do this to simulate the evolution of oxidized HOPG, an observation experimentally including the net removal of surface carbon atoms, the product species created, and the geometry of each pit. Molecular Dynamics simulations are performed with the LAMMPS molecular dynamics program, using the ReaxFF potential.

2.1 ReaxFF Potential

ReaxFF is a bond order dependent potential that uses a relationship between bond distance and bond order along with bond order and bond energy to describe bond dissociation propensity. This allows natural creation and destruction of bonds which is critical to our oxidation simulations. The complete energy of a system is given by a number of terms, including long range non-bonded terms such as Coulomb and Van der Waals interactions:

\[ E_{\text{total}} = E_{\text{bond}} + E_{\text{charge}} + E_{\text{overlap}} + E_{\text{electrostatic}} + E_{\text{vdW}} + E_{\text{EEDF}} + E_{\text{dualbond}} \]

The force field parameters used in the present simulations have already been optimized by Chenoweth et al. [1] and it has been demonstrated that graphite–oxygen interactions are accurately modeled with this potential.

2.2 Surface Preparation

The collision of a 5 eV O atom with the atomistic-scale HOPG surfaces in such MD simulations results in a significant increase in the temperature of the simulated ‘slab’ of graphite. Under low pressure experimental conditions[2] any transfer of energy to the surface would be conducted into the bulk material long before the next O atom collision. In our simulations we thermostat the bottom layer of the HOPG slab to maintain a constant surface temperature. However, in addition, we also had to wait roughly 12.5 ps before the increased temperature of the top layer cooled back to the thermostat temperature as shown in Fig. 2. If the next gas-phase atom is injected prior to this, it hits a surface at an physically high surface temperature, not the desired temperature of the experiment. Colliding atoms at 1 ps intervals without temperature control results in very high surface temperatures which causes the HOPG to ablate much faster than it would in the experiment. However, simulating the system 12.5 ps between collisions is computationally expensive and there are no reactions over this time scale. In fact, most reactions were observed to occur at short timescales (<1 ps).

Thus, we simulate the collision with a short one-for-one, ps, which is sufficiently to determine the outcome of the collision (rejection, adsorption, oxidation, etc.). After the reaction is over (after 1 ps), we then thermostat the entire system for 0.75 ps to restore the surface temperature to its proper value. This added complexity, compared to previous studies involving single isolated collisions, is essential for both physical accuracy and computational efficiency.

2.3 Surface Coverage

It is well known that pristine HOPG does not undergo oxidation due to O atoms colliding even with high energy O atoms (5eV). However, the HOPG surface does become populated with adsorbed O atoms either in epoxide form(C=O) or C-OH form, and possibly other intrinsic surface defects. This is reasonable to be taken into MD simulations with HOPG and this surface coverage. If we initialize our MD simulation with a complete epoxide coverage the oxygen atoms remain bonded to the surface in the epoxide configuration. The non-bonded atoms are removed from the system and the process is repeated for a few times. If this procedure is followed, it is physically more realistic in that full oxygen coverage would not occur instantaneously, an HOPG surface with epoxide coverage is obtained without buckling. This then, is how we prepare our HOPG surfaces prior to gas-phase oxygen impacts.

2.4 Continuous Collisions

Oxygen atoms at 5eV are continuously injected towards the HOPG surface. A total of 1000 continuous collisions were simulated. The products predict the pit growth in the interplanar direction to be much more rapid than in the inplane direction. This was observed experimentally[3] (fig. 5) where shallow but wide,etch pits were created. Our results predict that 1 carbon atom is approximately removed for every 6 O atoms injected. However, this ratio depends on the size of atomic beam flux compared to the size of the etch pit. The surface temperature was maintained at 373K. In another set of experiments[4] performed at 525 K, the experimental data predict the ratio of CO to CO₂ products as 1:2 while our simulations predict this ratio of products to be roughly 1:4. The fact that our simulations predict more CO products than CO₂ and in a reasonable proportion compared to experimental evidence is encouraging.

2.5 Effect of surface temperature

The work in Ref. [1] also shows that the rate of oxidation increases with an increase in surface temperature. The experiments were done in the temperature range of 298K – 573K. In Molecular Dynamics simulations, the variation in this narrow range of temperature would be difficult to capture, as a large number of ensemble averages (many simulations) may be required to reduce scatter in the results. We simulated the collisions over a much larger temperature range of 300K, 600K, 1000K, and 1500K. The results are tabulated in Table 1. As shown in Table 1, the simulations do indeed predict an increase in the oxidation rate which increases as the temperature increases compared to the experimental observation. Specifically, this trend with temperature should reveal the activation energies of the specific reactions in each. If determined, these mechanisms and activation energies could be useful for finite-rate models used in CFD simulations.

2.6 Conclusions and Future Work

In this work, we have studied the oxidation of HOPG by hyperthermal O atoms. To avoid long wait times between successive collisions, we thermostat the system to the desired target temperature. It was also observed that the pristine HOPG sheet does not oxidize even at the collision of hyperthermal O atoms. However, a surface covered with oxygen groups and small intrinsic defects lead to oxidation of the surface. We created a surface coverage of O atoms on the surface by allowing the O atoms to bond naturally to the surface instead of placing them in epitaxial form which results in delisting of the surface. Our continuous collision results are compared with the trends observed in molecular beam experiments. We observed that oxidation in the inplane direction is faster than in the interplanar direction as observed in experiments, and also that the oxidation rate increases with surface temperature. Finally, our simulations predicted higher production of CO₂ compared to CO in and relative amounts that were in agreement with experimental observations. These preliminary results are promising for the validation for our simulation techniques including the interatomic potentials and modeling assumptions.

In future work, we wish to characterize the rates quantitatively of all species formed on the surface and to run large number of simulations to validate our results as close as possible to available experimental data. We could then run simulations at high surface temperatures and see a variety of crystal orientations to ascertain oxidation reactions present under hypersonic conditions for more realistic carbon-based surface ablative materials.

3 References


Table 1: Surface Temperatures vs Number of Carbon atoms removed

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>Number of Carbon atoms removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>152</td>
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<tr>
<td>400</td>
<td>154</td>
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<td>600</td>
<td>246</td>
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<tr>
<td>700</td>
<td>290</td>
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