Reactive Molecular Dynamics of Fuel Oxidation and Catalytic Reactions

A thesis submitted for the degree of

Doctor of Philosophy

by

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Declaration

I, Muye Feng, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Signature: ___________________________ Date: ___________________________
Abstract

The present research employs the ReaxFF (a force field for reactive systems) molecular dynamics simulation method to investigate the detailed microscopic modelling for complex chemistry of fuel oxidation and catalytic reactions on graphene-based nanomaterials at the atomic level. Specifically, in total, four different systems are studied in detail. Firstly, the fundamental reaction mechanisms of hydrous ethanol oxidation in comparison with the ethanol oxidation under fuel-air condition is investigated. The results indicate that it is the addition of water that promotes the OH production due to the chemical effect of H_2O leading to the enhancement of ethanol oxidation and reduction of CO production. Secondly, the fundamental study on mechanisms of thermal decomposition and oxidation of aluminium hydride is conducted. It is found that the thermal decomposition and oxidation of aluminium hydride proceed in three distinctive stages ((1) Pre-diffusion; (2) Core-shell integration; (3) Post-diffusion, and (I) Oxygen adsorption; (II) Fast dehydrogenation; (III) Al oxidation), respectively. Thirdly, the catalytic mechanisms and kinetics of methane oxidation assisted by Platinum/graphene-based catalysts are studied. Platinum-decorated functionalized graphene sheet is reported to be the most effective catalyst among all the involved nanoparticle candidates and it improves the catalytic activity by dramatically lowering the activation energy by approximately 73% compared with pure methane oxidation. Fourthly, the initiation mechanisms of JP-10 pyrolysis and oxidation with functionalized graphene sheets in comparison with normal JP-10 reactions are revealed. The results suggest that both pyrolysis and oxidation of JP-10 are advanced and enhanced in the presence of functionalized graphene sheets. Additionally, the functional groups also participate in various intermediate reactions to further enhance the pyrolysis and oxidation of JP-10.
In summary, the new findings from the present research could contribute to the design and improvement of the future high-performance energy and propulsion systems, especially for the promising graphene-containing fuel/propellant formulations.
Impact Statement

The findings of the present thesis provide valuable microscopic insights into four fuel oxidation and catalytic reaction systems, which not only aid in the understanding of fundamental mechanisms of those systems, but also benefit their potential practical applications.

Chapter 4 studies the oxidation of hydrous ethanol and provides the scientific base for its direct use as a fuel for combustion systems with a low cost. Chapter 5 investigates the thermal decomposition and oxidation of aluminium hydride and contributes to its safe storage and efficient usage for a variety of propulsion and energy storage systems. Chapter 6 explores the catalytic methane oxidation on Platinum/graphene-based catalysts and sheds new light on the enhanced fuel/propellant combustion in the presence of Platinum-decorated functionalized graphene sheet. Chapter 7 extends the research to the pyrolysis and oxidation of JP-10 (exo-tetrahydrodicyclopentadiene) on functionalized graphene sheets and demonstrates its potential use as a promising catalyst for JP-10 and many other jet fuel systems.

The present thesis proves the feasibility and usefulness of ReaxFF reactive force field molecular dynamics simulation methodology for detailed investigation of reaction mechanisms of various fuel oxidation and catalytic reaction systems. It also lays the theoretical foundation for designing and improving the next-generation high-performance energy and propulsion systems.
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Chapter 1 – Introduction

1.1 Background and motivation

Energy and propulsion systems play a vital role in the development of human civilization ranging from land transportation to aviation. However, the success of such systems strongly depends on the fuel properties, which affect the performance and emissions. Currently, the primary interest is to design environmental-friendly fuels, which can offer high energy density, reliable and safe burning, short ignition delay and so on to power the next-generation energy and propulsion systems. Both conventional and alternative fuels need to be improved to enhance the fuel properties and combustion performance.

To study the fuel properties, the understanding of its fundamental reaction process is crucial. The macroscopic properties of fuel reaction can be easily investigated by experiments, but some microscopic insights such as the underlying mechanisms are difficult or even impossible to be determined by the existing experimental techniques (e.g. intermolecular and/or intramolecular interaction within the fuel system). Therefore, the methodology of molecular dynamics (MD) simulation is introduced to provide the detailed microscopic modelling for dynamic chemical reactions thereby benefiting the understanding of fundamentals of fuel oxidation and catalytic reactions.

The present research focuses on the applications of ReaxFF reactive force filed MD methods on the investigation of fundamental reaction mechanisms of thermal decomposition and oxidation of various kinds of fuel including hydrous ethanol, aluminium hydride, methane and JP-10. Particularly, catalytic reactions of methane and JP-10 on graphene-based nanomaterials are studied to provide atomic level insights as to their potential usage as promising catalysts for fuel oxidation. The new findings from
this research contribute to the specific area of application of each studied fuel type and could benefit the design and improvement of the next-generation high-performance energy and propulsion systems.

1.2 Aim of the research

The primary aim of the present research is to develop fundamental understanding of fuel oxidation and catalytic reactions by MD simulation methods to provide guidance for enhancing the fuel properties and performance. Various types of fuel oxidation system including conventional and novel approaches are studied in detail.
Chapter 2 – Literature Review

2.1 Introduction

This chapter firstly introduces the various methodologies of molecular simulation. Among all these methods, molecular dynamics (MD) is emphasized, with brief introduction of ReaxFF reactive force field MD simulation. Then, the applications of ReaxFF MD on the study of fuel oxidation and catalytic reactions are reviewed.

2.2 Brief introduction and development of molecular simulation

2.2.1 Quantum mechanics methods

Thanks to the rapid development of quantum mechanics (QM) from 20th century, almost all molecular properties such as structure, conformation, ionization potential and electron density can be calculated, which are in good agreement with experimental results. In addition, some information deduced from the QM calculations is extremely difficult or even impossible to be obtained by the existing experimental techniques. QM methods are based on the wave function, which is achieved by solving the Schrödinger equation [1]. Fundamental theories and comprehensive applications can be referred to textbooks by Griffiths [2] and Cramer [3].

2.2.1.1 Ab initio

Ab initio is one of the most widely used QM methods. In ab initio method, the concept of molecular orbitals is introduced and they are approximated by a linear combination of atomic orbitals, which is calculated using the variation principle. These atomic orbitals are defined as some specific basis sets such as Gaussian functions. This approach is accurate but computationally very expensive for large systems due to the involvement of calculation of many integrals.
2.2.1.2 Semi-empirical

In order to increase the efficiency of QM computations, semi-empirical QM methods were developed and applied since 1960s. The matrix elements related to the wave function interactions in these methods are built from a set of predetermined parameters instead of explicitly calculated integrals. These predetermined parameters are normally obtained from experimental results. Therefore, semi-empirical methods can be applied on larger systems and retain the comparable accuracy. However, a good parameterization is required and parameters are not directly transferable between different systems. Commonly used semi-empirical methods include CNDO (Complete Neglect of Differential Overlap), INDO (Intermediate Neglect of Differential Overlap) and NDDO (Neglect of Diatomic Differential Overlap). The selection of these different approaches depends on the studied system.

2.2.1.3 Density functional theory

Density functional theory (DFT) based on the use of electron density function as a basic descriptor of the electronic system, can be considered as a variant of ab initio methods, where exchange and correlation functionals are employed to describe the electron correlation energy [1]. The difference between DFT and conventional ab initio methods is the treatment of exchange and correlation energy. In general, DFT method is computationally more efficient than conventional ab initio methods while offering a similar high level of accuracy, which benefits the calculation of larger systems.

2.2.2 Molecular mechanics

The QM methods are suitable for simple and small systems as summarized above. However, in the nature and industry, many systems to be investigated are usually complicated such as those involving biochemical or polymer molecules, which contain a large amount of atoms and electrons. In addition, for the systems consisted of metallic
materials, viscous solution, solid mixture and nanomaterials, not only the properties of
an isolated molecule and the interactions between the molecules need to be studied, the
dynamic behaviours and thermodynamic properties are more important. The
investigation of these kinds of complex systems cannot fully rely on the QM
calculations. As a result, many non-QM methods were developed to solve the problems
of large and complicated systems.

An alternative approach is molecular mechanics (MM), also known as force field
or potential energy method, which is based on classical mechanics [1]. According
to the Born-Oppenheimer approximation, the potential energy of the system can be
represented as a function of the collective position of the nuclei and the motion of
electrons is ignored. Unlike QM methods, the potential function must be estimated
empirically. MM methods calculate the molecular properties by force fields containing
many parameters obtained from QM computations or/and experimental data. The
details of the concept of force field are shown in Section 2.2.4. A fundamental principle
in MM is that the molecular geometries and energies can be depicted by cumulative
physical forces. A molecule is regarded as a collection of atoms connected by spring
forces (bonds). Thus, those bonds of the molecule stretch, bend and rotate as a result of
inter and intramolecular forces. The ultimate spatial conformation is a naturally
adjusted geometry having a minimized total internal energy. In brief, the stable
conformation, thermodynamic properties, vibrational spectrum and etc. results of large
and complex systems can be obtained from MM calculations. Compared to QM
methods, MM is computationally much more cost-efficient. It is worth mentioning that
the hybrid QM/MM approach was firstly introduced in 1976 by Warshel and Levitt [4].
It combines the high accuracy of QM and fast speed of MM thereby offering an efficient
molecular simulation method.
2.2.3 Monte Carlo

Monte Carlo (MC) is widely used in statistical physics and chemistry, and it is one of the non-QM molecular simulation methods to solve problems for large-scale systems. Based on the stochastic motion of particles (molecules or atoms), MC employs the probability distribution principle in statistical mechanics to get the statistical and thermodynamics information of the system. The detailed introduction and theory can be found in textbooks by Hammersley & Handscomb [5] and Frenkel & Smit [6], and a review by Amar [7]. The limitation of MC method is that it can only calculate the statistical mean value and is unable to capture the dynamic behaviours of the system. Although some MC-derived approaches such as Quantum Monte Carlo (QMC) and Kinetic Monte Carlo (KMC) have been developed, the strengths of MD simulation (Section 2.3) make it more popular than MC.

2.2.4 Force field

The force field is the potential energy of a system, which is described as a mathematical function with sets of parameter. The function is correlated to particle coordinates and the parameters are derived from QM computations or/and experimental data. The force field lays the foundation for the MM, MC as well as MD calculations. Generally, the total potential energy of a system can be divided into bonded and non-bonded terms, where bonded terms include bond stretching, angle bending, torsions, and non-bonded terms include van der Waals and electrostatic/columbic interactions. Depending on the different force fields for their specific applications, the sub-terms included and the expression of the function may vary. Cross and additional terms may be involved in some cases. Prevailing classical force fields include but not limit to AMBER (Assisted Model Building and Energy Refinement), CHARMM (Chemistry at Harvard Macromolecular Mechanics), COMPASS (Condensed-phase Optimized
Molecular Potentials for Atomistic Simulation Studies), CVFF (Consistent Valence Force Field), OPLS (Optimized Potential for Liquid Simulations) and UFF (Universal Force Field). The second-generation force fields like CFF (Consistent Force Field) and MMFF (Merck Molecular Force Field) are more sophisticated than above both in terms of functional form of the potential energy and parameters, which can produce more accurate results. Apart from using a large amount of experimental data, the parameterization of those force fields also significantly relies on precise QM calculations. Polarizable force fields (charge distribution changes based on the local environment instead of fixed charges) with a better performance than second-generation’s can be called third-generation force fields. The force fields mentioned so far are all-atom force fields. These force fields provide parameters for every type of atom in the system. Moreover, some simplified potentials such as united-atom and coarse-grained potentials are also available for long time simulations with higher computing efficiency.

The classical force fields cannot model chemical reactions but many reactive force fields are available to overcome this limitation. Among them [8-14], ReaxFF is the most frequently used and popular reactive force field, which is able to describe dissociation, transition and formation of chemical bonds so that large-scale reactive systems can be simulated. This efficient MD technique for reactive simulations is the primary methodology for the present research. More details of the ReaxFF formalism and development can be seen in Chapter 3.

Every force field was designed and developed for a specific scope of applications. The selection of an appropriate force field is extremely important and has a significant impact on the accuracy of the results. Furthermore, a good parameterization is the
foundation for an effective force field. Therefore, ongoing works are being done to improve the parameters of current existing force fields.

2.2.5 Other methods

In addition to the aforementioned several molecular simulation methods and MD, which will be described in detail in Section 2.3, Brownian dynamics (BD) and dissipative particle dynamics (DPD) methods are briefly introduced here.

2.2.5.1 Brownian dynamics

It is unrealistic to use MD methods to study the particle dispersion problems, i.e. the dispersion or suspension consisted of fine particles dispersed in liquid, because of the significant difference of characteristic time of the motion between dispersed particles and solvent molecules [15]. Besides, the relatively slow motion leads to a considerably long simulation time, which makes it impractical for MD. An alternative approach is treating the solvent molecules as a continuum medium instead of focusing on the motion of each solvent molecule and then investigate the motion of dispersed particles in such a medium. The BD method was developed for tackling this type of problems based on the concepts of frictional and stochastic force. It can also be considered as an extension to the Langevin dynamics (LD) [16] without inertia. More fundamentals can be read from literatures [1, 15]. The advantage of BD method is that it can be used to study the long time scale motion such as the motion of macromolecules and biochemical molecules with remarkably lower computational resources.

2.2.5.2 Dissipative particle dynamics

The DPD method, firstly introduced by Hoogerbrugge and Koelman [17, 18], is a simulation technique laying between atomic scale and mesoscale. It is an approximated coarse-grained scheme, which is used to study the system containing very many
particles (millions or even billions of atoms) for a very long time (milliseconds to seconds), such as colloidal dispersions. It is obvious that MD methods are not applicable for such large-scale and complex systems. In the DPD simulation, groups or clusters of molecules are regarded as one particle (dissipative particle) and then the interaction between these dissipative particles can be studied. Although the DPD method is not able to provide an atomic insight of the system, it takes the advantage of producing correct hydrodynamics results on long length and time scales. This approach is similar to MD to some extent. The detailed theories can be found in textbooks by Frenkel & Smit [6] and Satoh [15].

2.3 Molecular dynamics simulation

2.3.1 Introduction

At present, MD simulation is one of the most popular methods for dynamic simulation of large-scale systems. It is a technique for calculating the equilibrium and transport properties of a classical many-body system [6]. With the rapid advance of MM, numerous force fields for various applications were developed and the accuracy of them was dramatically increased. The principle of MD approach is simple. The motion of a system based on the applied force field is estimated by the Newton’s equations of motion in classical mechanics. Hence, MD requires and provides complete information of position and momentum of atoms at all times. This is an excellent approximation for a wide range of applications because quantum effects only need to be taken into account under certain circumstances, for example, if the translational or rotational motion of light atoms or molecules such as He and H\textsubscript{2}, or vibrational motion with a specified range of frequency have to be considered. According to the position and momentum of all particles, the macroscopic quantities of the system can be computed via statistical mechanics, which bridges the gap between the results of
MD simulations are used to evaluate equilibrium and dynamics properties of complex systems, which cannot be estimated analytically as a counterpart to experiment, and they provide the insight for detailed microscopic modelling at the atomic level. The continually improved computational capability makes it practical to tackle problems of system with great complexity by MD methods. But due to the extensive calculation of mathematical integrals required, MD simulation has a limited time scale and is not applicable for modelling some long time problems. To understand and apply MD techniques, the knowledge of statistical mechanics, thermodynamics ensembles, time-correlation functions and basic simulation protocols are essential. More fundamental theories are introduced in textbooks by Schlick [1] and Rapaport [19]. To date, applications of MD can be found in many fields including physics, chemistry, biochemistry, material science and other engineering branches.

Figure 2.1 Main steps for conducting the MD simulation.
2.3.2 ReaxFF reactive force field molecular dynamics simulation

The present research primarily employs the ReaxFF reactive force field MD simulation method to investigate the fundamental reaction mechanisms of thermal decomposition and oxidation of various fuel systems. The methodology is introduced in detail in Chapter 3.

2.4 Applications of ReaxFF MD simulation on fuel oxidation and catalytic reactions

The review in this section is limited to the applications of ReaxFF MD simulation on the oxidation of hydrocarbon/oxygenated hydrocarbon and aluminium nanoparticles, and fuel oxidation assisted by graphene-based nanomaterials, which are highly relevant to the main subjects of the present research.

2.4.1 Hydrocarbon/oxygenated hydrocarbon fuel oxidation

The first ReaxFF force field, which only contains parameter sets of C and H element, was developed for hydrocarbons by van duin et al. [13] in 2001. It provides a simple and efficient method for describing hydrocarbon systems compared to other computational methods such as MM3, PM3, Brenner and DFT. ReaxFF was the only technique, which could be actually applied on predicting the reactivity of a system with large molecules or multi molecules except for Brenner potential at that time. The comparison with extensive literatures showed that ReaxFF is able to accurately describe the stability, geometry as well as the dissociation and formation of chemical bonds in hydrocarbon compounds. Furthermore, ReaxFF is much faster than QM and semi-empirical methods. Although it was not designed for solving the dynamic problem for complex systems, it did provide a new possibility for simulating dissociation and formation of chemical bonds in relatively large hydrocarbon systems.
Afterwards in 2008, the ReaxFF was extended to the first ReaxFF oxidation force field (CHO-2008) for the purpose of investigating the initial chemical events of high-temperature gas-phase oxidation of hydrocarbons [20]. A range of hydrocarbon-oxygen systems including methane, o-xylene, propene, benzene and their mixtures were tested to validate the ReaxFF potential. The reactions during the complete oxidation of isolated methane, propene and o-xylene were also tracked and it was found that the pathways produced agree well with QM results. The results showed difference of dominant initiation reaction mechanisms for oxidation of these hydrocarbons between fuel lean and rich conditions. Under fuel lean condition, the oxidation was initiated by the hydrogen abstraction of the methyl hydrogen by molecular oxygen forming hydroperoxyl and hydrocarbon radical species, while a different initiation mechanism for a mixture of these hydrocarbons was observed under fuel rich condition compared to the oxidation of isolated hydrocarbons, involving both decomposition of the hydrocarbon or attack by other radicals in the system. This ReaxFF potential not only successfully depicted the initiation mechanisms for hydrocarbon oxidation, but was also able to reproduce qualitative results including reaction rates and rate constants for the oxidation process. The results proved that ReaxFF can be used to elucidate fundamental steps for complex reactions thus benefiting the understanding of oxidation chemistry at the atomic level.

The classical CHO-2008 ReaxFF force field was extensively used for studying the hydrocarbon oxidation over the past ten years. Those applications are reviewed in the following sections.

2.4.1.1 Small hydrocarbons

The ignition of hydrogen oxidation was studied by Alaghemandi et al. [21] using the ReaxFF. By estimating the ignition time of H2/O2 mixtures with various equivalence
ratios, they found that the ignition delay was the shortest under fuel lean condition with an equivalence ratio of 0.5 and the time for ignition was uniformly increased with a higher or lower oxygen loading. Additionally, H\textsubscript{2}O\textsubscript{2} and HO\textsubscript{2} were determined to be the two intermediate species, which could be used to forecast the ignition at elevated temperatures and pressures. Therefore, it was believed that the ignition delay of hydrogen oxidation under high temperature and pressure could be controlled by adjusting the magnitude of those components. The thermal decomposition and oxidation of methane were also investigated. Lummen [22] studied the hydrocarbon growth under thermal decomposition of methane at a variety of temperatures and densities to understand the formation of large hydrocarbon molecules. It was concluded that the temperature had a significant impact on the cracking reactions while no obvious influence of density was observed. Specifically, at the temperature of 2500 K, molecular hydrogen, a wide range of hydrocarbons and carbon dimers were formed and the largest molecule, a 6-membered carbon ring structure was observed once at 3500 K but subsequently reacted with other products as it was unstable. In brief, the number of different kinds of molecules produced increased as the rising temperature within the simulation time scale. Döntgen et al. [23] developed a programme that could automatically determine the reaction pathways, rate constants and transition states for complex chemical reactions from ReaxFF outputs and verified the proposed methodology by studying the chemical kinetics of methane oxidation. The research proved the potential of ReaxFF MD simulation for developing quantitative reaction models. The low-temperature partial oxidation of methane was investigated by Page and Moghtaderi [24]. They found that the partial oxidation of methane was initiated by the hydrogen abstraction from methane by the molecular oxygen and the atomization
of methane itself. Furthermore, the primary pathways of hydrogen formation were the radical recombination between hydrogen atoms and the dehydrogenation of methane.

### 2.4.1.2 Long-chain hydrocarbons

Apart from small hydrocarbons, there are also many studies of the oxidation of large long-chain hydrocarbons using the CHO-2008 ReaxFF potential. Wang et al. [25] studied the pyrolysis and oxidation of \( n \)-dodecane. They observed that the main initiation mechanisms of the \( n \)-dodecane pyrolysis were the cleavage of C-C bond producing smaller hydrocarbon radicals and the dehydrogenation generating H and \( n \)-C\(_{12}\)H\(_{25}\) radicals. With regard to the oxidation of \( n \)-dodecane, formaldehyde was found to be an important intermediate, which was consistent with the kinetic modelling. The pyrolysis of \( n \)-heptane at high temperature was investigated by Ding et al. [26]. The results suggested that the entire pyrolysis process was dominated by the radicals and the main pathway was the unimolecular dissociation. Similar to \( n \)-dodecane, the pyrolysis of \( n \)-heptane was initiated by the C-C bond cleavage and the central C-C bond dissociation had a priority over the terminal ones. The H radical turned out to be the most important intermediate species. They also calculated the apparent activation energy of \( n \)-heptane pyrolysis, which was in good agreement with the experimental results. Chen et al. [27] conducted research on the pyrolysis of hexadecane under high-temperature and high-pressure conditions. According to the results of unimolecular simulations, eight different initiation mechanisms all beginning with the cleavage of C-C bond were proposed and it was found that the biradical mechanism led to a shorter pyrolysis process. In order to verify the enthalpy results from ReaxFF simulations, QM method was used and they agreed well with each other. Regarding the multimolecular simulations, the results indicated that both product distributions and reaction rates
strongly depended on the temperature. The calculated activation energy and pre-exponential factor were in accordance with the previous work.

2.4.1.3 Hydrocarbons with cyclic structures

In addition to the straight-chain hydrocarbons, the CHO-2008 ReaxFF force field is capable of describing the oxidation of hydrocarbons with cyclic structures as well. Chenoweth et al. [28] investigated the pyrolysis and oxidation of JP-10 jet fuel. They found that the primary decomposition mechanism was either forming an ethylene plus a C₈ hydrocarbon or resulting in two C₅ hydrocarbons. Moreover, the product distribution was dependent on the temperature and the obtained activation energy of JP-10 pyrolysis was comparable to the experimental value. The ReaxFF also produced a reasonable reaction pathway for the oxidation of JP-10, which is consistent with QM calculations thermodynamically. Similarly, Guo et al. [29] studied the initiation mechanism of JP-10 oxidation from a statistics perspective by analysing the radicals distribution. They proposed a detailed chain reaction pathway, i.e. 1. a radical pool including H, O, OH and HO₂ was developed; 2. the fragments decomposed from JP-10 were attacked by the radical pool forming oxygenated species such as formyls, alcohols and ketones; 3. these species were further oxidized leading to molecules such as H₂O and CO₂ and a new radical pool was developed for chain reactions. The research of toluene oxidation at high temperature was carried out by Cheng et al. [30]. Three initiation pathways were found: 1. the hydrogen abstraction by molecular oxygen or other small radicals to generate benzyl radical; 2. the C-H bond dissociation to produce benzyl and hydrogen radicals; 3. the C-C bond cleavage to form phenyl and methyl radicals. The results showed a decreasing oxidation reaction rate with the increasing equivalence ratio. The apparent activation energy extracted from ReaxFF MD simulations matched well with experimental results. Interestingly, Zhang et al. [31]
conducted a study on the effect of electromagnetic (EM) fields on the high temperature pyrolysis of toluene. It was indicated that the Arrhenius parameters could be affected by EM fields on the basis of various frequencies. Compared to ordinary oxidation without EM, the presence of EM reduced the total population of C-C bonds and restrained carbon build-up of pyrolysis residue. This research provides the possibility and validity of application of ReaxFF method coupled with an external physical force field.

2.4.1.4 Other large hydrocarbons and oxygenated hydrocarbons

The pyrolysis and oxidation of some large carbon material molecules such as fullerene [32] and graphite [33], as well as many other large oxygenated hydrocarbons including different ranks of coals (lignite/brown coal [34]; subbituminous coal [35, 36]; bituminous coal [37, 38]), phenolic [39, 40] and biomass [41-44], were also investigated by the CHO-2008 ReaxFF force field and they all produced excellent results proving the effectiveness of CHO-2008 for simulating the oxidation of large hydrocarbons and oxygenated hydrocarbons.

2.4.1.5 Upgrade of CHO-2008 to CHO-2016

In recent years, the classical CHO-2008 ReaxFF force field was systemically improved and upgraded to CHO-2016 by Ashraf and van Duin [45]. Two issues of the CHO-2008 parameter set were addressed. Firstly, the accuracy for describing the chemistry of oxidation of small hydrocarbons, especially the conversion of CO to CO2, was enhanced. Secondly, the problem that H abstraction from hydrocarbons by molecular oxygen was faster than expected resulting in the underestimation of the initiation temperature of oxidation, was solved. A series of high-temperature NVT (canonical)-MD simulations were performed to study the pyrolysis and oxidation of syngas, methane, JP-10 and n-butylbenzene and then the results were used to validate
the newly developed CHO-2016. The results showed that the \( \text{C}_1 \) chemistry described by CHO-2016 and the problem of low-temperature oxidation initiation was significantly improved while the accuracy for larger hydrocarbons was retained. Therefore, the new CHO-2016 can be used to study the pyrolysis and oxidation of a broad range of hydrocarbon/oxygenated hydrocarbon fuels and fuel mixtures irrespective of their molecular size or structure. Additionally, it has been proved that the CHO-2016 has the capability of studying both the solid and gas phase of carbon using the same parameter set. To sum up, different problems for varieties of hydrocarbon/oxygenated hydrocarbon fuels can now be solved with a single CHO-2016 ReaxFF force field as reviewed below.

Martin et al. [46] investigated the formation of giant fullerene through thermal treatment of fullerene soot and successfully demonstrated the integration of oxygen and the coalescence of two fullerenes. Song et al. [47] studied the blending influence on the oxidation of \( n \)-decane and toluene and showed that H/C ratio was a key parameter for the fuel oxidation. Chen et al. [48] conducted research on the initial mechanism and kinetics of incomplete oxidation of a multicomponent diesel fuel model. While the main products, influences of temperature and pressure, and mechanisms and pathways were elucidated, it was found that the main reason for the initial formation of coke was collision rather than gas phase thermal deposition under extremely high temperatures. The performance of various additives including ethanol, butanol, dimethyl carbonate, dibutyl carbonate, methyl tert-butyl ether and tri-tert amyl glycerol ether on the oxidation of a four-component diesel fuel model were also evaluated by Chen et al. [49]. They suggested that esters, ethers and alcohols with larger molecular weight such as 2-butanol were more suitable than alcohols with smaller molecular weight like ethanol as fuel additives. Ashraf et al. [50] studied the pyrolysis of binary fuel mixtures at
supercritical conditions and revealed that not only the activation energy of the most reactive component of a fuel mixture affected its overall pyrolysis characteristics, the role of pyrolysis products in assisting other less reactive molecules to decompose was more important. The effects of the electric field on the ethanol oxidation were investigated by Jiang et al. [51] and it was indicated that the reaction rate of the elementary reactions was altered and the reaction pathways were changed with the imposition of the electric field. The successful applications of the new CHO-2016 ReaxFF force field will make it become increasingly popular in the future.

2.4.2 Oxidation of aluminium nanoparticles

Aluminium nanoparticles (ANPs) are widely used in propulsion applications such as solid rocket propellants and have been extensively studied due to its remarkable advantages including high energy density, excellent catalytic activity, relative safety and low cost [52, 53]. Consequently, the investigation on complex oxidation mechanism of ANPs has attracted widespread attention, where ReaxFF MD is well utilized. Hong and van Duin [54] studied the mechanism of oxidation kinetics of the ANPs and the oxidation states in the oxide layer. They divided the oxidation mechanism into three stages and the results showed that the oxidation depended on both temperature and oxygen gas pressure, which resulted in different thickness and density of the oxide layer. Zheng et al. [55] explored the effect of ionization on the oxidation kinetics of core-shell Al/Al₂O₃ nanoparticles and found that Al atoms leaped over the interfacial gaps via thermal driving force and the energy barrier of Al ionization was higher with the increasing interfacial gap. They also proposed a competition mechanism between thermal driving force and ionization potential barrier to demonstrate the oxidation behaviour. Similarly, the ignition and oxidation of core-shell Al/Al₂O₃ nanoparticles were investigated by Chu et al. [56]. The results indicated that the
oxidation process proceeded in four stages, i.e. preheating, melting, fast Al core oxidation, and moderate oxide shell oxidation. The initial environmental temperature and the equivalent pressure were found to have significant impact on preheating but not on melting and the fast Al core oxidation was more sensitive to the equivalent pressure. Liu et al. [57] also studied the ignition and oxidation of core-shell ANPs and they focused on the thermodynamic and structure properties. It was suggested that the oxidation was controlled by diffusion behaviours of nanoparticles as well as oxygen molecules. Additionally, the ignition delay was shorter and oxidation temperature was higher in the case of ANPs with a thinner shell, which influenced the radiative heat transfer rate during the oxidation period.

Besides pure ANPs oxidation, the reaction of ANPs mixed with other components was also studied by ReaxFF MD. Hong and van Duin [58] developed a Al/C/H/O force field and used it to investigate the carbon coating and its effect on the oxidation of ANPs. A carbon coating layer was observed to be formed on the surface of bare ANPs and its growth strongly relied on the chosen hydrocarbon precursors. Furthermore, the oxidation of carbon coated ANPs at low temperatures was not as reactive as at elevated temperatures when the coating layer was removed. Their findings were in accordance with the experimental literature. Zhang et al. [59] studied the catalytic ethanol oxidation on ANPs with different oxidation states. The results showed that the initial temperature of ethanol oxidation was lowered in the presence of ANPs and the ethanol reactions were significantly affected by the different oxidation states of ANPs. Mei et al. [60] conducted research on the thermal decomposition of energetic explosives (TNT, RDX, HMX and CL-20) with ANPs, where they characterized the thermal decomposition mechanism as three main steps: i.e. adsorption period, diffusion period and formation period, and provided detailed analysis of energy, products formation, and distribution.
of structure and temperature. These successful applications demonstrate the feasibility and validity of ReaxFF MD on the study of aluminium-based nanoparticles.

### 2.4.3 Fuel oxidation assisted by graphene-based nanomaterials

Graphene-based nanomaterials have been considered as effective catalysts for the oxidation of fuel and propellant including nitromethane [61], nitrocellulose [62], carbon monoxide [63], methylcyclohexane [64], Jatropha Methyl Ester [65], diesel and biodiesel blends [66], and various jet fuels [67-69] in the past decade. Hence, the fundamental understanding of catalytic reaction mechanisms by graphene-based nanomaterials is highly desirable for improving their practical applications. Liu et al. [70] firstly carried out a study on the enhanced thermal decomposition of nitromethane on functionalized graphene sheets (FGS) using ab initio MD simulations. They revealed that the catalytic activity of FGS originated from lattice defect complex (carbon vacancies functionalized with oxygen-containing groups) within the graphene sheet, which remarkably improved the thermal decomposition of nitromethane and also its derivatives. A detailed mechanism involving the interaction between functional groups and various species was proposed. Moreover, the graphene sheets were not significantly changed or consumed during the oxidation showing consistency with experiments. Later on, Zhang et al. [71] used ReaxFF MD simulations to investigate the similar but larger nitromethane/FGS systems and further understand the catalytic effect of FGS. They compared the reactions of nitromethane with both FGS and pristine graphene sheets and reported that the catalytic activity was dependent on the temperature, functionalities of graphene sheets, and density of nitromethane. The interaction of functional groups on FGS and nitromethane was also detailed, which was found to agree with the previous ab initio MD simulations [70].
Although experimental studies have proved that graphene-based nanomaterials are promising catalysts for fuel and propellant oxidation, the underlying mechanisms are still poorly understood and the relevant research is very limited. The atomic-level insight into the catalytic reactions and processes are required to uncover the mechanisms and potentially benefit the design and improvement for the next-generation propulsion systems assisted by graphene-based nanomaterials. A part of the present research focuses on the atomistic study of hydrocarbon fuel oxidation enhanced by graphene-based nanomaterials using ReaxFF MD simulations.

2.5 Summary

MD is a very popular method for the dynamic simulation of large systems and provides the insight for detailed microscopic modelling at the atomic level. Particularly, ReaxFF MD is a powerful and efficient technique that can be used to describe the dynamic chemical reactions in large-scale complex systems. It bridges the gap between QM and classical force field based methods. According to Section 2.4, all the mentioned ReaxFF MD simulations produced comparable results with QM calculations and/or experimental data. Thus, it can be concluded that the ReaxFF method is competent to accurately detect the reaction pathways, produce the mechanisms, calculate the quantitative chemical kinetic parameters and estimate the product distribution thereby generating the detailed kinetic models for oxidation chemistry. To summarize, with ReaxFF technique, dynamic descriptions and highly accurate results of a large-scale reactive atomic system can be obtained.
Chapter 3 – Methods

3.1 Introduction

This chapter firstly gives a detailed introduction of ReaxFF reactive force field, followed by the general procedure of carrying out the ReaxFF MD simulation. Finally, the uncertainty and error of each force field used in the present research is evaluated.

3.2 ReaxFF reactive force field

As mentioned in Chapter 2, the classical MD simulation is unable to model chemical reactions as traditional force fields cannot describe breaking and forming of bonds and predefined rigid connectivity between atoms is required. The ReaxFF reactive force field, firstly developed by van Duin and co-workers [13] in 2001, is an excellent alternative, which is capable of modelling dissociation, transition and formation of bonds for chemical reactions based on the bond order concept. It bridges the gap between QM and classical force field based methods. A comprehensive review covering the development, applications and future directions of ReaxFF can be seen in the article [72].

Figure 3.1 ReaxFF in the hierarchy of computational chemical methods [73].
The concept of bond order is the kernel of ReaxFF and the force field parameters are obtained from QM calculations or/and experimental data. Bond orders are calculated directly from interatomic distances (Equation (3.1)) and continually updated at every iteration thereby allowing for connectivity changes [72].

\[
\text{BO}_{ij} = \text{BO}_{ij}^{\sigma} + \text{BO}_{ij}^{\pi} + \text{BO}_{ij}^{\pi\pi}
\]

\[
= \exp \left[ p_{bo1} \left( \frac{r_{ij}}{r_o^{\sigma}} \right)^{p_{bo1}} \right] + \exp \left[ p_{bo3} \left( \frac{r_{ij}}{r_o^{\pi}} \right)^{p_{bo3}} \right] + \exp \left[ p_{bo5} \left( \frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{bo5}} \right]
\]

(3.1)

where BO is the bond order between atoms \(i\) and \(j\), \(r_{ij}\) is interatomic distance, \(r_o\) terms are equilibrium bond lengths, and \(p_{bo}\) terms are empirical parameters. Equation (3.1) is continuous for transitions between \(\sigma\), \(\pi\), and \(\pi\pi\) bond character, producing a differentiable potential energy surface as required for calculating the interatomic forces.

Equation (3.2) describes the general energy contributions to the ReaxFF potential as below [72]:

\[
E_{\text{system}} = E_{\text{bond}} + E_{\overline{\text{o}r\overline{\text{e}}}\text{r}} + E_{\text{angle}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{specific}}
\]

(3.2)

\(E_{\text{system}}\): total potential energy of the system

\(E_{\text{bond}}\): a continuous function of interatomic distance and describes the energy associated with forming bonds between atoms

\(E_{\overline{\text{o}r\overline{\text{e}}}\text{r}}\): an energy penalty preventing the over coordination of atoms, which is based on atomic valence rules (e.g., a stiff energy penalty is applied if a carbon atom forms more than four bonds)

\(E_{\text{angle}} \& E_{\text{tors}}\): energies associated with three-body valence angle strain and four-body torsional angle strain
$E_{\text{Coulomb}} \& E_{\text{vdWaals}}$: electrostatic and dispersive contributions calculated between all atoms, regardless of connectivity and bond-order

$E_{\text{Specific}}$: system specific terms that are not generally included, unless required to capture properties particular to the system of interest, such as lone-pair, conjugation, hydrogen binding, and C2 corrections

The potential functions of each energy term excluding $E_{\text{Specific}}$ in Equation (3.2) are given below [20]:

$E_{\text{bond}}$:

$$E_{\text{bond}} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot \exp \left[ p_{\text{bel}} \left( 1 - \left( BO_{ij}^\sigma \right)^{\text{pos}} \right) \right] - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi^{\text{xx}}} \cdot BO_{ij}^{\pi^{\text{xx}}} \quad (3.3)$$

$E_{\text{over}}$:

$$E_{\text{over}} = \sum_{j=1}^{n_{\text{bond}}} \frac{p_{\text{ovun1}} \cdot D_e^\sigma \cdot BO_{ij}}{\Delta^\text{lp\text{corr}} + \text{Val}_j} \cdot \Delta^\text{lp\text{corr}} \left[ \frac{1}{1 + \exp \left( p_{\text{ovun2}} \cdot \Delta^\text{lp\text{corr}} \right)} \right] \quad (3.4a)$$

$$\Delta^\text{lp\text{corr}} = \Delta^\text{lp} - \frac{\Delta^\text{lp}}{1 + p_{\text{ovun3}} \cdot \exp \left\{ p_{\text{ovun4}} \cdot \left\{ \sum_{j=1}^{\text{neighbours}(i)} \left( \Delta_j - \Delta_j^\text{lp} \right) \cdot \left( BO_{ij}^\sigma + BO_{ij}^{\pi^{\text{xx}}} \right) \right\} \right\}} \quad (3.4b)$$

$E_{\text{angle}}$:

$$E_{\text{angle}} = f_5 \left( BO_{ij} \right) \cdot f_7 \left( BO_{jk} \right) \cdot f_8 \left( \Delta_j \right) \cdot \left\{ p_{\text{val1}} - p_{\text{val1}} \cdot \exp \left[ -p_{\text{val2}} \left( \Theta_o \left( BO \right) - \Theta_{ij} \right)^2 \right] \right\} \quad (3.5a)$$

$$f_5 \left( BO_{ij} \right) = 1 - \exp \left( -p_{\text{val3}} \cdot BO_{ij}^{\text{pw}^\text{xx}} \right) \quad (3.5b)$$

$$f_8 \left( \Delta_j \right) = \frac{p_{\text{val5}} - (p_{\text{val5}} - 1) \cdot 2 + \exp \left( p_{\text{val6}} \cdot \Delta_j^{\text{angle}} \right)}{1 + \exp \left( p_{\text{val6}} \cdot \Delta_j^{\text{angle}} \right) + \exp \left( -p_{\text{val7}} \cdot \Delta_j^{\text{angle}} \right)} \quad (3.5c)$$
SBO = \sum_{n=1}^{\text{neighbours}(j)} (BO_{jn}^z + BO_{jn}^{\pi}) + \left[1 - \prod_{n=1}^{\text{neighbours}(j)} \exp(-BO_{jn}^\delta) \right] \left(-\Delta_{j}^{\text{angle}} - p_{\text{val}} \cdot n_{p,j} \right) \tag{3.5d}

\Delta_{j}^{\text{angle}} = -\text{Val}_{j}^{\text{angle}} + \sum_{n=1}^{\text{neighbours}(j)} BO_{jn} \tag{3.5e}

SBO2 = 0 \text{ if } SBO \leq 0
SBO2 = SBO^{\text{vor}} \text{ if } 0 < SBO < 1
SBO2 = 2 - (2 - SBO)^{\text{vor}} \text{ if } 1 < SBO < 2
SBO2 = 2 \text{ if } SBO > 2

\Theta_0(BO) = \pi - \Theta_{0,0} \cdot \left[1 - \exp\left[-p_{\text{val10}} \cdot (2 - SBO2)\right]\right] \tag{3.5g}

E_{\text{tors}}:

E_{\text{tors}} = f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) \cdot \sin \Theta_{jk} \cdot \sin \Theta_{jkl} \cdot \left[\frac{1}{2} V_1 \cdot (1 + \cos \omega_{jkl}) + \frac{1}{2} V_2 \cdot \exp\left(p_{\text{tor1}} \cdot (BO_{jk} - 1 + f_{11}(\Delta_j, \Delta_k))^{2}\right) \right] \tag{3.6a} \left[1 - \cos 2 \omega_{jkl} + \frac{1}{2} V_3 \cdot (1 + \cos 3 \omega_{jkl}) \right]

f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) = \left[1 - \exp\left[-p_{\text{tor2}} \cdot BO_{ij}\right]\right] \cdot \left[1 - \exp\left[-p_{\text{tor2}} \cdot BO_{jk}\right]\right] \cdot \left[1 - \exp\left[-p_{\text{tor2}} \cdot BO_{kl}\right]\right] \tag{3.6b}

f_{11}(\Delta_j, \Delta_k) = \frac{2 + \exp\left[-p_{\text{tor3}} \cdot (\Delta_j^{\text{angle}} + \Delta_k^{\text{angle}})\right]}{1 + \exp\left[-p_{\text{tor3}} \cdot (\Delta_j^{\text{angle}} + \Delta_k^{\text{angle}})\right] + \exp\left[-p_{\text{tor4}} \cdot (\Delta_j^{\text{angle}} + \Delta_k^{\text{angle}})\right]} \tag{3.6c}

E_{\text{vdWaals}}:

E_{\text{vdWaals}} = Tap \cdot D_{ij} \cdot \left\{ \exp\left[\alpha_{ij} \left(1 - \frac{f_{13}(r_{ij})}{r_{\text{vdW}}}\right)\right] - 2 \cdot \exp\left[\frac{1}{2} \cdot \alpha_{ij} \left(1 - \frac{f_{13}(r_{ij})}{r_{\text{vdW}}}\right)\right]\right\} \tag{3.7a}
\[
\begin{align*}
    f_{ij} (r_{ij}) &= \left[ r_{ij}^{p_{\text{cut}}} + \left( \frac{1}{\gamma_w} \right)^{p_{\text{cut}}} \right]^{1/3} \\
    T_{\text{ap}} &= T_{\text{ap}_7} \cdot r_{ij}^7 + T_{\text{ap}_6} \cdot r_{ij}^6 + T_{\text{ap}_5} \cdot r_{ij}^5 + T_{\text{ap}_4} \cdot r_{ij}^4 + T_{\text{ap}_3} \cdot r_{ij}^3 + T_{\text{ap}_2} \cdot r_{ij}^2 + T_{\text{ap}_1} \cdot r_{ij} + T_{\text{ap}_0}
\end{align*}
\] (3.7b)

\[
\begin{align*}
    T_{\text{ap}_7} &= 20/R_{\text{cut}}^7 \\
    T_{\text{ap}_6} &= -70/R_{\text{cut}}^6 \\
    T_{\text{ap}_5} &= 84/R_{\text{cut}}^5 \\
    T_{\text{ap}_4} &= -35/R_{\text{cut}}^4 \\
    T_{\text{ap}_3} &= 0 \\
    T_{\text{ap}_2} &= 0 \\
    T_{\text{ap}_1} &= 0 \\
    T_{\text{ap}_0} &= 1 
\end{align*}
\] (3.7c)

\[
E_{\text{Coulomb}} = T_{\text{ap}} \cdot C \cdot \frac{q_i \cdot q_j}{\left[ r_{ij}^3 + \left( 1/\gamma_{ij} \right)^3 \right]^{1/3}}
\] (3.8)

The detailed description of the parameters and variables in Equation (3.1-3.8) are provided in the Supporting Information of the publication [20]. As described in Equation (3.2), the ReaxFF potential is divided into bonded and non-bonded terms and they are calculated independently, i.e. separate bond order dependent and independent contributions. The bond orders are incorporated in all valence terms, meaning that the energy contributions like angle and torsion are dependent on connectivity, which guarantees the energies and forces associated with these terms going to zero upon bonds dissociation. Moreover, ReaxFF computes non-bonded (van der Waals and Coulomb) interactions between all atoms with no exclusion, regardless of connectivity. Additionally, a shielding term is included in the van der Waals and Coulomb interaction.
for the purpose of circumventing the excessive short-range non-bonded interactions.

There is no information transferred between the bond order and non-bond order based terms. An overview and schematic of energy components of the ReaxFF potential is shown in Figure 3.2 [72].

![Figure 3.2 Schematic of energy components of the ReaxFF potential [72].](image)

ReaxFF features the long-time large-scale (more than 1000 atoms, even hundreds of thousands of particles) reactive MD simulations, which are impractical or impossible to be done by QM methods. It is computationally much cheaper than QM methods while retaining a high level of accuracy. But compared with classical MD methods, the computation of ReaxFF is more expensive due to the additional modelling of chemical reactions. A comparison of computational expense between DFT and ReaxFF can be seen in Figure 3.3 [74]. ReaxFF methodology has been extensively used in a broad range of areas including combustion, catalysis, fuel cells, and nanotubes in the last decade [75]. A ReaxFF development tree summarized by Senftle et al. [72] is illustrated in Figure 3.4. As can be seen in Figure 3.4, there are currently two major groupings, i.e. ReaxFF branches of combustion and aqueous, where parameter sets on a common ‘branch’ are fully transferable with one another. The current (by 2018) development st-
Figure 3.3 Comparison of computational expense between DFT and ReaxFF [74].

Figure 3.4 ReaxFF development tree summarized by Senftle et al. [72].
ations or/and experimental data. The development of new ReaxFF reactive force fields is still ongoing to enrich the ReaxFF methodology.

Figure 3.5 Current development status of ReaxFF referring to the periodic table [74].

Significant contributions of ReaxFF MD to the fuel oxidation and catalytic reactions have been made in the last decade since the first ReaxFF force field for oxidation was developed as reviewed in Chapter 2. However, there are still limitations. For example, one limitation of ReaxFF (or ‘standard’ ReaxFF) compared to QM methods is that it does not handle the reactions kinetically controlled by electron transfer very well such as electrolytic reactions. In other words, the explicit electron transfer issue is always a barrier in ‘standard’ ReaxFF. But the extension of the ‘standard’ ReaxFF to the recently developed new eReaxFF [76, 77] has now been able to (at least partially) solve the electron transfer problems. This sheds the light on the potential of ReaxFF to effectively deal with the electron issues in the near future thus narrowing its gap with QM methods. Additionally, the principal limiting factor is the high computational cost of ReaxFF MD, which sets a practical limitation on the size of the simulated system (to typically several millions of atoms at present [72]). This also sets a limit on the physical time that can be simulated up to microseconds. Therefore,
ReaxFF MD is best suited for fundamental studies of small and fast-changing systems, where the unknown mechanisms are dominated by molecular interactions. Such limitations have been significantly lifted in the past few decades, thanks to the rapid advancement in computing hardware and software. This trend is set to continue as the exascale computing era is fast approaching. As a result, some hybrid or accelerated ReaxFF methods and advanced computational techniques are desired to enhance the capability of ReaxFF-based simulations. The relevant developments are indeed in progress. To sum up, more and more unrevealed problems in the oxidation chemistry can be solved by the increasingly stronger ReaxFF technique.

3.3 General procedure of ReaxFF MD simulation

The key steps for carrying out a ReaxFF MD simulation are generalized as below and they are employed throughout the research.

3.3.1 Initial model building

The first step is to build an initial simulation model(s) for the studied system. Basically, it is a simulation box filled with target molecules or nanoparticles. Various software packages can help with the system modelling including Materials Studio [78], Packmol [79], LAMMPS [80] or in-house code if necessary. The final goal is to obtain the required information of the simulation box (e.g. position and dimension) and every atom (e.g. atom number, molecule number, atom type, and coordinates) in the simulation box. Therefore, after the initial model building, the configuration has to be converted to a data file, which will be used as an input file for the simulation.

3.3.2 Energy minimization

After inputting the model file, energy minimization procedure should be carried out to eliminate the artificial effects on the initial geometric configuration and optimize
the structure. The conjugate gradient algorithm is chosen for energy minimization. In the present research, the steps of energy minimization, and the following system equilibration and reactive simulation are all performed using the REAXC [81] package embedded in LAMMPS [80].

3.3.3 System equilibration

Before the reactive simulation, every system needs to undergo the equilibration process under specified conditions (e.g. temperature and duration depending on the studied system) to reach the steady state and it usually uses system potential energy as an indicator. No reaction should occur during the equilibration. For this purpose, some bond parameters (e.g. C-O, H-O) may be switched off by eliminating the bond parameters describing those interactions in the ReaxFF force field file to prevent the occurrence of reactions during the equilibration. The NVT ensemble (canonical ensemble: constant number of particles N, volume V, and temperature T) is selected as a suitable ensemble for equilibration of all of the systems studied in the present research. Other ensembles such as NPT (isothermal-isobaric ensemble: constant number of particles N, pressure P, and temperature T) could also be used for equilibration of different systems.

3.3.4 Reactive simulation

The reactive simulation process is the main and most crucial part in ReaxFF MD simulation. The reaction occurs and the desired results are calculated during the process. A wide range of results can be produced as needed. Among them, bonding information and dynamic trajectory are the most two essential and important results. The NVT and NVE (microcanonical ensemble: constant number of particles N, volume V, and total energy E) ensembles are adopted for the reactive simulations in the present research. For NVT, both ramped- and fixed-temperature simulations are involved; and for NVE,
the simulations start from a specified initial condition. Similarly, the choice of ensemble highly depends on the purpose of research and other ensembles could also be used for the reactive simulations.

3.3.5 Post-processing

Some of the results such as system temperature and potential energy can be outputted directly and used straightforwardly. However, most of the raw results need post-processing to be presented in the desired form. For example, bonding information has to be processed to obtain the product distribution. A script called ‘mol_fra.c’ included in the LAMMPS package was developed to analyse the bonding information. To run the code, the cutoff for bond orders describing the bond order threshold must be defined to recognize the species, above which atoms are considered connected. Specifically, a lower bond order cutoff leads to more sensitive species recognition, which means atoms are more ‘easily’ connected. A commonly used 0.3 bond order cutoff normally gives reasonable results but a lower value such as 0.2 could help with capturing all the reactions in order to detect all possible reaction pathways including those unsuccessful events producing very short-lived species [20, 28]. Hence, the bond order cutoff value can be adjusted to meet different requirements. Another essential result, dynamic trajectory, which mainly contains the information of atomic attributes, also requires processing for visualization. The two popular visualization packages, VMD [82] and OVITO [83], are employed to visualize the simulation results in the present research. These two packages are also able to produce some additional results based on the trajectory information. To obtain other results of interest, either available open source or self-developed codes should be used to process the simulation outputs.
3.4 Uncertainty and error analysis

The accuracy of the results obtained from the ReaxFF MD simulation significantly relies on the chosen force field. Therefore, it is necessary to evaluate the uncertainty and error of each used force field for their specific application in the present research. In total, five ReaxFF force fields are used, i.e. one in Chapter 4 (C/H/O/N [84]), one in Chapter 5 (Al/C/H/O [58]), two in Chapter 6 (C/H/O-2008 [20] and Pt/C/H/O [85]), and one in Chapter 7 (C/H/O-2016 [45]). These five force fields are examined individually by investigating the same fuel as in each chapter at two different temperatures using a simplified demonstrative system. The time evolution of one representative species is used as the indicator for demonstrating the uncertainty and error. The details of configuration for examination of each force field are given in Table 3.1.

Table 3.1 Details of configuration for examination of each force field used in the present research.

<table>
<thead>
<tr>
<th>Force Field</th>
<th>System Composition</th>
<th>Cubic Box Size (Å)</th>
<th>Temperature (K)</th>
<th>Indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/H/O/N</td>
<td>30 C₂H₅OH</td>
<td>28.42</td>
<td></td>
<td>C₂H₅OH</td>
</tr>
<tr>
<td>Al/C/H/O</td>
<td>AlH₃ (1.5 nm diameter sphere)</td>
<td>60.00</td>
<td>2300</td>
<td>H₂</td>
</tr>
<tr>
<td>C/H/O-2008</td>
<td>40 CH₄ + 80 O₂</td>
<td>32.85</td>
<td>&amp;</td>
<td>CH₄</td>
</tr>
<tr>
<td>Pt/C/H/O</td>
<td>40 CH₄ + 80 O₂ + 1 tetrahedral Pt cluster</td>
<td>32.87</td>
<td>2800</td>
<td>CH₄</td>
</tr>
<tr>
<td>C/H/O-2016</td>
<td>15 JP-10</td>
<td>25.70</td>
<td></td>
<td>JP-10</td>
</tr>
</tbody>
</table>

Figure 3.6 shows the configuration of each simulation system. For the examination of two force fields in Chapter 6 (Figure 3.6c & d), 80 oxygen molecules are introduced to accelerate the reaction because of the low reactivity of pure thermal decomposition
of methane. Following the general procedure, all of the five systems start with energy minimization, followed by 20 ps NVT equilibration at 1000 K (except 500 K for AlH$_3$ due to its high reactivity). Next, a series of reactive NVT MD simulations for each system are performed at 2300 and 2800 K for 500 ps. The damping constant is 100 fs and the time step is 0.1 fs. Simulation results are recorded every 0.1 ps. Consistent with Chapter 4-7, a 0.3 bond order cutoff is adopted for species recognition in the AlH$_3$ system and all of the other systems use a 0.2 cutoff value. Every simulation case (one system at one temperature) is run three times independently and the results are averaged for analysis.

**Figure 3.6** Illustration of configuration of each simulation system: (a) C$_2$H$_5$OH, (b) AlH$_3$, (c) CH$_4$ + O$_2$, (d) CH$_4$ + O$_2$ + Pt and (e) JP-10. C, H, O, Al and Pt atoms are represented in grey, white, red, purple and blue, respectively.

The demonstration of the uncertainty and error of each force field can be seen in Figure 3.7. The error bars presented in the figure are obtained from the standard error
Figure 3.7 Time evolution of the number of the representative species in each simulation system: (a) C$_2$H$_5$OH, (b) AlH$_3$, (c) CH$_4$ + O$_2$, (d) CH$_4$ + O$_2$ + Pt and (e) JP-10. The error bars are obtained from the standard error of the mean (SEM).

It is worth mentioning that the uncertainty and error is expected to be reduced with the increasing number of independent runs and increasing size of the...
simulation system. However, the balance between the accuracy and computational expense should be considered based on the results of interest.
Chapter 4 – Ethanol Oxidation with High Water Content

4.1 Introduction

The development of environmentally-friendly alternative fuels have been prompted by the severe problem of combustion emissions and the finite resources of conventional fossil fuels. Ethanol has numerous advantages as a widely acknowledged renewable resource. It can suppress soot formation and reduce pollutant emissions when used as a fuel additive in internal combustion (IC) engines [86]. Furthermore, the overall octane rating of blends of ethanol and fossil gasoline can be increased by the high knock resistance of ethanol, potentially permitting spark ignition (SI) engine operation at higher compression ratios and thus thermal efficiencies [87]. However, the water content of ethanol derived from biomass is inherently high, and the necessary distillation and dehydration processes to obtain anhydrous ethanol are both energy-intensive [88]. Data shows that the required energy for distilling ethanol grows exponentially as the fraction volume of ethanol increases and 37% of the total production cost is spent on dewatering activities [89]. It is therefore of great interest to study oxidation of ethanol containing high water concentration, as enabling the direct use of hydrous ethanol could significantly save energy and cost during production.

The study of hydrous ethanol oxidation has been lasted for a long time by both experiments and simulations. The combustion characteristics of wet ethanol by laser ignition was investigated by Rahman et al. [90]. They found that compared to the anhydrous ethanol, with the addition of water in ethanol, the combustion rate was accelerated and the laser ignition delay was shorter. Their simulation also demonstrated that the water blending reduced the adiabatic flame temperature and laminar burning velocity. The decrease of laminar burning velocity was also observed in Liang et al.’s
experiment and numerical modelling. Breaux and Acharya [92] studied the influence of water addition on swirl-stabilized ethanol/air flames and concluded that the exhaust temperature was decreased thereby reducing the nitrogen oxides emissions. Saxena et al. [93] developed a homogeneous charge compression ignition (HCCI) engine retrofitted with an exhaust heat recovery system and they explored the direct use of wet ethanol as the fuel. The results showed that burning hydrous ethanol could achieve the best operating conditions for the engine. Mack et al. [94] obtained the similar outcomes for the usage of wet ethanol in an HCCI engine. Munsin et al. [95] examined the performance and emissions of a SI engine running with hydrous ethanol and reported that both regulated and unregulated emissions could be reduced provided that a catalytic converter is employed. To summarize, it was indicated that direct use of hydrous ethanol could be more efficient [96] and cost-effective [97] than dehydrated ethanol in many combustion applications, including IC engines. On the other hand, the fuel calorific value is reduced by burning hydrous ethanol, and the presence of water blended with ethanol has seen increased specific fuel consumption in engine experiments, and can lead to higher NOx emissions if ignition timing is advanced in order to take advantage of enhanced knock resistance and produce higher power output [98]. In tests of hydrous ethanol in a SI engine at constant load and speed, Munsin et al. [95] observed increases in engine-out emissions of formaldehyde and acetaldehyde in addition to CO and HC with an increase in water content from 20 % to 40 %. Moreover, the stability and storage potential of the fuel blend is compromised because the use of hydrous ethanol in blends with fossil gasoline can result in phase separation [99].

Although previous research has proved hydrous ethanol to be a promising alternative fuel, the underlying mechanisms of hydrous ethanol oxidation are still poorly understood. In this study, the fundamental reaction mechanisms of hydrous
ethanol oxidation in comparison with ethanol oxidation under fuel-air conditions are investigated. The reaction rates and detailed reaction pathways are achieved by analysing the time evolution of the reaction and the atomic trajectory. Finally, the effects of water blending on ethanol oxidation are uncovered.

4.2 Simulation details

The ReaxFF force field of C/H/O/N parameters [84] is used for all the MD simulations. Three cubic and periodic simulation systems are built at the same density of 0.062 g/cm³ with different gas phase components. Table 4.1 shows the details of the studied reactive systems. All the three systems adopt the stoichiometric condition of ethanol and oxygen (1:3). System 1 represents the environment of fuel-air oxidation. (In the air, the proportion of oxygen and nitrogen molecules is approximately 1:4, which is calculated based on their volume fractions and the total density.) It is worth noting that Systems 2 and 3 are simplified with no nitrogen molecules from the perspective of setting up and running the simulations as nitrogen reaction is not observed within the studied time scale of simulations. In System 2, the 480 nitrogen molecules are simply replaced with 480 water molecules to study the effects of high water concentration. The number of water molecules is reduced to 20 in System 3 in order to investigate the ethanol oxidation with different ethanol/water ratios. To keep the same density for all the three systems, the size of the cubic simulation boxes is adjusted accordingly.

**Table 4.1** Construction details of the studied systems. Size is the length of cubic simulation box.

<table>
<thead>
<tr>
<th>System</th>
<th>No. of Molecules</th>
<th>Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₂H₆O</td>
<td>O₂</td>
</tr>
<tr>
<td>1</td>
<td>40</td>
<td>120</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>120</td>
</tr>
</tbody>
</table>
All the MD simulations use the canonical ensemble (NVT) in conjunction with the Nosé-Hoover thermostat and the damping constant is 100 fs. Every system undergoes energy minimization before the reactive simulation to optimize the initial geometric configuration, followed by the NVT for 50 ps at 1000 K. After the equilibration, a series of reactive NVT MD simulations for each system are performed for 1000 ps at temperatures ranging from 2000 K to 3000 K with an increment of 200 K. In previous ReaxFF MD simulations, particularly for combustion, to overcome the limitation of computing power, it is a common strategy to employ a high temperature to accelerate the reactions [20, 23, 28, 51, 100-107]. More importantly, the absolute temperature used in the present research is less important because it is a comparative study of different cases. A 0.1 fs time step is adopted for both the equilibrating and reactive simulations, which was found suitable for high-temperature (2500K) ReaxFF MD simulations [20]. The simulation results are outputted every 0.1 ps. A bond order cutoff of 0.2 is chosen to recognize the species forming during the simulation as a low cutoff value can help with capturing all the reactions involving those with very short-lived species [20]. Three parallel simulations, each of which has a unique starting configuration, are set up for every case (one system at one temperature), resulting in 54 simulations in total. The results for each simulation case are averaged for further analysis. Chemical Trajectory AnalYzer (ChemTraYzer) [23] scripts are employed to analyse the reaction pathways.

4.3 Results and discussions

4.3.1 Time evolution of potential energy

Figure 4.1 describes the time evolution of potential energy for ethanol oxidation in both O2/N2 and O2/H2O atmospheres at various temperatures from 2000 K to 3000 K. Overall, the potential energy firstly rises to a peak point and then drops down as the time passes. However, higher temperature leads to more rapid increasing and
decreasing of the potential energy, which means that the heat absorption and release are accelerated so that the ethanol oxidation is promoted by the elevated temperature. The comparison of Figure 4.1a and 4.1b clearly shows that the amount of the absorbed energy (potential energy difference between the starting point and the maximum point) at the initial stage of the reaction is much more in O$_2$/H$_2$O than in O$_2$/N$_2$ environment (e.g. 4026.50 and 3298.00 Kcal/mol at 3000 K, respectively), as is the amount of the heat release (potential energy difference between the maximum point and the end point) at a later stage (e.g. 9634.97 and 7246.57 Kcal/mol at 3000 K, respectively). Likewise, the processes of heat absorption (e.g. average 84.06 and 41.02 Kcal/mol/ps from the starting to the maximum point of potential energy at 3000 K, respectively) and release (e.g. average 10.12 and 7.88 Kcal/mol/ps from the maximum to the end point of potential energy at 3000 K, respectively) are faster in H$_2$O environment. These results imply that water does participate in and facilitate the reaction of ethanol oxidation.

![Figure 4.1](image_url)

**Figure 4.1** Time evolution of potential energy during NVT MD simulations of ethanol oxidation from 2000 K to 3000 K in (a) O$_2$/N$_2$ and (b) O$_2$/H$_2$O (System 2) environments.

### 4.3.2 Reaction rate under various conditions

The time evolution of the number of ethanol molecules over a temperature range from 2000 K to 3000 K for all three systems is used to investigate the reaction rate und-
Figure 4.2 Time evolution of ethanol molecule number during NVT MD simulations of ethanol oxidation from 2000 K to 3000 K in O$_2$/N$_2$ (hollow symbol) and O$_2$/H$_2$O (solid symbol) environments.

Figure 4.2 shows the results of ethanol oxidation in N$_2$ and H$_2$O environments. The reaction rate of ethanol increases remarkably as temperatures rise in both cases. In addition, the consumption of ethanol is faster in O$_2$/H$_2$O than in O$_2$/N$_2$ at all studied temperatures, which indicates that ethanol oxidation is enhanced by replacing N$_2$ with H$_2$O. This phenomenon of improved ethanol oxidation with water was also observed in a previous experiment [90]. From 2400 K, the reaction rate of ethanol in O$_2$/H$_2$O is almost the same and even slightly higher than in O$_2$/N$_2$ at the next temperature point. This means that a similar reaction rate of ethanol in N$_2$ environment can be achieved at a 200 K lower temperature in H$_2$O environment when the temperature of ethanol oxidation in N$_2$ environment goes beyond 2600 K. The aforementioned results can also be supported by the time evolution of species number as illustrated in Figure 4.3. Firstly, the peak value of species number is successively reached by a descending temperature order and the climbing rate is faster with the boosted temperature, which is consistent with the fact that higher temperature results in
quicker reaction. Although there is not a significant difference in the maximum species number generated during the reactions at each temperature between ethanol oxidation in N2 and H2O environments, other distinctions are obvious. The time to reach the peak species number is shorter in O2/H2O than in O2/N2 at each temperature, which agrees with experimental results that the presence of water in ethanol advances the ionisation process and accelerates the radical production rate [90]. In addition, the rising and falling rates of the species number are more rapid in H2O environment verifying the enhancement of ethanol oxidation with water compared to nitrogen.

![Figure 4.3](image)

Figure 4.3 Time evolution of species number during NVT MD simulations of ethanol oxidation from 2000 K to 3000 K in (a) O2/N2 and (b) O2/H2O environments.

The results of ethanol oxidation with two different ethanol/water ratios are depicted in Figure 4.4. Generally, the reaction rate increases as the water content decreases, as would be expected. However, the difference in reaction rate between the two becomes smaller with increasing temperature. At 3000 K, the two lines nearly collapse into each other. This suggests that the water content of ethanol plays a vital role in the reaction rate at low temperatures but is significantly less important at high temperatures. Further studies are needed to determine whether a threshold of effect of water content on reaction rate exists under certain conditions.
4.3.3 Reaction pathways and time evolution of key species

All the simulation results from different temperatures and replicas are merged into one single mechanism to explore the reaction pathways of ethanol oxidation in N2 and H2O environments, respectively. The full list of elementary reactions (Table A.1 in the Appendices) is generated by filtering out the pathways with less than 40 accumulated total flux, resulting in 23 reactions for O2/N2 and 38 reactions for O2/H2O. The flux here represents the number of times that one reaction happens during the studied time period. These extracted mechanisms are in good agreement with previous experimental results under similar conditions [87, 108-111]. Table 4.2 displays a reduced list of reactions which has more than 50 accumulated total flux for ethanol oxidation. Finally, there are 17 and 30 reactions remaining for O2/N2 and O2/H2O, respectively. Time evolution of some relevant key species is also shown in Figure 4.5.
Table 4.2 Reduced list of elementary reactions during NVT MD simulations of ethanol oxidation in (a) O2/N2 and (b) O2/H2O environments. Different reactions within the two pathways are marked with asterisk.

<table>
<thead>
<tr>
<th>ID</th>
<th>(a) Reaction (O2/N2)</th>
<th>Total Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C2H6O → C2H5 + OH</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>H + O2 → HO2</td>
<td>222</td>
</tr>
<tr>
<td>3</td>
<td>* HO2 → OH + O</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>* HO2 + OH → H2O + O2</td>
<td>110</td>
</tr>
<tr>
<td>5</td>
<td>H2O2 → OH + OH</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>C2H6O + OH → C2H5O + H2O</td>
<td>179</td>
</tr>
<tr>
<td>7</td>
<td>* C2H6O + HO2 → C2H5O + H2O2</td>
<td>74</td>
</tr>
<tr>
<td>8</td>
<td>C2H5O → C2H4 + OH</td>
<td>82</td>
</tr>
<tr>
<td>9</td>
<td>C2H5O → CH2O + CH3</td>
<td>149</td>
</tr>
<tr>
<td>10</td>
<td>* C2H5 + O2 → C2H4 + HO2</td>
<td>66</td>
</tr>
<tr>
<td>11</td>
<td>C2H4 + OH → C2H3 + H2O</td>
<td>63</td>
</tr>
<tr>
<td>12</td>
<td>CH3O → CH2O + H</td>
<td>56</td>
</tr>
<tr>
<td>13</td>
<td>CH3 + OH → CH3O</td>
<td>61</td>
</tr>
<tr>
<td>14</td>
<td>* CH3 + O2 → CH3O2</td>
<td>56</td>
</tr>
<tr>
<td>15</td>
<td>CH2O + OH → CHO + H2O</td>
<td>96</td>
</tr>
<tr>
<td>16</td>
<td>CHO → CO + H</td>
<td>57</td>
</tr>
<tr>
<td>17</td>
<td>CHO + O2 → CO + HO2</td>
<td>68</td>
</tr>
<tr>
<td>ID</td>
<td>(b) Reaction (O₂/H₂O)</td>
<td>Total Flux</td>
</tr>
<tr>
<td>----</td>
<td>-----------------------</td>
<td>------------</td>
</tr>
<tr>
<td>1</td>
<td>C₂H₆O → C₂H₅ + OH</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>H + O₂ → HO₂</td>
<td>301</td>
</tr>
<tr>
<td>3</td>
<td>* H₂O + HO₂ → H₂O₂ + OH</td>
<td>468</td>
</tr>
<tr>
<td>4</td>
<td>* H₂O + H → H₂ + OH</td>
<td>209</td>
</tr>
<tr>
<td>5</td>
<td>* H₂O + O → OH + OH</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>H₂O₂ → OH + OH</td>
<td>302</td>
</tr>
<tr>
<td>7</td>
<td>* H₂O₂ + HO₂ → H₂O + O₂ + OH</td>
<td>79</td>
</tr>
<tr>
<td>8</td>
<td>* H₂O₂ + H → H₂O + OH</td>
<td>77</td>
</tr>
<tr>
<td>9</td>
<td>* H + OH → H₂O</td>
<td>81</td>
</tr>
<tr>
<td>10</td>
<td>C₂H₆O + OH → C₂H₅O + H₂O</td>
<td>320</td>
</tr>
<tr>
<td>11</td>
<td>* C₂H₆O + OH → CH₂O + CH₃ + H₂O</td>
<td>60</td>
</tr>
<tr>
<td>12</td>
<td>C₂H₅O → C₂H₄ + OH</td>
<td>98</td>
</tr>
<tr>
<td>13</td>
<td>C₂H₅O → CH₂O + CH₃</td>
<td>171</td>
</tr>
<tr>
<td>14</td>
<td>* C₂H₅O → C₂H₄O + H</td>
<td>51</td>
</tr>
<tr>
<td>15</td>
<td>* C₂H₄O + OH → C₂H₃O + H₂O</td>
<td>62</td>
</tr>
<tr>
<td>16</td>
<td>C₂H₄ + OH → C₂H₃ + H₂O</td>
<td>118</td>
</tr>
<tr>
<td>17</td>
<td>* C₂H₃O → C₂H₂O + H</td>
<td>60</td>
</tr>
<tr>
<td>18</td>
<td>* C₂H₂O + OH → C₂HO + H₂O</td>
<td>61</td>
</tr>
<tr>
<td>19</td>
<td>* CH₃O + OH → CH₃O + H₂O</td>
<td>66</td>
</tr>
<tr>
<td>20</td>
<td>CH₃O → CH₂O + H</td>
<td>54</td>
</tr>
<tr>
<td>21</td>
<td>CH₃ + OH → CH₄O</td>
<td>128</td>
</tr>
<tr>
<td>22</td>
<td>CH₂O + OH → CHO + H₂O</td>
<td>219</td>
</tr>
<tr>
<td>23</td>
<td>* CHO₂ → CO₂ + H</td>
<td>159</td>
</tr>
<tr>
<td>24</td>
<td>* CHO₂ + O₂ → CO₂ + HO₂</td>
<td>56</td>
</tr>
<tr>
<td>25</td>
<td>CHO → CO + H</td>
<td>92</td>
</tr>
<tr>
<td>26</td>
<td>* CHO + OH → CH₂O₂</td>
<td>81</td>
</tr>
<tr>
<td>27</td>
<td>CHO + O₂ → CO + HO₂</td>
<td>86</td>
</tr>
<tr>
<td>28</td>
<td>* CO₃ → CO₂ + O</td>
<td>53</td>
</tr>
<tr>
<td>29</td>
<td>* CO + OH → CHO₂</td>
<td>98</td>
</tr>
<tr>
<td>30</td>
<td>* CO + O₂ → CO₃</td>
<td>61</td>
</tr>
</tbody>
</table>
Figure 4.5 Time evolution of some key species during NVT MD simulations of ethanol oxidation from 2000 K to 3000 K in (a1~f1) O$_2$/N$_2$ and (a2~f2) O$_2$/H$_2$O environments.
According to the extracted mechanisms, as expected, ethanol oxidation is initiated by the decomposition of ethanol forming C₂H₅ radicals, until CHO and CO radicals are seen at a very late stage. Additionally, key intermediate products such as C₂H₄, CH₃ and CH₂O are found in the reactions as well. The accordance with previous experimental results [87, 108-111] proves the effectiveness and accuracy of the present ReaxFF MD method to study the reaction mechanism of ethanol oxidation. More specifically, all reactions shown in Table 4.2a are covered by the previous detailed kinetics studies of ethanol oxidation from Marinov [109] and Norton & Dryer [110] except a couple of minor differences. For example, R14a shows the reaction of CH₃ + O₂ → CH₃O₂ instead of CH₃ + O₂ → CH₃O + O, which appears in the both aforementioned two studies. But the CH₃O₂ → CH₃O + O reaction can be found in the present mechanism if a lower total flux filter is used. The total flux in Table 4.2a can also be comparable to the activation energy in Marinov’s [109] study, which is applicable to high temperature ethanol oxidation and similar to the present research. Excluding those prerequisite initiation decomposition reactions (R1a and R9a), R2a, R6a and R4a have the largest three numbers of the total flux. The corresponding activation energy of these three reactions are 0, 0.600 - 1.634 and 3.500 Kcal/mol, respectively. In contrast, for those reactions with low total flux number such as R16a, R11a and R10a, the activation energy is relatively higher (17.000, 5.936 and 7.585 Kcal/mol, respectively). All the reactions displayed in Table 4.2 are obtained by setting specified conditions in the present research within the simulation time scale (not totally completed ethanol oxidation). Therefore, compared to some previous studies having hundreds of elementary reactions, this study focuses more on the significant differences of reaction pathways between ethanol oxidation in N₂ and H₂O environments.
4.3.3.1 Chemical effects of water addition

The different reactions within the two pathways are marked with asterisk in Table 4.2. As can be seen, the main discrepancies are the way of producing OH radicals and consuming the main intermediates. Figure 4.5 depicts that the OH production is always higher in O$_2$/H$_2$O than in O$_2$/N$_2$. Previous experiments have proved that water addition into ethanol can promote the OH production due to the chemical effect of H$_2$O thereby accelerating the oxidation reactions [90, 91]. Because of the high content of water, O$_2$/H$_2$O system is able to generate a large amount of OH radicals also by several other different reactions involving H$_2$O molecules (R3b, R4b and R5b), whereas the main sources of OH radicals in O$_2$/N$_2$ are only HO$_2$ and H$_2$O$_2$. Moreover, the reaction H$_2$O$_2$ → OH + OH happens much less frequently in O$_2$/N$_2$ than in O$_2$/H$_2$O. Comparing R3a with R3b, H$_2$O promotes the reaction of HO$_2$ producing OH and H$_2$O$_2$ as well, which is the main reason for the much higher frequency of reaction H$_2$O$_2$ → OH + OH in O$_2$/H$_2$O. This can also explain that the level of HO$_2$ produced is lower and the maximum number of H$_2$O$_2$ created is more in O$_2$/H$_2$O as shown in Figure 4.5. In contrast, HO$_2$ in O$_2$/N$_2$ has a high possibility consuming the OH radicals by reaction R4a and consequently decreases the reactivity of OH with other intermediates. This HO$_2$/OH mechanism combined with R4a and R9b accounts for the experimental fact that the reaction HO$_2$ + OH → H$_2$O + O$_2$ is suppressed while the reaction H + OH → H$_2$O is promoted with the presence of water in ethanol [91]. As a main source of OH formation in O$_2$/N$_2$, H$_2$O$_2$ in O$_2$/H$_2$O also reacts with HO$_2$ and H (R7b and R8b) which further enhance the OH generation. It is worth mentioning that high water concentration contributes to increased H$_2$ production (displayed in Figure 4.5), primarily by reaction R4b.

As discussed above, the other significant difference between the two mechanisms lies in how they consume the main intermediates. Based on Table 4.2, for the O$_2$/N$_2$
system, there are 3 and 4 events for C₁ & C₂ intermediates reaction with O₂ and OH, respectively, whereas the number count for O₂/H₂O system is 3 and 10. The large number of reaction events involving OH indicates that the C₁ & C₂ intermediate products favour the reaction pathway of CₓHₓOₓ + OH → CₓHᵧ₋₁Oₓ + H₂O (situations are different for reactions R21b, R26b and R29b, where there is no H₂O generated) in O₂/H₂O due to the high level of OH production. Besides, reactions R14b, R17b, R23b show that the presence of a large amount of water advances the dehydrogenation of C₁ & C₂ intermediates via the reaction pathway of CₓHₓO → CₓHᵧ₋₁O + H and these 3 reactions are not seen in the reduced O₂/N₂ mechanism. The generated H radicals either directly react with OH to form H₂O (reaction R9b) or participate in the OH production related events (reactions R2b, R4b and R8b) to create more OH radicals.

4.3.3.2 CO and CO₂ production

As shown in Figure 4.5, the number of CO molecules is always greater than CO₂ in O₂/N₂ during the simulation time, while at a late stage from 2400 K in O₂/H₂O, the number of CO₂ molecules becomes larger than CO and this turning point occurs earlier as the temperature goes up. This phenomenon cannot be seen at the low temperatures of 2000 K and 2200 K because the simulation time is not long enough to allow the reaction to proceed to that stage. Similarly, it is apparent that the number of CO molecules in O₂/H₂O has reached its maximum value and started to decrease within the simulation time at the high temperatures of 2800 K and 3000 K. Furthermore, the maximum number of CO produced is lower in O₂/H₂O than in O₂/N₂ and the CO number in O₂/N₂ is still increasing which has not reached its peak value at the end of the simulation. This elucidates why the number of CO molecules is close or even slightly more in O₂/H₂O than in O₂/N₂ at the temperatures below 2800 K. It is because of the faster CO production rate at the initial stage of the O₂/H₂O simulation and the
insufficient simulation time for O$_2$/N$_2$. Therefore, it is believed that the number of CO molecules generated is less in O$_2$/H$_2$O than O$_2$/N$_2$ provided that the simulation time is long enough to witness both of their peaks, and CO production is therefore reduced with the presence of high content water. This outcome agrees well with the previous experimental results [91, 95].

The above results can also be interpreted by the two different mechanisms. In the full list of O$_2$/N$_2$ reaction pathways, it can be seen that CO firstly reacts with O$_2$ to form unstable CO$_3$ and then decomposes to CO$_2$ and O (reactions R23a and R22a in Table A.1). Apart from this same pathway, CO in O$_2$/H$_2$O has an alternative way to be transformed into CO$_2$, where OH is involved. CHO$_2$ is formed by the reaction of CO with OH (reaction R29b). Afterwards, CHO$_2$ can either directly decompose to CO$_2$ and H (reaction R23b) or be oxidized by O$_2$ producing CO$_2$ and HO$_2$ (reaction R24b). Hence, the CO/CO$_2$ ratio is decreased in O$_2$/H$_2$O by converting CO to CO$_2$ via the aforementioned pathways so that CO$_2$ production is significantly higher in O$_2$/H$_2$O than in O$_2$/N$_2$ as presented in Figure 4.5. Similar CO/OH/CO$_2$ pathways were also obtained from the experiment of hydrous ethanol oxidation [91]. Once again, it is the high water concentration that promotes the OH generation and then advance the conversion of CO to CO$_2$. On the whole, the CO production is reduced.

### 4.4 Summary

The fundamental reaction mechanisms of hydrous ethanol oxidation in comparison with ethanol oxidation under fuel-air conditions are investigated by ReaxFF MD simulations. The effect of water addition on ethanol oxidation is scrutinized via reaction rates and detailed reaction pathways. The potential energy evolution shows that compared with in O$_2$/N$_2$ environment, the heat absorption and release are much more and faster in O$_2$/H$_2$O, which indicates that water does participate
in and facilitate the reaction of ethanol oxidation. The higher reaction rate of ethanol oxidation with water addition at all studied temperatures further confirm this conclusion. On the basis of species number evolution, the ionisation process is advanced and the radical production rate is accelerated in the presence of water thus enhance the ethanol oxidation. By comparing the cases of two different ethanol/water ratios, it is suggested that water content plays a vital role in the reactions at low temperatures but that effect can be neglected at high temperatures. The detailed reaction pathways and time evolution of relevant key species provide a new insight into water effect on ethanol oxidation. The main discrepancies between the two pathways are found to lie in the way of producing OH radicals and consuming the main intermediates, which are not revealed previously. In O₂/H₂O environment, the reaction of some important species like HO₂, H and O is promoted by H₂O as well as the associated reactions involving H₂O₂ indirectly producing a large amount of OH radicals due to the high water content whereas the main sources of OH formation in O₂/N₂ environment are only the decomposition of HO₂ and H₂O₂. In addition, the reaction of OH with C₁ & C₂ intermediates is also advanced on account of the high level of OH production in water environment. Moreover, the presence of water improves the dehydrogenation of C₁ & C₂ intermediates. Finally, the oxidation of hydrous ethanol reduces the CO production owning to the reaction of CO with OH converting CO to CO₂ ultimately, which is not observed in O₂/N₂ mechanism. Therefore, it is concluded that the addition of water promotes the OH production as a result of the chemical effect of H₂O leading to the enhanced ethanol oxidation and reduced CO production. The results obtained from the present research are applicable to the oxidation of hydrous ethanol in combustion applications such as IC engines. This research provides the scientific base for using hydrous ethanol solely in combustion systems that can save energy and cost.
Chapter 5 – Fundamental Mechanisms of Thermal Decomposition and Oxidation of Aluminium Hydride

5.1 Introduction

Aluminium hydride (AlH$_3$) has great potential for a broad range of propulsion and energy storage applications, including explosive, solid or hybrid rocket propulsion and hydrogen source for low temperature fuel cells [112-116]. The gravimetric and volumetric hydrogen capacity of AlH$_3$ (10.1 wt % and 0.148 g/ml, respectively) is twice as much as the value of liquid hydrogen (0.070 g/ml), and it also has rapid low temperature decomposition kinetics (below 100°C) [117-119]. There are seven known different AlH$_3$ polymorphs, among which, α-AlH$_3$ is the most stable one thus has been considered to be the most desirable polymorph in practical applications [113, 120, 121]. The presence of the oxide layer effectively prevents the dehydrogenation of metastable α-AlH$_3$ at room temperature [117]. Finholt et al. [122] firstly prepared AlH$_3$ in an ether solvated form in 1947. Later in the early 1960s, it was considered for military applications and formulated into propellants. The addition of AlH$_3$ into solid propellant can decrease the overall molecular weight with expected H$_2$ formation in the combustion gases and supply a higher combustion heat, which improves the specific impulse by more than 7% compared with aluminium and enhances the rocket performance [123-125]. However, the generation of excessive amounts of hydrogen gas may occur during the storage of solid propellant as a result of the low thermal stability of AlH$_3$. Hence, the instability and high production costs of AlH$_3$ disbanded most of the development work in the USA by the early 1970s [126]. Thanks to the advances in safe and cheap production methods and the improvements in storage, the interest in AlH$_3$ has been recently renewed [127].
A great many literatures investigated the characterization, decomposition kinetics and vacuum thermal stability of AlH₃. Paraskos et al. [128] studied the AlH₃ thermal decomposition and it was found that AlH₃ rapidly decomposes at about 180 °C with a weight loss of 10 wt % during the heating process, which is in accordance with the theoretical hydrogen content. The isothermal decomposition of AlH₃ using nuclear magnetic resonance (NMR) was investigated by Tarasov et al. [129] and they indicated that the process is divided into three stages, namely, the induction, acceleration and deceleration period, with the activation energy of 97, 108 and 112 kJ/mol, respectively. Ismail and Hawkins [127] studied the kinetics and mechanism of thermal decomposition of AlH₃ in argon environment by thermogravimetric analysis in order to further understand the dehydrogenation of AlH₃. It was revealed from the results that the liberation of hydrogen from an external surface and pre-existing pores and cracks initiated the decomposition. In addition, the decomposition is composed of two main steps: the slowest step controlled by the solid-state nucleation of aluminium crystals, which is the rate-determining step, and the fastest step due to the crystal growth, which is postulated as the growth of an aluminium layer toward the particle centre. Weiser et al. [130] conducted experiments on the thermoanalytical oxidation of AlH₃ and the results suggested that after dehydrogenation, the particles presented similar oxidation behaviour as Al nanoparticles with a diameter of less than 100 nm. A chemically controlled reaction between 650 and 850 K and a subsequently diffusion controlled reaction step above 900 K were involved in the oxidation reaction. Moreover, it was also demonstrated from the previous research that many factors including particle size, impurities, crystal defects, temperature and heating rate have impacts on the characteristics of thermal decomposition of AlH₃ [126, 127, 129, 131-134].
To sum up, extensive experimental works have been done to study the thermal decomposition and oxidation of AlH₃ but the understanding of the microscopic process and underlying mechanisms is still limited. Fundamental research is desired for gaining a physicochemical insight of AlH₃ reactions, which could benefit the optimization of the design and application of practical AlH₃ systems. In this study, the fundamental reaction mechanisms of thermal decomposition and oxidation of AlH₃ are investigated at the atomic level. Both gas and solid phase reactions are scrutinised to obtain the overall microscopic understanding of the AlH₃ reaction process. The effects of the oxide layer and defect are also studied.

5.2 Simulation details

The ReaxFF force field of Al/C/H/O interactions [58], which was extended from the original Al/H description [135] specifically parameterized for aluminium hydride, is selected as a suitable force field for the present research. Four cubic and periodic simulation systems, including two for thermal decomposition and two for oxidation, are built with the box size of 150 Å × 150 Å × 150 Å. In order to approximate the real experimental condition, a spherical α-AlH₃ nanoparticle wrapped by a thin α-alumina shell is constructed due to the existence of the oxide layer covering the aluminium hydride. The effect of the oxide layer defect is also taken into consideration for the same purpose. A spherical nanoparticle model is chosen because the initial tests show the evolution of a nanoscale AlH₃ crystal structure to a spherical structure at the very early stage of the reaction.

To prepare the core-shell model, these steps are followed: (1a) a 5 nm diameter α-AlH₃ nanoparticle is cut from the crystal structure; (1b) the nanoparticle is relaxed for 100 ps; (1c) the 3 nm diameter core is cut from the relaxed AlH₃ nanoparticle; (2a) a 6 nm diameter α-alumina nanoparticle is cut from the crystal structure; (2b) the nanoparti-
Figure 5.1 (a) Nanoparticle structures and a typical simulation system: 1. core-shell structure (Step 3a); 2. central cross section of relaxed core-shell nanoparticle (Step 3b); 3. core-shell nanoparticle with a defect; 4. oxidation simulation system. Atoms colouring scheme: core Al – blue; shell Al – purple; H – white; shell O – green; oxygen O – red. (b) Potential energy profiles of relaxation processes.

cle is relaxed for 100 ps; (2c) the 0.4 nm thickness shell is cut from the relaxed α-alumina nanoparticle (radius range from 1.5 to 1.9 nm); (3a) the AlH₃ core and Al₂O₃ shell is combined together; (3b) the core-shell structure is relaxed for 200 ps. A 0.4 nm thickness oxide shell is adopted as it is neither too thick with respect to the AlH₃ core nor too thin to lose the Al₂O₃ structure. The nanoparticle structures and a typical
simulation system are depicted in Figure 5.1a. For the defect-containing case (Figure 5.1a3), a small hole is excavated throughout the oxide shell at Step (3a), followed by the 100 ps relaxation of the nanoparticle. The structure produced after Step (1c) is simply relaxed for another 50 ps for the bare AlH₃ nanoparticle case. NVT simulations at 300 K are performed for all the relaxation processes. Each specified time for relaxation is determined based on when the potential energy reaches a stable value, and Figure 5.1b displays the corresponding profiles of potential energy. Table 5.1 summarizes the detailed configuration for each simulation system.

Table 5.1 Configuration details of simulation systems.

<table>
<thead>
<tr>
<th>Case</th>
<th>System</th>
<th>NP Structure</th>
<th>No. of O₂</th>
<th>No. of Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thermal Decomposition</td>
<td>bare 3 nm AlH₃</td>
<td>0</td>
<td>2097</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>3 nm AlH₃ + 0.4 nm Al₂O₃</td>
<td>0</td>
<td>3772</td>
</tr>
<tr>
<td>3</td>
<td>Oxidation</td>
<td>3 nm AlH₃ + 0.4 nm Al₂O₃</td>
<td>1000</td>
<td>5772</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>3 nm AlH₃ + 0.4 nm Al₂O₃ + Defect</td>
<td>1000</td>
<td>5751</td>
</tr>
</tbody>
</table>

NVT simulations at 2000, 2500 and 3000 K for thermal decomposition and NVE simulations starting from 300 K for oxidation are conducted for 500 ps after the relaxation. The time step used in this study is 0.2 fs and the damping constant of thermostat for NVT simulations is 0.1 ps. The simulation results are outputted every 1000 time steps. A common bond order cutoff value of 0.3 is employed to recognize the species formed during the simulation.
5.3 Results and discussions

5.3.1 Thermal decomposition of bare and perfect core-shell AlH₃

5.3.1.1 Gas products formation

The process and mechanism of hydrogen formation are of great interest in AlH₃ reactions. An illustration of how H₂ is typically released from bare AlH₃ is shown in Figure 5.2a. Along with the diffusion of H atoms, two surface H atoms combine with each other and are released as a H₂ molecule mainly in four formats. They can be both adhered to the same Al atom before ejecting (Figure 5.2a1), or bonded together first with one of them attached on an Al atom and then leave this Al atom (Figure 5.2a2). Alternatively, the two H atoms can be separately from (Figure 5.2a3) or shared by (Figure 5.2a4) two adjacent Al atoms prior to H₂ discharge. The situation is similar for H₂ production in the perfect core-shell AlH₃ case. As seen in Figure 5.1a2, during the relaxation, a small amount of H atoms in the core AlH₃ have already diffused into the oxide shell and even to the surface of nanoparticle. Additionally, a thin core-shell interface consisting of both core Al/H and shell Al/O atoms can be identified. However, the interface and effect of thickness of the oxide shell layer are not studied in this research, which will be investigated in the follow-on work. As the reaction proceeds, more H atoms diffuse through the oxide shell to the surface. The subsequent procedure of H₂ release is as described in the case of bare AlH₃, but the H atoms could also be adhered to O and/or Al atoms. Due to the existence of the oxide layer, O atoms are present and H₂O formation is observed, where Figure 5.2b demonstrates the generation steps. Initially, surface H and O atoms in close proximity to one another adhere to the same Al atom (Figure 5.2b1). Next, they move closer to each other (Figure 5.2b2) until the H atom is bonded directly to the O atom (Figure 5.2b3). Following this, a further nearby H atom, also attracted by the O of OH, bonds with the OH group to form a H₂O
unit (Figure 5.2b4). Finally, the preformed H$_2$O unit disengages from the Al atom as an independent H$_2$O molecule. It is found that the H$_2$O unit could slide on the surface for a while before departing from an Al atom. Moreover, there is a simpler way of producing H$_2$O, which directly starts from the step of Figure 5.2b3. The OH involved in this way is pre-existing and integrated during the diffusion of atoms.

**Figure 5.2** Illustration of formation of (a) H$_2$ from bare AlH$_3$ and (b) H$_2$O from perfect core-shell AlH$_3$. The highlighted H and O atoms are in yellow and orange, respectively.

The number of H$_2$ molecules produced over time from the thermal decomposition of perfect core-shell AlH$_3$ and bare AlH$_3$, and the number of H$_2$ and H$_2$O molecules from thermal decomposition of perfect core-shell AlH$_3$ at 2000, 2500 and 3000 K are exhibited in Figure 5.3a and Figure 5.3b, respectively. In general, the decomposition reactions are temperature dependent, with high temperature enhancing the thermal decomposition with a faster reaction rate. This temperature dependency relationship is also confirmed by many experimental studies [120, 129, 131, 136]. Because the H atoms of AlH$_3$ have to travel across the oxide layer to the nanoparticle surface, this resistance makes H$_2$ production of perfect core-shell AlH$_3$ slower than that of bare AlH$_3$, which is consistent with the previous experimental literature [137]. At the early stage (
Figure 5.3 Time evolution of (a) number of H\textsubscript{2} molecules for thermal decomposition of perfect core-shell AlH\textsubscript{3} and bare AlH\textsubscript{3}, and (b) number of H\textsubscript{2} and H\textsubscript{2}O molecules for thermal decomposition of perfect core-shell AlH\textsubscript{3} at 2000, 2500 and 3000 K.

about 0 – 16 ps) of thermal decomposition of perfect core-shell AlH\textsubscript{3} at 2000 K, a dramatically fast production of H\textsubscript{2}O (much faster than H\textsubscript{2}) is observed, followed by the relatively smooth fluctuation to the end. Similar results were observed at 2500 and 3000 K, with the only difference that the peak and rate of H\textsubscript{2}O production is larger and quicker due to the higher temperature. This suggests that H\textsubscript{2}O is much more easily formed than H\textsubscript{2} at the beginning of the reaction primarily as a result of the great availability of O atoms in the oxide layer. However, as the reaction progresses, the shell O atoms penetrate inside and the core H atoms diffuse outside simultaneously (more details presented in the next section), restraining the further rapid growth of H\textsubscript{2}O production because H\textsubscript{2}O (as well as H\textsubscript{2}) is only formed on the nanoparticle surface as shown in Figure 5.2. It is worth noting that in almost all the experiments [120, 131, 136-142], H\textsubscript{2} was a normal product of AlH\textsubscript{3} thermal decomposition, but H\textsubscript{2}O was not observed or mentioned. Only Ismail and Hawkins [127] traced a tiny amount of H\textsubscript{2}O but they did not give any further explanation. The main reason of the significant H\textsubscript{2}O production in the present research is the huge difference of employed particle size and relative scale of oxide shell to AlH\textsubscript{3} core between the simulation and experiment. The
micron-size AlH$_3$ was usually adopted in the experiment with a natural nano-size alumina surface layer [142], leading to an extremely small oxide shell to core ratio. In contrast, the particle size used in ReaxFF MD simulation is normally in nanometers as it is very computationally expensive to perform ReaxFF MD simulation on a micro-size particle. Consequently, in the experiment, the amount of H$_2$O produced at the very beginning of the reaction would be too small and the process would be too fast to be captured by the detecting instrument. The greater number of core H atoms relative to shell O atoms makes the H$_2$ production absolutely dominant later on (after the initial fast release of H$_2$O). Previous literature [120, 129, 132, 136, 143] also reported particle size as a significant factor.

### 5.3.1.2 Structural evolution of perfect core-shell AlH$_3$

Figure 5.4 visualizes the structural evolution of perfect core-shell AlH$_3$ nanoparticle at 2000 K by taking a snapshot of the nanoparticle central cross-section at different time instants. Compared with $t = 0$ ps (Figure 5.1a2), at $t = 2$ ps, plenty of H atoms diffuse into the shell and to the nanoparticle surface. Meanwhile, it can be seen that some shell O atoms move inward slightly. At $t = 5$ ps, while this H and O two-way movement continues, the core and shell Al atoms also start to exchange and the core-shell boundary is shrinking. At $t = 10$ ps, the amount of core H atoms is obviously less and shell O atoms move further inward but the exchange of core and shell Al atoms does not progress much. By time 40 ps, the core-shell structure becomes vague and the area of mixed core and shell Al atoms increases. At t = 130 ps, the core-shell structure completely disappears and all core-shell atoms are mutually blended. There is no apparent difference between the structure at 500 ps and 130 ps, during which the atomic diffusion is steadily progressing. In short, the structural evolution of perfect core-shell AlH$_3$ nanoparticle proceeds in three main stages: (1) Pre-diffusion: core H atoms
diffuse outward throughout the shell to the surface and shell O atoms move inward; (2) Core-shell integration: core and shell Al atoms exchange and mix accompanied by the shrinking of core-shell boundary; and (3) Post-diffusion: core-shell structure completely vanishes and all mixed core-shell atoms steadily diffuse around. If the simulation is long enough, it would be expected to see that most of the H atoms are released as H₂, leaving the pure Al core with limited O atoms inside. The whole process agrees well with the hydrogen desorption mechanism proposed by Kato et al. [144] based on their in situ x-ray photoelectron spectroscopy surface analysis, which found that AlH₃ only decomposes into Al and H₂ at the free surface instead of the bulk, and is comparable with the recognized mechanism of Al nucleation and growth [120, 127]. More importantly, the results in the present study provide a detailed atomistic insight of the process.

Figure 5.4 Snapshots of the central cross sections of perfect core-shell AlH₃ nanoparticle structure in the thermal decomposition reaction at 2000 K. The snapshot at 0 ps is shown in Figure 5.1a2.
5.3.1.3 Diffusion of atoms

The mean square displacement (MSD) of Al, H and O atoms of perfect core-shell AlH₃ nanoparticle over time at 2000, 2500 and 3000 K are calculated and displayed in Figure 5.5. Only the nanoparticle atoms are considered for calculating the MSD, which means the atom is excluded in the calculation from the instant when it leaves the nanoparticle. The initial sharp increase of MSD_H is caused by the rapid movement and outward diffusion of core H atoms into the shell. The MSD_O line is above the MSD_Al line because shell O atoms diffuse into the core and they travel a longer distance with a quicker speed than Al atoms. The results are consistent with the findings in Section 5.3.1.2. As time progresses, the MSD_H becomes the lowest line among the three, when the diffusion of O and Al atoms plays a more leading role in the reaction, and this moment comes earlier as the temperature increases.

**Figure 5.5** Mean square displacement of Al, H and O atoms of perfect core-shell AlH₃ nanoparticle during thermal decomposition at (a) 2000 K, (b) 2500 K and (c) 3000 K.

Within the studied simulation time scale, all of the three MSDs show a faster rate (faster diffusion of atoms) at the early stage with rising temperature. Although the MSDs at 2500 K have the highest peak values in Figure 5.5, those maximums should actually be the highest at 2000 K if the simulation is extended enough to witness those peaks. On the one hand, it can be seen from the figure that the MSDs at 2000 K are still climbing and their end values are close to those peak values at 2500 K; the MSDs at
2500 K have reached their peaks and just start to decrease; the MSDs at 3000 K have already shown a smooth vibration. Consequently, it is reasonable to deduce that the peak MSD values at 2000 K should be higher than those at 2500 K. On the other hand, because the focus is on the diffusion of atoms within the nanoparticle, it is necessary to exclude the atoms which have left the nanoparticle and are able to move much faster and more freely in the MSD calculation as mentioned above. For this reason, combined with the observation that high temperature enhances the thermal decomposition with a faster reaction rate (second paragraph of Section 5.3.1.1), more atoms leave the nanoparticle as gas products or radicals at the early stage and the reaction progresses to the steady diffusion stage earlier at high temperature than at low temperature. As a result, the internal diffusion of atoms rather than rapid release of products at low temperature is more dominant than that at high temperature leading to the highest MSD peak values at 2000 K among the three temperatures. However, the most important is that the evolution tendency of the MSD lines at the three temperatures should be the same (provided that the simulations are long enough) and the evolution progresses faster at higher temperatures, which also backs up the concluded temperature dependency relationship.

5.3.2 Oxidation of perfect and defective core-shell AlH₃

5.3.2.1 Effects of defect and time evolution of potential energy, temperature and main species

As can be seen in Figure 5.6, the existence of the defect clearly accelerates the oxidation of core-shell AlH₃. Specifically, the decrease of relative potential energy, increase of temperature and consumption rate of O₂ is faster in the system with defective core-shell AlH₃, which indicates a faster reaction rate. The defectiveness was reported to be an important factor on the kinetics of AlH₃ reactions in previous
experimental [129, 136, 145] and theoretical [146] studies. It is believed that defects play a crucial role in the initiation of AlH$_3$ reaction and that a higher defect concentration could result in faster reaction. In the present study, it is found that the defect actually provides a fast track for the diffusion of atoms, especially H and O atoms. In other words, it facilitates the direct contact of core AlH$_3$ and ambient O$_2$. Therefore, in and around the defect area, the H and O atoms could easily diffuse outward and inward, respectively, and do not have to pass through the oxide layer. Then, with the outward diffusion of H atoms and consequent shrinking of core AlH$_3$, the surface layer defect closes gradually. Finally, after the closure of the defect, the whole nanoparticle acts like the perfect core-shell AlH$_3$ at the same stage. In brief, the defect enhances the initiation of AlH$_3$ oxidation and accelerates the oxidation at the early stage of the reaction. It is foreseeable that the reaction could be much faster with the increasing size and number of the defect.

![Figure 5.6](image1)

**Figure 5.6** Time evolution of (a) relative energy and temperature, and (b) main species for oxidation of perfect and defective core-shell AlH$_3$.

Similar to the thermal decomposition of perfect core-shell AlH$_3$, the production of H$_2$O is significant in the oxidation simulations. In the oxygen environment, likewise, H$_2$O is preferentially formed relative to H$_2$ at the early stage of the reaction, the
significant extent of which can be seen in Figure 5.6b. However, in a reported experiment [147], H2O was considered as a product of H2/O2 reaction after the H2 release. In addition to the discussion and explanation given in the second paragraph of Section 5.3.1.1, the high surface-to-volume ratio of nanoparticle also contributes to the great amount of H2O generated. Because of the relatively much larger surface area than a micron-size particle, the contact area of the nanoparticle with O2 is much larger, thereby adsorbing more O2 molecules. Together with the small radius, the penetrability of O atoms is better. As a result, the abundant availability of O atoms leads to the remarkable and fast production of H2O at the early stage. The oxygen pressure and equivalence ratio could be other influential factors and will be investigated in the future work. After about 200 ps and when the H2O production is steady, production of H2 starts to increase. However, most of the H atoms are consumed as H2O due to the aforementioned reasons, which accounts for the minor observation of H2 in the present simulation. It is certain that H2 production would dominant in a later stage if a micro-size particle is adopted. Apart from H2O and H2, OH is also a noticeable species in the oxidation reaction. It begins to form from nearly the same time (slightly after) as H2O production and before H2 release. The OH generation in the thermal decomposition reaction is negligible. Hence, it is the O2 that promotes the production of OH.

5.3.2.2 Reaction of perfect core-shell AlH3 with O2

The detailed interaction of perfect core-shell AlH3 with O2 is monitored to investigate the oxidation process. It is observed that O2 molecules head towards the nanoparticle surface rapidly when the reaction starts. After reaching the surface, one O atom could be attached to one single Al atom or located in the middle of two adjacent Al atoms with the other O atom vertically (to the surface) hanging in the air (Figure 5.7a). After a while, in the same way, the other O atom would lay down on the surface
Figure 5.7 Illustration of how O₂ molecules are (a) initially and (b) finally adsorbed on the nanoparticle surface, and (c) how OH is produced on top of the adsorbed O₂ molecule. The highlighted H and O atoms are in yellow and orange, respectively. sticking to another one or two Al atoms (Figure 5.7b). Next, the O-O bond is broken and the two O atoms are able to move freely. This explains why Figure 5.6b demonstrates that the number of O₂ reduces from the very beginning but there is no product formation during the first tens of ps. It is as a result of this oxygen adsorption-decomposition process, which sees increased O availability for the next stage of the reaction but does not itself produce any oxidation species. This process goes quicker as the temperature increases. Subsequently, along with the outward diffusion of core H atoms, the products start to form and be released successively. The formation mechanisms of H₂O and H₂ are the same as elucidated in the first paragraph of Section 5.3.1.1. The nanoparticle simply includes far more O atoms derived from the ambient O₂ molecules. The OHs mentioned before are mainly generated from the nanoparticle but a small number of OHs are found to be the product of reaction of some species like HO₂ at high temperature, which is not detailed here. It is noteworthy that the OH is not directly released from an OH unit (Figure 5.2b3) on the nanoparticle surface but has connection with the adsorbed O₂ molecules. When the O₂ molecule is vertically adsorbed on the surface with one O atom freely hanging in the air, a nearby H atom could bond to it (Figure 5.7c) and then this OH is detached from the adsorbed O atom, which is the preferred way of producing OH. Therefore, this is the reason that OH
production in the thermal decomposition reaction is negligible and illustrates how $O_2$ promotes the production of $OH$.

The structural evolution of the nanoparticle is shown in Figure 5.8. Corresponding to Figure 5.6b, at $t = 50$ ps when there is no product formation, many $O_2$ molecules are adsorbed on the nanoparticle surface. The O-O bond has not been broken yet and no O atom from the ambient $O_2$ has penetrated inside the nanoparticle. In the meantime, more core H atoms diffuse into the shell and to the surface compared with $t = 0$ ps (Figure 5.1a2). Shell O atoms start to diffuse into the core as well. With the fast reaction, at $t = 120$ ps, a large amount of H atoms (417, mainly in released $H_2O$, $H_2$, and $OH$) have left the nanoparticle and shell O atoms enter into the core. Simultaneously, the ambient O atoms advance into the nanoparticle as free O atoms. Coming to $t = 160$ ps, the H atoms are lesser and ambient O atoms go further towards the nanoparticle core. Core and shell

![Snapshots of the central cross sections of perfect core-shell AlH$_3$ nanoparticle structure in the oxidation reaction. The snapshot at 0 ps is shown in Figure 5.1a2.](image)

**Figure 5.8** Snapshots of the central cross sections of perfect core-shell AlH$_3$ nanoparticle structure in the oxidation reaction. The snapshot at 0 ps is shown in Figure 5.1a2.
Al atoms begin to exchange and the core-shell boundary is shrinking. Until $t = 180$ ps, only a small amount of H atoms can be seen in the nanoparticle. The whole nanoparticle is distributed with ambient O atoms, and core/shell Al atoms are mixed interchangeably. From this point to the end of the simulation, a massive number of ambient O atoms gradually flow into the nanoparticle and core/shell Al atoms are uniformly integrated. At last, the nanoparticle consists primarily of Al and O with only few H atoms. Briefly, the oxidation process includes following three main stages: (I) Oxygen adsorption: ambient O$_2$ molecules are quickly adsorbed on the nanoparticle surface accompanied by the diffusion of inner atoms; (II) Fast dehydrogenation: O-O bond of O$_2$ is broken and these ambient O atoms penetrate into the nanoparticle with the fast products formation; and (III) Al oxidation: after most of the H atoms are released, the ambient O atoms oxidize the remaining nanoparticle. While the oxidation process is generally in agreement with the simplified model that dehydrogenation of AlH$_3$ occurs first followed by the Al oxidation [138], it is also observed in the present study that the dehydrogenation and oxidation actually proceed simultaneously although the oxidation rate is limited during the dehydrogenation period. Figure 5.9 describes the evolution of temperature distribution of the nanoparticle. Initially at $t = 50$ ps, a lot of hot spots ($\sim$ 2000 K) and high temperature areas ($\sim$ 1000 K) can be seen inside the nanoparticle and on the surface, which induce the adsorption and diffusion of the oxygen. At $t = 120$ ps, part of these high temperature regions stand out and their temperature further rises to about 4000 K. The temperature of the remaining area goes up accordingly. Then as the reaction progresses, the number and size of the high temperature regions (around or higher than 4000 K) both increase, which is attributed to the dominant exothermic oxidation of Al. Finally, the temperature distribution of the nanoparticle is equilibrated.
(t = 250 ps and 500 ps) because the potential energy tends to be stable after about 200 ps.

![Snapshots of the central cross sections of perfect core-shell AlH3 nanoparticle temperature distribution in the oxidation reaction.](image)

**Figure 5.9** Snapshots of the central cross sections of perfect core-shell AlH3 nanoparticle temperature distribution in the oxidation reaction.

### 5.4 Summary

The fundamental reaction mechanisms of thermal decomposition and oxidation of AlH3 are investigated using ReaxFF MD simulations. The process and mechanism of H2 and H2O formation during the AlH3 reaction are illustrated in detail. The results show that thermal decomposition is temperature dependent, and the reaction is promoted at a higher temperature with a faster reaction rate (e.g. the ratio of the average H2 release rate during the thermal decomposition of bare AlH3 within the simulation time scale at 2000, 2500 and 3000 K is about 1:2.96:5.42). As the H atoms have to travel across the oxide layer to the nanoparticle surface, H2 production of perfect core-
shell AlH₃ is slower than that of bare AlH₃ during the thermal decomposition. The significant amount of H₂O is produced in the thermal decomposition of perfect core-shell AlH₃ and it is indicated that compared with H₂, H₂O is much more easily formed at the beginning of the reaction. The thermal decomposition of perfect core-shell AlH₃ includes three main stages: (1) Pre-diffusion; (2) Core-shell integration; and (3) Post-diffusion. The above temperature dependency relationship is further confirmed by the results of mean square displacement, which agree with the findings from the structural evolution. As far as oxidation is concerned, it is suggested that with the defect, the initiation of core-shell AlH₃ oxidation is enhanced and the oxidation is accelerated at the early stage of the reaction. A fast track is provided for the diffusion of atoms, especially H and O atoms, which facilitates the direct contact of core AlH₃ and ambient O₂. Similar to the thermal decomposition process, in the oxidation, pronounced H₂O production is also observed and H₂O is preferentially formed with respect to H₂ at the beginning of the reaction. In addition to H₂O and H₂, OH is a notable species in the oxidation reaction. To demonstrate how O₂ promotes the production of OH, the detailed interaction of perfect core-shell AlH₃ with O₂ is monitored. It is concluded that the oxidation of perfect core-shell AlH₃ also involves three main stages: (I) Oxygen adsorption; (II) Fast dehydrogenation; and (III) Al oxidation. The dehydrogenation and oxidation are found to proceed simultaneously although the oxidation rate is limited during the dehydrogenation period. The results obtained from the present research are applicable to high-temperature thermal decomposition and oxidation reactions of AlH₃, which normally occur in propulsion systems. The revealed mechanisms may be beneficial for the control of hydrogen release resulting in the safe storage and efficient usage of AlH₃. This research lays the theoretical foundation for the improvement of the practical applications of AlH₃.
Chapter 6 – Methane Oxidation Assisted by Platinum/Graphene-Based Catalysts

6.1 Introduction

Graphene possesses many extraordinary properties including extreme mechanical strength, high thermal and excellent electronic conductivity, and it is well known as the first two-dimensional atomic crystal which has been extensively used in a broad range of areas [148, 149]. In recent years, the metal nanoparticles [63, 150] or functional groups [61] decorated graphene-based materials have been considered as effective catalysts for fuel combustion. A representative of these effective catalysts is Functionalized Graphene Sheet (FGS), which can enhance the reaction primarily due to its various active sites. Adding nano-sized metal particles into the fuel has many advantages, e.g. increasing energy density, shortening ignition delay and improving burning rates [151, 152]. It is therefore of great interest to study the metal-decorated functionalized graphene sheet as a novel catalyst for fuel and propellant combustion. Platinum (Pt) is able to promote oxidation of hydrocarbons [153, 154] and resist sulphur poisoning in exhaust gas after-treatment [155] as an effective metal catalyst. The foundation for improving fuel combustion with Pt-decorated functionalized graphene sheet (Pt@FGS) is laid on the successful synthesis of Pt-graphene composite [63, 156]. Methane is the main constituent of natural gas, which is one of the most ideal alternatives to other fossil fuels. Carbon dioxide emissions can be reduced considerably as a result of the low C/H ratio of methane. In addition, methane has high specific energy content and heat sink capacity [157]. Recently, the interest in using methane as a propellant for reusable boosters and rocket engines has been increasing, where combustion occurs at extremely high temperatures and pressures [158]. However,
among all the saturated hydrocarbons, the C-H bond strength of methane is the greatest (with an H-CH₃ bond dissociation energy of 104 kcal/mol) leading to unsatisfactory performance of gas phase combustion [103]. For the purpose of improving combustion performance, Pt@FGS may be considered as a catalyst for the methane/air system.

As reviewed in Section 2.4.3, although graphene-based materials have proven to be good catalysts, it is difficult to explore the underlying mechanisms using the existing experimental techniques. In this study, the fundamental catalytic mechanisms and kinetics of methane oxidation mixed with nanoparticle additives are investigated. Major catalytic mechanisms are proposed via the observation of atomic trajectory and analysis of key species evolution. The rate constant $k$ is determined and the activation energy ($E_a$) of each simulation case is calculated based on the Arrhenius Plot by following the first-order reaction model. Finally, the catalytic effect of each nanoparticle additive is scrutinized to compare their performance.

### 6.2 Simulation details

The ReaxFF force fields of C/H/O [20] and Pt/C/H/O [85] parameters are used for MD simulations. In total, four periodic systems are built at the same density of 0.0325 g/cm³ with different sizes of simulation box. The equivalent initial gas phase pressure is about 30 atm, which is high enough to ensure the occurrence of reaction within the time scale of ReaxFF MD simulation. To clarify the fundamental catalytic mechanisms and kinetics of methane oxidation and its mixture with various nanoparticle additives, the stoichiometric condition of CH₄ and O₂ is chosen as a representative. The base system consists of 50 CH₄ and 100 O₂ gas phase molecules, and three specific catalysts are included in the other three systems, namely, a Functionalized Graphene Sheet (FGS), two Tetrahedral Pt Clusters (Pt) and a Pt-decorated Functionalized Graphene Sheet (Pt@FGS), respectively. The systems of pure CH₄/O₂ and with FGS use the C/H/O
force field, and the systems with Pt and with Pt@FGS use the Pt/C/H/O force field. Because with the introduction of the Pt element, the interaction between each atom type pair is changed. Hence, using two different force fields for specific systems in the present study is appropriate and necessary. Figure 6.1 illustrates the details of system construction and structure of each catalyst. To be specific, the FGS (Figure 6.1b) is modified from a pristine graphene sheet (PGS) containing 1269 C atoms. In total, 16 identical functional groups are embedded in the PGS leading to a C/O ratio of 13. Each functional group has a divacancy decorated by two ethers with four additional hydroxyls attached to C atoms nearby [70]. Regarding the Pt@FGS (Figure 6.1d), two tetrahedral Pt clusters are adsorbed on the two single-vacancies in a triangle contact way, which was found to be the most stable form from DFT calculations [159, 160]. For such a small system, using a tetrahedral Pt cluster instead of a larger one is believed to be appropriate to study the combined catalytic activity of Pt and FGS. Otherwise, rather than showing the combined effect of Pt and FGS, the large Pt cluster would dominate the catalytic reaction within this small system. The simulation box for the system of CH₄/O₂ with Pt@FGS (Figure 6.1d) is cubic and its side length is 60 Å. While other parameters remain the same, the z-axial length of the box for the other three systems is adjusted accordingly to keep the constant density. A Conolly surface with a radius of 1.0 Å is created to evaluate the volume of the catalysts.
Figure 6.1 System configurations for methane oxidation mixed with various catalysts: (a) pure CH₄/O₂, (b) with FGS, (c) with Pt and (d) with Pt@FGS. Top panel is a perspective view of the simulation box and bottom panel is the top view of the catalyst. C, H, O and Pt atoms are represented in grey, white, red and blue, respectively.
All of the ReaxFF MD simulations employ the canonical ensemble (NVT) with a damping constant of 50 fs. To eliminate artificial effects of the structure, energy minimization is carried out for every simulation at the very beginning. The methane oxidation is studied by performing both ramped- and fixed-temperature NVT simulations. Each simulation system undergoes 100 ps equilibration with a time step of 0.1 fs at its starting temperature. C-O and H-O bond parameters are turned off for those fixed-temperature simulations starting from a high temperature (higher than 1000 K) by eliminating the corresponding bond parameters in the force field to prevent the occurrence of reactions during the equilibration [20]. For the systems involving Pt element, Pt-O and Pt-H bond parameters are also switched off during the equilibration. To ensure the structures of those catalysts could remain intact at high temperatures, the catalysts containing FGS (i.e. FGS and Pt@FGS) and surrounding gas molecules are equilibrated separately. A series of reactive MD simulations are performed for 4000 ps (ramped-temperature simulations) or 1000 ps (fixed-temperature simulations) with a time step of 0.2 fs after the equilibration. The species formed during the simulation is recognized employing a bond order cutoff value of 0.2, which could be helpful for detecting all possible reaction pathways [20, 28]. Three independent simulations with unique starting configurations are conducted and the results are averaged for each fixed-temperature simulation case.

6.3 Results and discussions

6.3.1 Reaction rate and time evolution of key species

The temperature ramping NVT MD simulations from 300 to 3000 K with heating rate of 0.90 K/ps are performed to investigate the reaction rate and mechanisms of methane oxidation mixed with catalytic nanoparticles. An additional 1000 ps
simulation at the constant temperature of 3000 K is appended to the 3000 ps simulation for further consumption of CH$_4$ as shown in Figure 6.2.

**Figure 6.2** Time evolution of CH$_4$ molecule number for systems with different catalysts during temperature ramping NVT MD simulations from 300 K to 3000 K.

In Figure 6.2, the fastest reaction rate of Pt@FGS case suggests that Pt@FGS has the most remarkable catalytic effect on methane oxidation among all the nanoparticle candidates. In contrast, FGS does accelerate the methane consumption to some extent, but hinders the oxidation at the late stage of the reaction (from $t_2$ in Figure 6.2). Moreover, the results show that the reaction rate of Pt is significantly quicker than FGS after about 3000 ps but is slightly slower than FGS before that time point ($t_1$ in Figure 6.2). In this research, methane molecules are observed to be adsorbed on the graphene-containing nanoparticles at low temperatures (~300 - 600 K), which is consistent with previous experimental [161] and computational [162] studies. The time evolution of some key species is shown in Figures 6.3 and 6.4. After the initial equilibration and when CH$_4$ starts to decay, the first drop in the number of CH$_4$ molecules in the FGS system is observed due to direct dehydrogenation of CH$_4$ on FGS. For the Pt and Pt@FGS systems, the CH$_4$ molecule is firstly adsorbed on the Pt surface at the end of
Figure 6.3 Time evolution of key species for systems with different catalysts during temperature ramping NVT MD simulations from 300 to 3000 K: (a) pure CH$_4$/O$_2$, (b) with FGS, (c) with Pt and (d) with Pt@FGS.

The equilibration and then dehydrogenated by the Pt cluster. The adsorption energy of CH$_4$ and O$_2$ on the surface of each catalyst is calculated using Equation (6.1) and given in Table 6.1.

\[
E_{\text{ads}} = E_{\text{catalyst+gas}} - E_{\text{catalyst}} - E_{\text{gas}}
\]  

(6.1)

where $E_{\text{ads}}$ is the adsorption energy, $E_{\text{catalyst+gas}}$ is the total energy of the gas-adsorbed catalyst, $E_{\text{catalyst}}$ is the energy of the catalyst and $E_{\text{gas}}$ is the energy of the gas.
Figure 6.4 Time evolution of adsorbed CH$_4$ and O$_2$ on the catalysts: (a) with FGS, (b) with Pt and (c) with Pt@FGS.

Table 6.1 Adsorption energy of CH$_4$ and O$_2$ on the surface of each catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Gas</th>
<th>$E_{ads}$ (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>CH$_4$</td>
<td>-11.83</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>-31.94</td>
</tr>
<tr>
<td>FGS</td>
<td>CH$_4$</td>
<td>-17.00</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>-43.17</td>
</tr>
<tr>
<td>Pt@FGS</td>
<td>CH$_4$</td>
<td>-39.51</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>-86.81</td>
</tr>
</tbody>
</table>

6.3.2 Catalytic mechanisms of methane oxidation with Pt/graphene-based catalysts

Based on the analysis of species and the observation of atomic trajectories, major catalytic mechanisms concerning interatomic exchange can be deduced as shown in Figure 6.5.
Figure 6.5 Proposed overall catalytic mechanism for methane oxidation catalysed by Pt@FGS: catalytic mechanisms for (a) Pt and (b) FGS. C, H, O and Pt atoms are represented in grey, white, red and blue, respectively. (a1~a4) demonstrate the dehydrogenation of CH₄ on Pt (a1) followed by the H radical participating in either H₂ (a2) or H₂O (a3, a4) formation related reactions, while (b1~b7) illustrate the OH functional groups on FGS (b1) contributing to the production of H₂ (b2) and H₂O (b3~b5), and show the recovery of the OH functional group on FGS (b6) as well as the increased functionality at the edge of the graphene (b7). The integrated Pt and FGS combines the catalytic mechanisms of (a) and (b) and the two catalytic cycles interact with each other.
6.3.2.1 Catalytic mechanisms of methane oxidation with Pt and FGS

Firstly, Pt is known to be capable of accelerating dehydrogenation of hydrocarbons to yield hydrogen [154, 163, 164]. Specifically in the present study, an H radical of CH₄ molecule is adsorbed on the Pt surface (Figure 6.5a1) followed by the H radical participating in subsequent reactions. The H radical can abstract another H radical from CH₄ molecule or other hydrocarbon radicals like CH₃ or CH₂ to form a hydrogen molecule (Figure 6.5a2). Also, this H radical can interact with the O radical from the O₂ molecule, forming an OH radical (Figure 6.5a3). In turn, both free OH radical and the OH group from intermediate reaction products like CH₃OH or CH₂OH tend to attract the H radical adsorbed on the Pt surface forming a water molecule (Figure 6.5a4). These observed catalytic mechanisms were also reported in previous experimental [165, 166] and computational [167, 168] studies. Similarly, in the FGS case, the hydroxyl functional group contributes an H radical to the formation of hydrogen and water molecules (Figures 6.5b2 to b5). However, some hydroxyl groups are found to be detached from the graphene sheet (Figure 6.5b4) during reactions generating more hydroxyl radicals, which could participate in the reaction. Afterwards, another H radical, usually from the methane molecule or other hydrocarbon radicals, is adsorbed on the O atom (hydroxyl group which loses the H radical) attached to the graphene sheet recovering to a hydroxyl group (Figure 6.5b6). Then this hydroxyl group undergoes the same process again. Additionally, the graphene sheet is further oxidized to increase the functionality, especially at the edge of the graphene (Figure 6.5b7), which can also be confirmed by the more rapid O₂ consumption of FGS and Pt@FGS compared to pure CH₄/O₂ and Pt in Figure 6.3. Only a few O radicals are observed adhering on the internal defect-free C atoms later and the sheet structure is retained during the whole simulation period, which agrees with the previous simulation results [71]. The attachment of H and
OH radicals to defect-free C atoms is occasional and does not last long. Instead, these radicals react with other intermediate species frequently. The catalytic cycle starting from the H transfer process repeats after the functionalization. Thus, the original active sites on the FGS can be considered as the internal edge of the graphene sheet. Similar mechanism is also corroborated by previous studies [70, 71, 169].

6.3.2.2 Catalytic mechanisms of methane oxidation with Pt@FGS

The integrated Pt and FGS shows the most outstanding catalytic performance, which can be attributed to the combined catalytic mechanisms of Pt and FGS. Figure 6.5 depicts the overall catalytic mechanism for methane oxidation catalysed by Pt@FGS. The two Pt clusters and functional groups on the FGS conduct the H transfer process simultaneously. Each of the two processes forms a catalytic cycle. Briefly, the H radical adsorbed on the Pt surface or from the hydroxyl on FGS interacts with the H-containing intermediates producing a H₂ molecule. In turn, the OH group from this particular H radical abstracted by the O radical from the O₂ molecule, the hydroxyl partitioned from the graphene sheet or all the OH-containing products, can react, as feedback, with the H radical on the Pt surface or H radical on hydroxyl of FGS to form water. Besides, the graphene sheet is further oxidized to enhance the functionality, enabling more functional groups to participate in the catalytic reactions. After losing the H radical, the Pt and the O atoms attached on graphene sheet adsorb another H radical from the H-containing species, which drives the catalytic cycle. Moreover, the intermediate products of either cycle could also interact with each other, thereby increasing the CA. These findings suggest that the improved CA is attributed to the acceleration of interatomic exchange, rather than the creation of new reactions to form new species. Based on the catalytic mechanisms of Pt@FGS, the proximity of the Pt and OH group sites would not have effects on the CA because the Pt and OH group do
Table 6.2 Branching ratios for some important competing pathways in the catalytic mechanisms of methane oxidation with Pt@FGS (Pathway numbers refer to Figure 6.5).

<table>
<thead>
<tr>
<th>Competing Pathway</th>
<th>Branching Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>a2 / a3</td>
<td>2.75</td>
</tr>
<tr>
<td>b2 / b3</td>
<td>0.35</td>
</tr>
<tr>
<td>b3 / b4</td>
<td>0.59</td>
</tr>
<tr>
<td>a2 / b2</td>
<td>4.13</td>
</tr>
<tr>
<td>a3 / b3</td>
<td>0.52</td>
</tr>
<tr>
<td>(a2 + a3) / (b2 + b3)</td>
<td>1.45</td>
</tr>
</tbody>
</table>

not interact with each other and they both have their own catalytic cycle. The branching ratios for some important competing pathways are determined by analysing the atomic trajectory and evolution of species together and the results are shown in Table 6.2. Figure 6.3 shows that CH₃ and OH radicals appear at the initial stage of the reaction (when CH₄ starts to decay) and subsequently disappear fast as the number of CH₄ molecules decreases. This phenomenon indicates that methane oxidation is initiated by the cleavage of C-H bond and catalytic production of hydroxyl. In addition, the extremely short lifetime of H radical validates the rapid H transfer process during the reaction. The main methane oxidation products are CO₂ and H₂O, which is consistent with the conventional methane oxidation without catalysts. A number of H₂ molecules are also observed during the reaction because both pyrolysis of methane and dehydrogenation of methane over catalysts can generate hydrogen under high temperature [170, 171]. Importantly, all the graphene structures are monitored and their structures are retained throughout the whole simulation period. However, it is noteworthy that most active sites of Pt@FGS are consumed eventually leaving the structure like a PGS but most active sites of FGS are retained at the end of the
simulation. This finding proves that the combination of Pt and FGS can further enhance the CA.

6.3.3 Global kinetics of methane oxidation with Pt/graphene-based catalysts

Figure 6.6 shows the CH₄ decay of systems with different catalysts over time within the temperature range from 2000 to 3000 K with an increment of 200 K. As expected, the consumption rate of CH₄ molecules is higher as temperature increases, which means that high temperature benefits the catalytic functions. Furthermore, in accordance with the results of temperature ramping MD simulations, Pt@FGS has the most significant catalytic effect on methane oxidation compared to other candidates. The bottom three panels confirm that FGS hinders the methane oxidation at the late stage of the reaction under high temperatures, which also agrees with the results shown.

![Figure 6.6](image)

**Figure 6.6** Time evolution of CH₄ molecule number for systems with different catalysts at the same temperature during fixed-temperature NVT MD simulations ranging from 2000 K to 3000 K: (a) 2000 K, (b) 2200 K, (c) 2400 K, (d) 2600 K, (e) 2800 K and (f) 3000 K.
in Figure 6.2. Combing the aforementioned analysis of sheet structural differences between Pt@FGS and FGS during the simulation (end of the Section 6.3.2.2), it is believed that methane oxidation is impeded in the presence of FGS at the late stage of the reaction probably due to the limited activity of active sites on FGS during that time period. Due to this low catalytic activity, the reactions with FGS could compete with those with CH₄, leading to the slower methane oxidation.

According to the results of fixed-temperature NVT MD simulations shown in Figure 6.6, the kinetics of pure methane oxidation and its mixtures with various catalysts can be studied. Following the first-order reaction model, the rate constant $k$ at each temperature and $E_a$ of the Arrhenius Equation (Equation (6.2)) are determined for the four cases (as shown in Figure 6.7).

$$\ln k = \ln A - \left(\frac{E_a}{R}\right) \cdot \left(\frac{1}{T}\right)$$  \hspace{1cm} (6.2)

where $k$ is the rate constant, $A$ pre-exponential factor, $E_a$ activation energy, $R$ gas constant and $T$ absolute temperature.

![Figure 6.7 Arrhenius Plot: determination of activation energy for methane oxidation and its mixture with various nanoparticle additives.](image)
Table 6.3 Calculated activation energy for methane oxidation and its mixture with various nanoparticle additives and comparison with previous results from the literature.

<table>
<thead>
<tr>
<th>System</th>
<th>Fitting formula (R²)</th>
<th>$E_a$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Study</td>
<td>Literature</td>
</tr>
<tr>
<td>CH₄/O₂</td>
<td>$\ln k = 2.49 - 26529.82/T$ (0.96)</td>
<td>52.68</td>
</tr>
<tr>
<td>w/FGS</td>
<td>$\ln k = 1.22 - 19948.43/T$ (0.99)</td>
<td>39.62</td>
</tr>
<tr>
<td>w/Pt</td>
<td>$\ln k = 0.32 - 17099.41/T$ (0.97)</td>
<td>33.96</td>
</tr>
<tr>
<td>w/Pt@FGS</td>
<td>$\ln k = -1.92 - 7284.79/T$ (0.96)</td>
<td>14.47</td>
</tr>
</tbody>
</table>

The calculated $E_a$ for all these systems are summarized in Table 6.3. From Table 6.3, the descending order of $E_a$ is: Pure CH₄/O₂ > with FGS > with Pt > with Pt@FGS. Pt@FGS reduces $E_a$ dramatically by 72.53% compared with pure CH₄/O₂, which results from the combined CA of Pt and FGS. By contrast, the other two catalysts (FGS and Pt) lower the $E_a$ of pure CH₄/O₂ by 24.79% and 35.54%, respectively. The results obtained from this research are also verified by previous studies (also summarized in Table 6.3), which proves the validity of the adopted ReaxFF MD simulation methodology. The difference in the overall activation energy determined by the present study and that reported in the literature is generally acceptable, considering the various different conditions applied (e.g. temperature, pressure, equivalence ratio, catalyst loading, catalyst structure, combustion environment, etc.) and uncertainties in both the numerical modelling and experiment. Although there is no straightforward comparison available for the systems with FGS and with Pt@FGS, some indirect evidence can be found. Sirijaraensre and Limtrakul [178] calculated an $E_a$ of 28.2 kcal/mol for partial oxidation of methane to methanol over the graphene supported Au₄Pt nanocluster by DFT calculations. In addition, experimental research revealed that $E_a$ for thermal and catalytic decomposition of $n$-dodecane ($n$-C₁₂H₂₆) with FGS and Pt@FGS is 63.5
kcal/mol and 57.3 kcal/mol, respectively (the ReaxFF MD simulation results in the same research are 54.0 kcal/mol and 32.3 kcal/mol, respectively) [179]. These values validate the effectiveness of data from the present research.

6.4 Summary

The catalytic mechanisms and kinetics of methane oxidation mixed with Pt/graphene-based nanoparticle additives are investigated by ReaxFF MD simulations. Pt@FGS is found to have the best catalytic performance among all the nanoparticles studied in the present research, and it improves the catalytic activity by significantly reducing the activation energy by approximately 73% compared with pure methane oxidation. Furthermore, during the reaction, it is observed that FGS is further oxidized to increase the functionality, especially at the edge of the graphene sheet. The most important is that rather than creating new reactions to form new species, the enhanced dehydrogenation of Pt@FGS and interatomic exchanges dominate the catalytic process and drive the catalytic cycle, which involves various intermediate products. In addition, the results from species analysis suggest that the C-H bond breaking and OH production initiate the catalytic methane oxidation. All of the graphene-containing structures are monitored throughout the simulation and it is found that the reactive sites are diminished but no destruction of graphene structures is observed. At the late stage of the reaction, the presence of FGS has a negative impact on methane oxidation due to the limited activity of active sites on FGS during that time period. The results obtained from the present research are applicable to high-temperature and high-pressure heterogeneous catalytic oxidation of methane with Pt/graphene-based nanoparticle additives, which could be potentially used in propulsion systems such as reusable boosters and rocket engines. This research sheds light on the usage of Pt@FGS to improve the performance of fuel combustion.
Chapter 7 – Initiation Mechanisms of Enhanced Pyrolysis and Oxidation of JP-10 (Exo-Tetrahydrodicyclopentadiene) on Functionalized Graphene Sheets

7.1 Introduction

The single-component hydrocarbon fuel Jet Propellant-10 (JP-10) possesses extraordinary properties such as high energy density (39.4 MJ/L) [180], high heat capacity [181], high thermal stability [182] and low freezing point (-79 °C) [183], which is used in aviation applications including detonation engines, missiles, ramjets and scramjets. In pulse-detonation engines using JP-10 as a fuel, the operational conditions can reach up to 2500 K and 100 bar [184]. Numerous experimental [181, 185-193] and theoretical [184, 194-200] works have been conducted to study the pyrolysis and oxidation of JP-10 due to its superior qualities and broad applications. However, one problem is that the slow ignition and combustion kinetics of JP-10 and many other liquid hydrocarbon fuels could result in poor performance for applications like pulse-detonation engines or ramjets [180]. Hence, it is of theoretical and practical importance for the research into the catalytic reaction of JP-10. Furthermore, the energy density of the fuel system can be increased with the addition of additives [151, 152]. Especially, the catalytic dehydrogenation and cracking of endothermic hydrocarbons like JP-10 offers a better chemical heat sink for aeropropulsion systems, where the cooling requirements are demanding [201]. Metal-based materials are the primary catalysts for JP-10 reactions so far [180, 201-205] but some disadvantages of these catalysts cannot be neglected. For example, during the combustion process, non-energetic oxide passivation layers and undesired solid oxide reaction byproducts are produced, which have negative impacts on the combustion performance.
Graphene-based materials such as functionalized graphene sheets (FGS) have recently proven to be effective catalysts for fuel and propellant combustion [61, 62, 65-69]. The advantages are that they can enhance fuel combustion reactions, be energetically involved in the combustion process, and be ultimately consumed without producing residual particles. Sabourin et al. [61] undertook a pioneering research, which investigated the effects of addition of FGS colloidal particles on the combustion performance of monopropellant nitromethane. The results showed that the presence of FGS reduced the ignition temperature and increased the burning rate up to 175% compared with neat nitromethane, outperforming more conventional additives such as amorphous silica oxide and aluminium oxyhydroxide nanoparticles. Jain et al. [62] also observed the flame speed enhancement (up to 8 times) of another monopropellant nitrocellulose with graphene microstructures in their experiments. The influence of adding graphene oxide (GO) nanoparticles into Jatropha Methyl Ester (JME) in a compression ignition (CI) engine was studied by EL-Seesy et al. [65]. They indicated that while reducing the duration of combustion and exhaust emissions of CO, UHC and NOx, the brake thermal efficiency, peak cylinder pressure, highest rate of pressure rise, and peak heat release rate were increased using JME-GO. Likewise, the impact of graphene nanoparticles addition into a diesel and biodiesel blend in a CI engine was examined by Paramashivaiah et al. [66] and similar effects on engine performance and emission were reported.

The interest in using graphene-based materials as additives for jet fuels has also been increasing. Huang and Li [68] tested the ignition and combustion characteristics of graphene-containing jet fuel liquid film. The results suggested that the ignition of graphene occurred earlier than that of the jet fuel and the mixture could be ignited with a shorter delay time. The combustion characteristics of colloidal droplets of Jet-A fuel
with various carbon-based nanoparticles were explored by Ghamari and Ratner [67]. It was found that graphene nanoplatelets had an outstanding performance by obtaining more than a 7% increase in burning rate at only a 0.1% particle loading. Recently, Li et al. [69] reported that the combustion performance of Jet A-1 fuel in air was improved in the presence of GO nanosheets, which decreased the strength and speed of initial transmitted wave, reduced the ignition delay and accelerated the initial linear burning velocity. In contrast to those jet fuels containing extremely complex hydrocarbon mixtures, the investigation on the FGS as a promising additive for enhancing the reactions of the single-component hydrocarbon fuel JP-10, where ignition and combustion kinetics are crucial, is certainly of great interest.

To summarize, although graphene-based materials are well known as effective catalysts for improving the combustion performance of fuel and propellant, the underlying mechanisms are still poorly understood. Moreover, the potential enhancement by FGS on the reactions of complex hydrocarbons like JP-10 comprising a tricyclic structure has not been investigated computationally. Compared with other jet fuels consisting of many hundreds of dissimilar hydrocarbons, it is much easier to study JP-10 as a single-component hydrocarbon fuel. In this study, the initiation mechanisms of enhanced pyrolysis and oxidation of JP-10 on FGS and the transition state and energy barrier for key initiation reactions are investigated. The catalytic effects of FGS on the pyrolysis and oxidation of JP-10 are uncovered finally.

7.2 Simulation details

The upgraded C/H/O-2016 ReaxFF force field parameters [45] are used for all of the MD simulations. In total, four cubic and periodic simulation systems, i.e. pyrolysis and oxidation of JP-10 and their mixture with FGS, are built at the same density of 0.15 g/cm³ with different box sizes. 20 JP-10 molecules are included in each system. In addi-
Figure 7.1 System configurations for pyrolysis and oxidation of JP-10 and their mixture with FGS: (a) JP-10 pyrolysis, (b) JP-10 structure, (c) JP-10 oxidation, (d) JP-10 pyrolysis with FGS, (e) FGS structure and (f) JP-10 oxidation with FGS. C, H and O atoms are represented in grey, white and red, respectively.

For pyrolysis, 10 oxygen molecules are introduced in the two systems of JP-10 oxidation and its mixture with FGS to focus on the comparison of initiation mechanisms instead of complete oxidation. Figure 7.1 shows the details of system construction and structure of JP-10 and FGS. To be specific, the FGS placed in the centre of the simulation box is modified from a pristine graphene sheet, containing 64 C, 12 O and 30 H atoms. Two identical functional groups are implanted in the graphene sheet and each one has a divacancy decorated by two ethers with four additional OH groups attached to the C atoms nearby [70]. H atoms are attached to the edge C atoms of the graphene sheet. As a result, the weight ratio of JP-10 and FGS is about 2.75:1, which is smaller than those
used in experiments mentioned in Introduction in order to accelerate the simulation.
The size of the cubic simulation box is changed accordingly to maintain the same
density for every system. A Conolly surface with a radius of 1.0 Å is created to evaluate
the volume of the FGS. Consequently, the size is 31.11 Å (Figure 7.1a), 32.29 Å (Figure
7.1c), 31.38 Å (Figure 7.1d) and 32.53 Å (Figure 7.1f) for the four systems, respectively.

All of the ReaxFF MD simulations use the canonical ensemble (NVT) with a
damping constant of 0.1 ps. To eliminate the artificial effects on the initial geometric
configuration, energy minimization is conducted for every system at the very beginning,
followed by the 50 ps equilibration at the starting temperature 300 K. Next, during a
time period of 1000 ps, the temperature is raised linearly from 300 to 2300 K with a
heating rate of 2 K/ps. Finally, the temperature is fixed at 2300 K for another 1000 ps.
Figure 7.3 shows the proposed heating strategy. It has been checked that the
temperature variation of more than 85% of the data points is within 5% of their target
values. The present study employs a 0.1 fs time step. The bonding and trajectory results
are recorded at a frequency of 0.1 fs. The species formed during the simulation is
recognized using a bond order cutoff value of 0.2, which could be beneficial for the
detection of all possible reaction pathways [20, 28].

In order to find the transition state and calculate the energy barrier of a specific
reaction where the reactants and products are known, nudged elastic band (NEB)
method is adopted. Basically, the NEB calculation is a simultaneous procedure of
energy minimization, which is carried out by damped dynamics. For the purpose of
finding the minimum energy path, a spring force is applied between a number of
inserted intermediate replicas. The methodology of NEB developed by Henkelman and
co-workers [206, 207] has been extensively used in the field of computational chemistry.
In the present research, a spring constant of 1 kcal/(mol·Å) is employed to connect each
replica. Depending on the complexity of each studied reaction, two or three intermediate replicas are produced, and all of the initial and final structures are fully relaxed.

7.3 Results and discussions

7.3.1 Detailed initiation reactions of pyrolysis and oxidation of JP-10 and their mixture with FGS

The time evolution of the number of JP-10 molecules for all the four systems is shown in Figure 7.2. Both pyrolysis and oxidation of JP-10 are enhanced in the presence of FGS, resulting in the earlier decomposition of JP-10 at a lower temperature. Also, the average reaction rate of JP-10 is faster with the addition of FGS in both cases. The enhancement is further confirmed by the change in relative potential energy between JP-10 pyrolysis/oxidation with FGS and JP-10 pyrolysis/oxidation as shown in Figure 7.3. These two lines have a similar trend, which increases to a peak firstly and then keeps decreasing. The increase in the difference of relative potential energy means that the heat absorption is accelerated in the systems with FGS. After about 1000 ps, the po-

![Figure 7.2](image)

**Figure 7.2** Time evolution of JP-10 molecule number during NVT MD simulations of: (a) JP-10 pyrolysis and its mixture with FGS and (b) JP-10 oxidation and its mixture with FGS.
potential energy of the systems with FGS reaches their peak values and starts to drop down proceeding to the heat release stage but the potential energy of the systems without FGS is still climbing. As a result, the change in relative potential energy subsequently decreases. This also suggests that the reactions of both pyrolysis and oxidation are advanced and enhanced in the presence of FGS. In order to gain deeper insight into the enhancement, the detailed initial decomposition pathway of every JP-10 molecule is tracked by analysing the evolution of species together with the visualization of trajectories. The results are summarized in Tables 7.1 and 7.2.

![Figure 7.3](image.png)

**Figure 7.3** Heating strategy and time evolution of relative potential energy between JP-10 pyrolysis/oxidation with FGS and JP-10 pyrolysis/oxidation. The noises of two sets of relative potential energy data are reduced by the Savitzky-Golay filter.
Table 7.1 Detailed initial decomposition pathways of every JP-10 molecule in the systems of: (a) JP-10 pyrolysis and (b) JP-10 pyrolysis with FGS.

<table>
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<tr>
<th>No.</th>
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<th>Time (ps)</th>
<th>No.</th>
<th>(a) Decomposition Reaction</th>
<th>Time (ps)</th>
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<td>Time (ps)</td>
<td>No.</td>
<td>(b) Decomposition Reaction</td>
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Table 7.2 Detailed initial decomposition pathways of every JP-10 molecule in the systems of: (a) JP-10 oxidation and (b) JP-10 oxidation with FGS.

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<th>No.</th>
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<td>633.5</td>
<td>12</td>
<td><img src="image6" alt="Reaction 12" /> + H₃C=CH₂</td>
<td>1092.7</td>
</tr>
<tr>
<td>3</td>
<td><img src="image7" alt="Reaction 3" /> + OH → <img src="image8" alt="Product 3" /></td>
<td>643.5</td>
<td>13</td>
<td><img src="image9" alt="Reaction 13" /> + H₃C=CH₂</td>
<td>1093.6</td>
</tr>
<tr>
<td>4</td>
<td><img src="image10" alt="Reaction 4" /> + OH → <img src="image11" alt="Product 4" /> + H₂O</td>
<td>729</td>
<td>14</td>
<td><img src="image12" alt="Reaction 14" /> + H₃C=CH₂</td>
<td>1099.3</td>
</tr>
<tr>
<td>5</td>
<td><img src="image13" alt="Reaction 5" /> + O₂ → <img src="image14" alt="Product 5" /> + HO₂</td>
<td>777.2</td>
<td>15</td>
<td><img src="image15" alt="Reaction 15" /> + <img src="image16" alt="Product 15" /></td>
<td>1125.3</td>
</tr>
<tr>
<td>6</td>
<td><img src="image17" alt="Reaction 6" /> + H₂C=CH₂ → <img src="image18" alt="Product 6" /> + H₂C=CH₂</td>
<td>832.2</td>
<td>16</td>
<td><img src="image19" alt="Reaction 16" /> + H → <img src="image20" alt="Product 16" /> + H₂</td>
<td>1136</td>
</tr>
<tr>
<td>7</td>
<td><img src="image21" alt="Reaction 7" /> + HO₂ → <img src="image22" alt="Product 7" /> + H₂O₂</td>
<td>848.2</td>
<td>17</td>
<td><img src="image23" alt="Reaction 17" /> + H₃C=CH₂</td>
<td>1181.8</td>
</tr>
<tr>
<td>8</td>
<td><img src="image24" alt="Reaction 8" /> + H₃C=CH₂ → <img src="image25" alt="Product 8" /></td>
<td>957.4</td>
<td>18</td>
<td><img src="image26" alt="Reaction 18" /> + H₂</td>
<td>1190.1</td>
</tr>
<tr>
<td>9</td>
<td><img src="image27" alt="Reaction 9" /> + H₃C=CH₂ → <img src="image28" alt="Product 9" /></td>
<td>957.6</td>
<td>19</td>
<td><img src="image29" alt="Reaction 19" /> + H₂C=CH₂</td>
<td>1241.3</td>
</tr>
<tr>
<td>10</td>
<td><img src="image30" alt="Reaction 10" /> + H → <img src="image31" alt="Product 10" /></td>
<td>1012.1</td>
<td>20</td>
<td><img src="image32" alt="Reaction 20" /> + H₃C=CH₂</td>
<td>1260.6</td>
</tr>
</tbody>
</table>
7.3.1.1 Validation of the ReaxFF method

In previous studies, the ReaxFF MD has proven to be an effective method for investigating the pyrolysis and oxidation of JP-10 [28, 29]. Especially, Chenoweth et al. [28] carried out a comprehensive comparison of the JP-10 decomposition products between various experimental [180, 186-188, 208, 209] and their ReaxFF MD results, where a high similarity was found. Among those many decomposition products discovered in experiments, only a couple of them such as C₂H₆ and C₁₀H₈ (napthalene) are not observed in the present research. Both Chenoweth et al.’s [28] and the present study capture some decomposition products like C₃H₅ (allyl radical) and C₅H₈ (1,4-pentadiene), which were not found in those experiments, but were obtained in several recent experimental studies [185, 191, 193]. In addition to the comparison with experimental results, Chenoweth et al. [28] also validated the ReaxFF method by performing QM calculations and the results were in good agreement with each other. Moreover, the latest C/H/O ReaxFF force field parameters used in the present study have proven to be able to produce comparable results of decomposition pathways and Arrhenius parameters (activation energy and pre-exponential factor obtained from ReaxFF and experiment are 56.8, 62.4 Kcal/mol, and 25 × 10¹⁴, 0.57 × 10¹⁴ s⁻¹, respectively) for JP-10 as in experiments [45]. Therefore, it is appropriate to investigate the chemistry of JP-10 pyrolysis and oxidation using the ReaxFF MD method with the latest C/H/O parameters.

7.3.1.2 Effects of FGS addition on JP-10 pyrolysis

The initial step of decomposition for every JP-10 molecule in the systems of JP-10 pyrolysis and its mixture with FGS is presented in Table 7.1 and the corresponding time of occurrence is given. The JP-10 pyrolysis has been well studied by both experiment [191-193] and numerical modelling [28, 196, 198, 199] before, so this
section focuses on the analysis of effects of FGS addition on the JP-10 pyrolysis. In consistency with Ashraf and van Duin’s [45] results, for normal pyrolysis, the JP-10 molecules mainly decompose into various smaller hydrocarbons by some dominant pathways (i.e. C₈ & C₂, C₅ & C₅, C₇ & C₃ or C₁₀H₁₅ & H), whereas with FGS, the decomposition of the first four JP-10 molecules begins with the dehydrogenation by the OH group on FGS forming H₂O and the initiation of these four JP-10 molecules all occurs earlier than the first JP-10 decomposition without FGS. After the initial dehydrogenation, it is also found that the secondary decomposition into smaller hydrocarbons of these four C₁₀H₁₅ radicals happens at 883.8 ps, 893.4 ps, 959.6 ps and 995 ps, respectively, which is more efficient than those JP-10 molecules in normal pyrolysis reactions. Additionally, the dehydrogenation of JP-10 without FGS (R13, R14 and R17 in Table 7.1a) is only observed at a high temperature (2300 K), which also agrees well with the previous results [45].

There are in total eight OH functional groups on the FGS. The results show that six of them are consumed and the remaining two groups are retained at the end of the simulation. Hence, further to the first four OH groups, the complete reactions of the 5th and 6th OH group during the whole simulation time are analysed as well and they are summarized in Table 7.3. As can be seen, the two series of reactions both start from the separation of OH from the FGS. Then the OH quickly reacts with a hydrocarbon radical forming an oxygenated hydrocarbon. Subsequently, the oxygenated hydrocarbon either reacts with another hydrocarbon or directly decomposes to produce a smaller oxygenated hydrocarbon. Next, this smaller oxygenated hydrocarbon goes through various reactions or decompositions generating H₂O or CO eventually. It can be expected that the last two OH groups could also take part in similar intermediate
reactions to enhance the pyrolysis reaction, provided that the simulation time is long enough.

**Table 7.3** Complete reactions of the 5th and 6th OH group during the whole simulation time of JP-10 pyrolysis with FGS.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Time (ps)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 5 OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1631.5</td>
<td>OH leaves the FGS</td>
</tr>
<tr>
<td>2</td>
<td>1637.9</td>
<td>OH + C₅H₅ → C₅H₆O</td>
</tr>
<tr>
<td>3</td>
<td>1771</td>
<td>C₅H₆O + C₇H₁₂ → C₁₀H₁₅ + C₂H₃O</td>
</tr>
<tr>
<td>4</td>
<td>1916.1</td>
<td>C₂H₃O → C₂H₂ + OH</td>
</tr>
<tr>
<td>5</td>
<td>1917.7</td>
<td>OH + C₃H₈ → C₃H₇ + H₂O</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No. 6 OH</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1947.3</td>
<td>OH leaves the FGS</td>
</tr>
<tr>
<td>2</td>
<td>1947.8</td>
<td>OH + C₆H₁₀ → C₆H₁₁O</td>
</tr>
<tr>
<td>3</td>
<td>1954.7</td>
<td>C₆H₁₁O → C₄H₇ + C₂H₄O</td>
</tr>
<tr>
<td>4</td>
<td>1967.7</td>
<td>H + C₂H₄O → H₂ + C₂H₃O</td>
</tr>
<tr>
<td>5</td>
<td>1976.2</td>
<td>C₂H₃O → C₂H₃ + CO</td>
</tr>
</tbody>
</table>

Combing the above two paragraphs, the catalytic reaction steps for JP-10 pyrolysis on FGS can be summarized as follow (Figure 7.4): (1) OHs leave the FGS; (2) OHs initiate the pyrolysis reaction by reacting with JP-10 forming C₁₀H₁₅ and H₂O; (3) more OHs leave the FGS; (4) OHs take part in various intermediate reactions involving oxygenated hydrocarbons. It is indicated that the OH functional groups on the FGS can not only advance the initiation of JP-10 pyrolysis, but also participate in various intermediate reactions to further enhance the pyrolysis reaction.
Figure 7.4 Catalytic reaction steps for JP-10 pyrolysis on FGS: (1) OHs leave the FGS; (2) OHs initiate the pyrolysis reaction by reacting with JP-10 forming $C_{10}H_{15}$ and $H_2O$; (3) more OHs leave the FGS; (4) OHs take part in various intermediate reactions involving oxygenated hydrocarbons.

7.3.1.3 Effects of FGS addition on JP-10 oxidation

Table 7.2 presents the initial decomposition step for every JP-10 molecule and its corresponding time of occurrence in the systems of JP-10 oxidation and its mixture with FGS. The analysis of effects of FGS addition rather than the simple JP-10 oxidation is emphasized in this section. The results show that the initiation of normal JP-10 oxidation includes two main stages, i.e. (1) decomposition of JP-10 and (2) reaction of JP-10 and other decomposed products with radicals like $O_2$, $O$, $H$, $OH$, $HO_2$ and $H_2O_2$, which is in accordance with previous experimental [185] and computational [29, 184] results. In contrast to JP-10 pyrolysis with FGS, the pathways are different although the decomposition of the first four JP-10 molecules in the system of JP-10 oxidation with FGS is still initiated by the reaction with OH. A new pathway is found, which involves the C-C bond cleavage followed by OH attachment to one of those two C atoms (R1 and R3 in Table 7.2b). The complete reactions that these two $C_{10}H_{16}OH$ molecules undergo during the simulation time are listed in Table 7.4. They both firstly decompose
into a smaller oxygenated hydrocarbon and then this oxygenated hydrocarbon goes through a series of reactions to finally form CO and H₂O, respectively. It is worth noting that a short exchange between intermediate products and FGS (R3 and R4 in Table 7.4 – No. 2 C₁₀H₁₆OH) is observed in the reactions of the second C₁₀H₁₆OH molecule. Similar to JP-10 pyrolysis reactions, the initiation of the first four JP-10 molecules in the system of JP-10 oxidation with FGS all proceed earlier than the first JP-10 decomposition without FGS and the dehydrogenation of JP-10 without FGS (R12, R13, R15, R16 and R17 in Table 7.2a) only takes place at a high temperature (2300 K).

Table 7.4 Complete reactions of two C₁₀H₁₆OH molecules during the whole simulation time of JP-10 oxidation with FGS. The subscript of FGS represents the different forms of FGS containing different numbers of C, H and/or O atoms.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Time (ps)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No. 1 C₁₀H₁₆OH (1st JP-10 molecule)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>674.2</td>
<td>C₁₀H₁₇O → C₂H₅O + C₈H₁₂</td>
</tr>
<tr>
<td>2</td>
<td>961</td>
<td>OH + C₂H₅O → C₂H₆O₂</td>
</tr>
<tr>
<td>3</td>
<td>1196.2</td>
<td>C₂H₆O₂ → CH₃ + CH₃O₂</td>
</tr>
<tr>
<td>4</td>
<td>1328.2</td>
<td>H + CH₃O₂ → H₂ + CH₂O₂</td>
</tr>
<tr>
<td>5</td>
<td>1594.9</td>
<td>H + CH₂O₂ → CH₃O₂</td>
</tr>
<tr>
<td>6</td>
<td>1595.2</td>
<td>CH₃O₂ → H₂O + CHO</td>
</tr>
<tr>
<td>7</td>
<td>1597.7</td>
<td>C₂H₅ + CHO → C₃H₆O</td>
</tr>
<tr>
<td>8</td>
<td>1598.4</td>
<td>C₃H₄O → H + C₃H₃O</td>
</tr>
<tr>
<td>9</td>
<td>1616.2</td>
<td>C₃H₃O → C₂H₃ + CO</td>
</tr>
<tr>
<td><strong>No. 2 C₁₀H₁₆OH (3rd JP-10 molecule)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1063.3</td>
<td>C₁₀H₁₇O → C₉H₁₄O + CH₃</td>
</tr>
<tr>
<td>2</td>
<td>1117.2</td>
<td>C₉H₁₄O → C₆H₁₀O + C₃H₄</td>
</tr>
<tr>
<td>3</td>
<td>1123.1</td>
<td>C₆H₁₀O + FGS₁ → FGS₂</td>
</tr>
<tr>
<td>4</td>
<td>1124.7</td>
<td>FGS₂ + C₁₀H₁₄ → FGS₁ + C₆H₁₀O + C₂H₄ + C₈H₁₀</td>
</tr>
<tr>
<td>5</td>
<td>1353</td>
<td>H + C₆H₁₀O → C₆H₁₁O</td>
</tr>
<tr>
<td>6</td>
<td>1353.1</td>
<td>C₆H₁₁O → C₆H₉ + H₂O</td>
</tr>
</tbody>
</table>
Table 7.5 Complete reactions of the 5th, 6th and 7th OH groups during the whole simulation time of JP-10 oxidation with FGS. All reactions involving FGS relate to the OH group on it. The subscript of FGS represents the different forms of FGS containing different numbers of C, H and/or O atoms.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Time (ps)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No. 5 OH</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1018.7</td>
<td>H + FGS₁ → FGS₂</td>
</tr>
<tr>
<td>2</td>
<td>1018.8</td>
<td>FGS₂ → FGS₃ + H₂O</td>
</tr>
<tr>
<td><strong>No. 6 OH</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1030.5</td>
<td>H + FGS₃ → FGS₄ + H₂</td>
</tr>
<tr>
<td>2</td>
<td>1986.6</td>
<td>CO leaves the FGS</td>
</tr>
<tr>
<td><strong>No. 7 OH</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1755.3</td>
<td>FGS₅ → FGS₆ + H</td>
</tr>
<tr>
<td>2</td>
<td>1759</td>
<td>H + C₈H₁₀ → C₈H₉ + H₂</td>
</tr>
</tbody>
</table>

With respect to the eight OH functional groups on the FGS, six of them are consumed, leaving one OH group and one attached O (lose the H) at the end of the simulation. The complete reactions of the 5th, 6th and 7th OH groups during the simulation time are shown in Table 7.5. Unlike those OHs in pyrolysis reactions which react with hydrocarbon intermediates, the 5th and 6th OH groups are attracted by an H radical directly generating H₂O and H₂, respectively, while the H is found to detach from the 7th OH and then dehydrogenize a hydrocarbon producing H₂. This difference results from the introduction of O₂ generating more OHs from HO₂ and H₂O₂ as well as some oxygenated hydrocarbons which both react with hydrocarbon radicals. Besides, the O₂ itself can also compete with OH’s reaction with hydrocarbons. Due to these reasons, O-H bond cleavage of the OH group on the FGS is only observed in the oxidation reactions. In addition, the H of OH can transfer between different O atoms on
the FGS. For example, at 1228.4 ps, an H of OH moves to a nearby O of ether and transfers back to the original O of that OH later at 1512.6 ps. Similarly, in the two reactions of No. 6 OH in Table 7.5, after losing the H, the O of OH shifts to another edge C atom of FGS and finally leaves the FGS as CO. The remaining one OH group and one attached O could also be involved in the intermediate reactions to further accelerate the JP-10 oxidation if the simulation is continued.

To summarize, the catalytic reaction steps for JP-10 oxidation on FGS follow the procedure (Figure 7.5): (1) OHs leave the FGS; (2) OHs initiate the oxidation reaction by reacting with JP-10 via different pathways; (3) OH or H of OH is abstracted from or leaves the FGS; (4) OH or H take part in intermediate reactions involving the direct formation of H₂O and H₂. Again, it is the OH functional group that advances the initiation of JP-10 oxidation and further enhances the oxidation reaction by participating in various intermediate reactions.

**Figure 7.5** Catalytic reaction steps for JP-10 oxidation on FGS: (1) OHs leave the FGS; (2) OHs initiate the oxidation reaction by reacting with JP-10 via different pathways; (3) OH or H of OH is abstracted from or leaves the FGS; (4) OH or H take part in intermediate reactions involving the direct formation of H₂O and H₂.
7.3.2 Transition state and energy barrier for key initiation reactions

**Figure 7.6** Transition state and energy barrier for some frequently occurring and key JP-10 decomposition reactions from ReaxFF-NEB simulations. Figures a–f are placed in the descending order of energy barrier and the calculated value of energy barrier is labelled in the bottom right corner in each figure. The C atoms of JP-10 molecule are numbered in the last figure.
Figure 7.6 depicts the transition state and energy barrier for some frequently occurring and key JP-10 decomposition reactions extracted from Tables 7.1 and 7.2 by ReaxFF-NEB simulations. It is checked that all of the obtained transition states from NEB calculations accord with the dynamic trajectories of ReaxFF MD simulations. Among all these studied reactions, the decomposition of JP-10 to cyclopentene and 1,4-pentadiene (Figure 7.6a) has the highest energy barrier of 156.81 kcal/mol. This decomposition procedure follows the sequential cleavage of C-C bonds: C₈-C₉ → C₁-C₂ → C₆-C₇, which is the same as Chenoweth et al.’s results [28]. The sequence of C-C bond dissociation for the reaction producing allyl in Figure 7.6b is C₁-C₂ → C₇-C₁₀ → C₈-C₉ and the H attached to C₆ shifts to C₂ before the cleavage of C₇-C₁₀ bond. These reaction steps are also found in DFT calculations [199]. Figure 7.6c demonstrates the formation of ethylene resulting from the successive breaking of C-C bonds between C₁ & C₉ and C₇ and C₈. The C₂-C₆ bond broken is seen at a later stage of the simulation leading to 1,5-cyclooctadiene structure. The JP-10 decomposition products of 1,5-cyclooctadiene and ethylene agree with the DFT [197] and ReaxFF MD [28] simulation results. These two reactions in Figures 7.6b and c have very close energy barrier values. Figures 7.6d and e illustrate the two scenarios of dehydrogenation of JP-10 at C₂ and C₄, respectively. Zhao et al. [193] computed the energy of C-H bond cleavage for every C position of JP-10 by DFT and found that the dehydrogenation at C₂, C₃, C₄ and C₉ are more preferable with the energy ranging from 92.73–97.04 kcal/mol. Three (C₂, C₃ and C₄) of these four dehydrogenations are observed in the present study and the calculated energy barrier for dehydrogenation at C₂ (89.31 kcal/mol) and C₄ (83.28 kcal/mol) is in good agreement with Zhao et al.’s DFT calculations. The conversion of JP-10 to two five-member ring structures were discovered in many studies [185, 186, 191, 193, 196]. The C₁-C₂ bond is broken first followed by further fragmentation via
C₆-C₇ separation. In the present study (Figure 7.6f), before the C₆ is separated from C₇, one H attached to C₁₀ moves to C₁ producing two cyclopentenes eventually. Figure 7.6g describes the formation of 2-norbornene and propene from consecutive C₅-C₆ and C₂-C₃ bond scissions [185, 186, 196, 198], which also involves the H transfer from C₄ to C₅ prior to the cleavage of C₂-C₃ bond.

Other species, i.e. O₂, OH, H and HO₂ are introduced in the JP-10 initiation reactions in Figures 7.6h–n and the energy barriers of these reactions are all lower than the above unimolecular JP-10 decompositions as expected. Except for the two reactions in Figures 7.6i and j, the remaining five all relate to the dehydrogenation of JP-10 at various C positions. It can be seen that the dehydrogenation of JP-10 by O₂ has the highest energy barrier of 44.38 kcal/mol among these reactions, followed by the formation of two C₁₀H₁₆OHs with OH attaching to C₄ and C₃, respectively. The OH is more likely to attach to C₃ compared to C₄ because the energy barrier is much lower. Figures 7.6k and l show the dehydrogenation of JP-10 by the OH functional group on FGS at C₁ and C₈ producing H₂O and the energy barriers for these two reactions are almost the same. It is indicated that JP-10 decomposition initiated by OH is easier than by O₂. The H₂ formation via dehydrogenation of JP-10 by the H radical in Figure 7.6m has a similar energy barrier as those decompositions initiated by OH. As presented in Table 7.5, the FGS can release the H of OH to participate in intermediate reactions, which could also be helpful for JP-10 initiation. It can be expected to see the JP-10 reaction with H of OH on FGS if the size of FGS is increased with more OH functional groups. The energy barrier of the dehydrogenation of JP-10 by HO₂ generating H₂O₂ is slightly lower than those reactions in Figures 7.6k–m. However, it needs HO₂ as a precursor and the formation of HO₂ is not that straightforward and easy as the release of OH or H from FGS. Based on the above analysis, it can be concluded that the energy
barrier for JP-10 decomposition reactions initiated by the OH or potential H of OH on FGS is much lower than the unimolecular decomposition of JP-10 by the C-C or C-H bond scission. This considerable reduction in the energy barrier makes the reactions of JP-10 with OH or H on FGS more preferable than those cleavages of C-C or C-H bonds thereby changing and enhancing the JP-10 initiation.

7.4 Summary

The initiation mechanisms of pyrolysis and oxidation of JP-10 with FGS in comparison with normal JP-10 reactions are investigated by ReaxFF MD simulations. Furthermore, the transition state and energy barrier for key initiation reactions are studied by ReaxFF-NEB calculations. It is indicated that the presence of FGS advances and enhances both the pyrolysis and oxidation of JP-10, which results in earlier JP-10 decomposition at a lower temperature as well as a faster reaction rate. To scrutinize the effect of the addition of FGS, detailed initiation reactions of JP-10 pyrolysis and oxidation and their mixtures with FGS are obtained. The results show that the decomposition of JP-10 with FGS in the pyrolysis system begins with the dehydrogenation by the OH functional groups on the FGS producing H₂O, whereas the pyrolysis of pure JP-10 primarily decomposes to diverse smaller hydrocarbons. Likewise, the decomposition of JP-10 with FGS is initiated by its reaction with OH in the system of oxidation, and another pathway involving the C-C bond breaking followed by OH attachment to one of those two C atoms, is discovered in addition to the formation of H₂O. With the proceeding of the reaction in both the pyrolysis and oxidation of JP-10, more OH groups from FGS participate in various intermediate reactions that involves oxygenated hydrocarbons or direct production of H₂O and H₂. Furthermore, in the absence of FGS, the dehydrogenation of JP-10 is only observed at high temperatures. As a result, the OH functional groups on the FGS not only advance
the JP-10 initiation, but also take part in various intermediate reactions, which further enhance the pyrolysis and oxidation of JP-10. The results of transition state and energy barrier for key initiation reactions provide a deeper insight into the enhancement caused by the FGS. It is suggested that the energy barrier of unimolecular decomposition of JP-10 or its reaction with O₂ is higher than the JP-10 decomposition triggered by OH or H, which leads to the preferential reactions of JP-10 with OH or H on the FGS. This is why the JP-10 initiation is changed and enhanced in the presence of FGS. The results obtained from the present research are applicable to and lay the scientific foundation for the potential use of FGS as a promising nanoparticle additive for enhancing the homogeneous combustion of JP-10 fuel system in aviation applications.
Chapter 8 – Conclusions and Future Work

The present research explores the fundamental reaction mechanisms of thermal decomposition and oxidation of various kinds of fuel including hydrous ethanol, aluminium hydride, methane and JP-10 using ReaxFF reactive force field MD simulations. Particularly, catalytic reactions of methane and JP-10 on graphene-based nanomaterials are studied to provide fundamental insights for their potential usage as promising fuel additives for the next-generation fuel/propellant systems. Each of these studies contributes to their specific area of application and is concluded as below.

Chapter 4 demonstrates the fundamental reaction mechanisms of hydrous ethanol oxidation as well as the feasibility and advantages of burning hydrous ethanol solely as a fuel. The understanding of the mechanisms, especially the important role of water and its resulting effects, could be helpful for designing the direct application of hydrous ethanol in combustion applications such as IC engines. However, the quantitative relationship between the operating conditions of using hydrous ethanol and the output performance under given circumstances still needs further investigation. For example, the threshold of temperature and water content for optimal performance could be studied in detail in the future. This research provides the scientific base for the direct use of hydrous ethanol as a fuel for combustion systems with a low cost.

Chapter 5 reveals the fundamental reaction mechanisms of thermal decomposition and oxidation of AlH₃ occurred in propulsion systems, which could contribute to the safe storage and efficient usage of AlH₃. For example, to reduce the instability resulting from the defects and preserve the high hydrogen capacity during storage, an additional thin oxide layer or other suitable organic layer could be coated on the AlH₃ surface that potentially makes it a more efficient propellant. Many other important influential
factors, including the thickness of the oxide shell layer, size/amount of the defect, oxygen pressure, and equivalence ratio, could also be investigated in the future work to add to the growing understanding of the AlH₃ reaction. This research provides new fundamental information about thermal decomposition and oxidation of AlH₃ that may impact on its practical applications.

Chapter 6 studies the mechanisms and kinetics of heterogeneous catalytic oxidation of methane with Pt/graphene-based additives, which has potential applications on propulsion systems. Pt@FGS is found to improve the catalytic activity by dramatically lowering the activation energy of methane oxidation by approximately 73% thereby demonstrating that Pt@FGS is a promising nanoparticle additive for catalytic fuel combustion. Based on the catalytic mechanisms, the effect of Pt loading on the FGS and the functionality of the FGS could be further explored. Additionally, the optimal equivalence ratio for the catalytic methane oxidation in this case should be specified. This research sheds light on the enhanced fuel combustion in the presence of Pt@FGS.

Chapter 7 investigates the initiation mechanisms of enhanced pyrolysis and oxidation of JP-10 on FGS. The proposed mechanisms demonstrate the catalytic effect of FGS on the homogeneous combustion of JP-10 fuel system thus offer guidelines for designing such a system, which could be used in aviation applications. Similar to Chapter 6, in addition to the mechanisms, the effect of FGS loading, functionality of FGS and equivalence ratio should be studied in detail in the future work to construct a more complete theoretical framework. This research provides the scientific insight as to the potential use of FGS as a promising additive for JP-10 fuel systems.
To conclude, the present research provides guidelines for studying the complex chemistry of a broad range of fuel oxidation and catalytic reactions, which could benefit the improvement of current and the design of future high-performance energy and propulsion systems.
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Appendices

Appendix A – Supplementary Information for Chapter 4

Table A.1 Full list of elementary reactions during NVT MD simulations of ethanol oxidation in (a) O$_2$/N$_2$ and (b) O$_2$/H$_2$O environments. Different reactions within the two pathways are marked with asterisk.

<table>
<thead>
<tr>
<th>ID</th>
<th>(a) Reaction (O$_2$/N$_2$)</th>
<th>Total Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$_2$H$_6$O $\rightarrow$ C$_2$H$_5$ + OH</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>H + O$_2$ $\rightarrow$ HO$_2$</td>
<td>222</td>
</tr>
<tr>
<td>3</td>
<td>* HO$_2$ $\rightarrow$ OH + O</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>* HO$_2$ + OH $\rightarrow$ H$_2$O + O$_2$</td>
<td>110</td>
</tr>
<tr>
<td>5</td>
<td>H$_2$O + O $\rightarrow$ OH + OH</td>
<td>46</td>
</tr>
<tr>
<td>6</td>
<td>H$_2$O$_2$ $\rightarrow$ OH + OH</td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$O$_2$ + H $\rightarrow$ H$_2$O + OH</td>
<td>47</td>
</tr>
<tr>
<td>8</td>
<td>C$_2$H$_6$O + OH $\rightarrow$ C$_2$H$_5$O + H$_2$O</td>
<td>179</td>
</tr>
<tr>
<td>9</td>
<td>* C$_2$H$_6$O + HO$_2$ $\rightarrow$ C$_2$H$_5$O + H$_2$O</td>
<td>74</td>
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<tr>
<td>10</td>
<td>C$_2$H$_6$O + O$_2$ $\rightarrow$ C$_2$H$_5$O + HO$_2$</td>
<td>42</td>
</tr>
<tr>
<td>11</td>
<td>C$_2$H$_5$O $\rightarrow$ C$_2$H$_4$ + OH</td>
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<tr>
<td>12</td>
<td>C$_2$H$_3$O $\rightarrow$ CH$_2$O + CH$_3$</td>
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<td>13</td>
<td>C$_2$H$_5$ + O$_2$ $\rightarrow$ C$_2$H$_4$ + HO$_2$</td>
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<td>CH$_3$O $\rightarrow$ CH$_2$O + H</td>
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<td>17</td>
<td>CH$_3$ + OH $\rightarrow$ CH$_4$O</td>
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<tr>
<td>18</td>
<td>CH$_3$ + O$_2$ $\rightarrow$ CH$_3$O$_2$</td>
<td>56</td>
</tr>
<tr>
<td>19</td>
<td>CH$_2$O + OH $\rightarrow$ CHO + H$_2$O</td>
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<tr>
<td>20</td>
<td>CHO $\rightarrow$ CO + H</td>
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<tr>
<td>21</td>
<td>CHO + O$_2$ $\rightarrow$ CO + HO$_2$</td>
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<td>22</td>
<td>CO$_3$ $\rightarrow$ CO$_2$ + O</td>
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<tr>
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<td>* H₂O + HO₂ → H₂O₂ + OH</td>
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<td>* H₂O + H → H₂ + OH</td>
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<td>H₂O + O → OH + OH</td>
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<tr>
<td>6</td>
<td>H₂O₂ → OH + OH</td>
<td>302</td>
</tr>
<tr>
<td>7</td>
<td>* H₂O₂ + HO₂ → H₂O + O₂ + OH</td>
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<td>H₂O₂ + H → H₂O + OH</td>
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<td>9</td>
<td>* H + OH → H₂O</td>
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<td>12</td>
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<tr>
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<td>C₂H₅O → C₂H₄ + OH</td>
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<tr>
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<td>C₂H₅O → CH₂O + CH₃</td>
<td>171</td>
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<tr>
<td>15</td>
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Appendix B – List of Publications and Conferences

Journal Articles


Conferences
