Initiation mechanisms of enhanced pyrolysis and oxidation of JP-10 (exo-tetrahydrodicyclopentadiene) on functionalized graphene sheets: Insights from ReaxFF molecular dynamics simulations

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Abstract

Functionalized graphene sheets (FGS) have proven to be an effective nanoparticle additive for jet fuels. In this study, the reactive force field (ReaxFF) molecular dynamics (MD) simulation is employed to investigate the initiation mechanisms of JP-10 pyrolysis and oxidation with FGS in comparison with normal JP-10 reactions. ReaxFF-nudged elastic band (NEB) calculations are performed to study the transition state and energy barrier for key initiation reactions in order to reveal the catalytic effect of FGS on JP-10 pyrolysis and oxidation. The results show that both pyrolysis and oxidation of JP-10 are advanced and enhanced in the presence of FGS, leading to earlier decomposition of JP-10 at a lower temperature and a faster reaction rate. It is found that the OH functional group on the FGS not only advances the initiation of JP-10 but also participates in various intermediate reactions to further enhance the pyrolysis and oxidation of JP-10. Moreover, the

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dehydrogenation of JP-10 without FGS is only observed at high temperatures. A deeper insight into the enhancement resulting from the FGS is provided through the analysis of the results of transition state and energy barrier for key initiation reactions. It is found that JP-10 decomposition initiated by OH or H on the FGS occurs at a lower energy barrier than unimolecular decomposition or through reaction with O_2 thereby changing and enhancing the JP-10 initiation. In summary, this research provides the scientific insight as to the potential use of FGS as a promising catalyst for JP-10 fuel systems.

Keywords: JP-10; Functionalized graphene sheet; Molecular dynamics; Reactive force field; Nudged elastic band calculation; Catalysis.

1. Introduction

Jet Propellant-10 (JP-10, exo-tetrahydrodicyclopentadiene) is a single-component hydrocarbon fuel, which is used in aviation applications such as missiles, detonation engines, ramjets and scramjets due to its extraordinary properties including high energy density [1], high heat capacity [2], high thermal stability [3] and low freezing point [4]. The operational conditions for use of JP-10 as a fuel in pulse-detonation engines can reach up to 2500 K and 100 bar [5]. Because of its broad applications and superior qualities, numerous experimental [2, 6-14] and theoretical [5, 15-21] studies have been reported for the pyrolysis and oxidation of JP-10. However, one problem of JP-10 and many other liquid hydrocarbon fuels, is that the slow ignition and combustion kinetics could lead to poor performance for applications like pulse-detonation engines or ramjets [1]. Therefore, research into the catalytic reaction of JP-10 is of theoretical and practical importance. Moreover, the addition of additives can further increase the energy density of the fuel system [22, 23]. Particularly for aeropropulsion systems where the cooling requirements are demanding, the catalytic dehydrogenation and cracking of endothermic hydrocarbons like JP-10 is able to offer a better chemical heat sink [24]. To date, the majority of the catalysts used for JP-10 reactions are metal-based materials [1, 24-28] but these suffer from some disadvantages that cannot be ignored. For

47 example, there are non-energetic oxide passivation layers on the particles and undesired solid oxide

48 reaction byproducts produced during the combustion process.

49   In recent years, graphene-based materials, especially functionalized graphene sheets (FGS) have

50 been considered as effective catalysts for fuel and propellant combustion [29-35]. They can not only

51 catalyse fuel combustion reactions, but also be energetically involved in the combustion process, and

52 finally be consumed without producing residual particles. A pioneering work was undertaken by

53 Sabourin et al. [29], who studied the combustion of monopropellant nitromethane enhanced by FGS

54 colloidal particles. They found that the ignition temperature was lowered with the addition of FGS

55 and the burning rate increased up to 175% over neat nitromethane, outperforming more conventional

56 additives such as aluminium oxyhydroxide and amorphous silica oxide nanoparticles. Flame speed

57 enhancement of another monopropellant nitrocellulose by graphene microstructures was also

58 observed in Jain et al.'s [30] experiments. EL-Seesy et al. [31] investigated the impact of adding

59 graphene oxide (GO) nanoparticles to Jatropha Methyl Ester (JME) in a compression ignition (CI)

60 engine and reported that the JME-GO increased the brake thermal efficiency, peak cylinder pressure,

61 highest rate of pressure rise, and peak heat release rate while reducing the duration of combustion

62 and exhaust emissions of CO, UHC and NO_x. Similarly, Paramashivaiah et al. [32] examined the

63 effects of graphene nanoparticles addition to a diesel and biodiesel blend in a CI engine and observed

64 similar effects on engine performance and emission.

65   There has also been increasing interest in using graphene-based materials as additives for jet

66 fuels. Huang and Li [33] explored the ignition and combustion characteristics of jet fuel liquid film

67 containing graphene powers and indicated that the mixture could be ignited with a shorter delay time

68 and that the ignition of graphene occurs prior to that of the jet fuel. Ghamari and Ratner [34] tested

69 the combustion characteristics of colloidal droplets of Jet-A fuel and various carbon-based

70 nanoparticles. Graphene nanoplatelets were found to have an outstanding performance by yielding

71 more than a 7% increase in burning rate at only a 0.1% particle loading. Li et al. [35] recently

reported that the application of GO nanosheets on Jet A-1 fuel improved its combustion performance

in air in terms of acceleration of initial linear burning velocity, reduction in ignition delay and

decrease in strength and speed of initial transmitted wave. Compared with those jet fuels consisting

of extremely complex hydrocarbon mixtures, it is certainly of great interest to study the FGS as a

promising catalyst for enhancing the reactions of the single-component hydrocarbon fuel JP-10

where ignition and combustion kinetics are crucial.

To sum up, graphene-based materials are effective catalysts for enhancing fuel and propellant

combustion but the understanding of the underlying mechanisms is very limited. Following Sabourin

et al.'s [29] pioneering work, Liu et al. [36] studied the enhanced thermal decomposition of

nitromethane on FGS by ab initio molecular dynamics (MD) simulations and demonstrated that the

catalytic activity originates from the lattice defect complex within the graphene sheet. A reactive

force field (ReaxFF) MD simulation research on self-enhanced catalytic activity of FGS in the

combustion of nitromethane was completed by Zhang et al. [37]. However, no computational

research has been conducted to investigate the potential enhancement by FGS of the reactions of

complex hydrocarbons like JP-10 comprising a tricyclic structure. The study of JP-10 as a single-

component hydrocarbon fuel is much easier relative to other jet fuels that consist of many hundreds

of dissimilar hydrocarbons. In this study, ReaxFF MD simulations are performed to investigate the

initiation mechanisms of enhanced pyrolysis and oxidation of JP-10 on FGS and ReaxFF-nudged

elastic band (NEB) calculations are conducted to study the transition state and energy barrier for key

initiation reactions. Finally, the catalytic effects of FGS on JP-10 pyrolysis and oxidation are

revealed.

2. Methodology

2.1. Reactive force field (ReaxFF) molecular dynamics (MD) simulation

The ReaxFF MD is a powerful method for modelling dissociation, transition and formation of

chemical bonds within a reactive system. In contrast to quantum mechanics (QM)-based methods,

97   ReaxFF features the long-time large-scale reactive MD simulations, which are impractical or

98   impossible to achieve with QM methods. It is computationally much cheaper than QM methods

99   while maintaining a high level of accuracy. The concept of bond order is the kernel of ReaxFF and

100   the force field parameters are obtained from QM calculations or/and experimental data. Bond orders

101   are calculated directly from interatomic distances (Eq. (1)) and continually updated at every iteration

102   thereby allowing for connectivity changes [38].

103
$$\mathrm{BO}_{ij} = \mathrm{BO}_{ij}^{\sigma} + \mathrm{BO}_{ij}^{\pi} + \mathrm{BO}_{ij}^{\pi\pi}$$
$$= \exp\left[p_{\mathrm{bo1}} \left(r_{ij} / r_o^{\sigma} \right)^{p_{\mathrm{bo2}}} \right] + \exp\left[p_{\mathrm{bo3}} \left(r_{ij} / r_o^{\pi} \right)^{p_{\mathrm{bo4}}} \right] + \exp\left[p_{\mathrm{bo5}} \left(r_{ij} / r_o^{\pi\pi} \right)^{p_{\mathrm{bo6}}} \right]$$
(1)

104   where BO is the bond order between atoms i and j, r_{ij} is interatomic distance, r_o terms are

105   equilibrium bond lengths, and p_{bo} terms are empirical parameters. Equation (1) is continuous for

106   transitions between σ, π, and ππ bond character, producing a differentiable potential energy surface

107   as required for calculating the interatomic forces. Equation (2) describes the general energy

108   contributions to the ReaxFF potential as shown below [39]:

109   $E_{\mathrm{system}} = E_{\mathrm{bond}} + E_{\mathrm{over}} + E_{\mathrm{under}} + E_{\mathrm{lp}} + E_{\mathrm{val}} + E_{\mathrm{tor}} + E_{\mathrm{vdWaals}} + E_{\mathrm{Coulomb}}$ (2)

110   where E_{system}, E_{bond}, E_{over}, E_{under}, E_{lp}, E_{val}, E_{tor}, E_{vdWaals} and E_{Coulomb} represent total energy, bond

111   energy, overcoordination energy penalty, undercoordination stability, long pair energy, valence angle

112   energy, torsion angle energy, van der Waals energy, and Coulomb energy, respectively.

113   Further details of the ReaxFF formulation and development can be found in previous articles [38, 40-

114   42]. Additionally, ReaxFF MD has proven to be an effective method for studying

115   hydrocarbon/oxygenated hydrocarbon oxidation with [43-45] or without [39, 46, 47] catalysts.

116   All the ReaxFF MD simulations are performed using the REAXC package embedded in

117   LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software [48, 49], with the

118   latest C/H/O ReaxFF force field parameters [39]. In total, four (pyrolysis and oxidation of JP-10 and

119   their mixture with FGS) three-dimensional and cubic systems with different sizes are established at

120   the same density of 0.15 g/cm^3. Periodic boundary conditions are applied in all the three directions.

121   Each system contains 20 JP-10 molecules. For the two systems of JP-10 oxidation and its mixture

122   with FGS, 10 oxygen molecules are introduced to focus on the comparison of initiation mechanisms

123   rather than complete oxidation. The details of system construction as well as structure of JP-10 and

124   FGS are shown in Fig. 1. Specifically, the FGS used in this study, which is modified based on a

125   pristine graphene sheet, has 64 carbon, 12 oxygen and 30 hydrogen atoms, and it is placed in the

126   centre of the simulation box. There are 2 identical functional groups on the graphene sheet and each

127   functional group includes a divacancy decorated by 2 ethers with 4 additional OH groups attached to

128   the C atoms nearby [36]. The edge C atoms of the graphene sheet are adjusted with H atoms. To keep

129   the same density, the size of the cubic simulation boxes is accordingly changed for every system and

130   the volume of the FGS is evaluated by creating a Conolly surface with a radius of 1.0 Å. As a result,

131   the size of all the four systems (Fig. 1a, c, d and f) is 31.11 Å, 32.29 Å, 31.38 Å and 32.53 Å,

132   respectively.

(a) JP-10 pyrolysis   (b) JP-10 structure   (c) JP-10 oxidation

133   (d) JP-10 pyrolysis with FGS   (e) FGS structure   (f) JP-10 oxidation with FGS
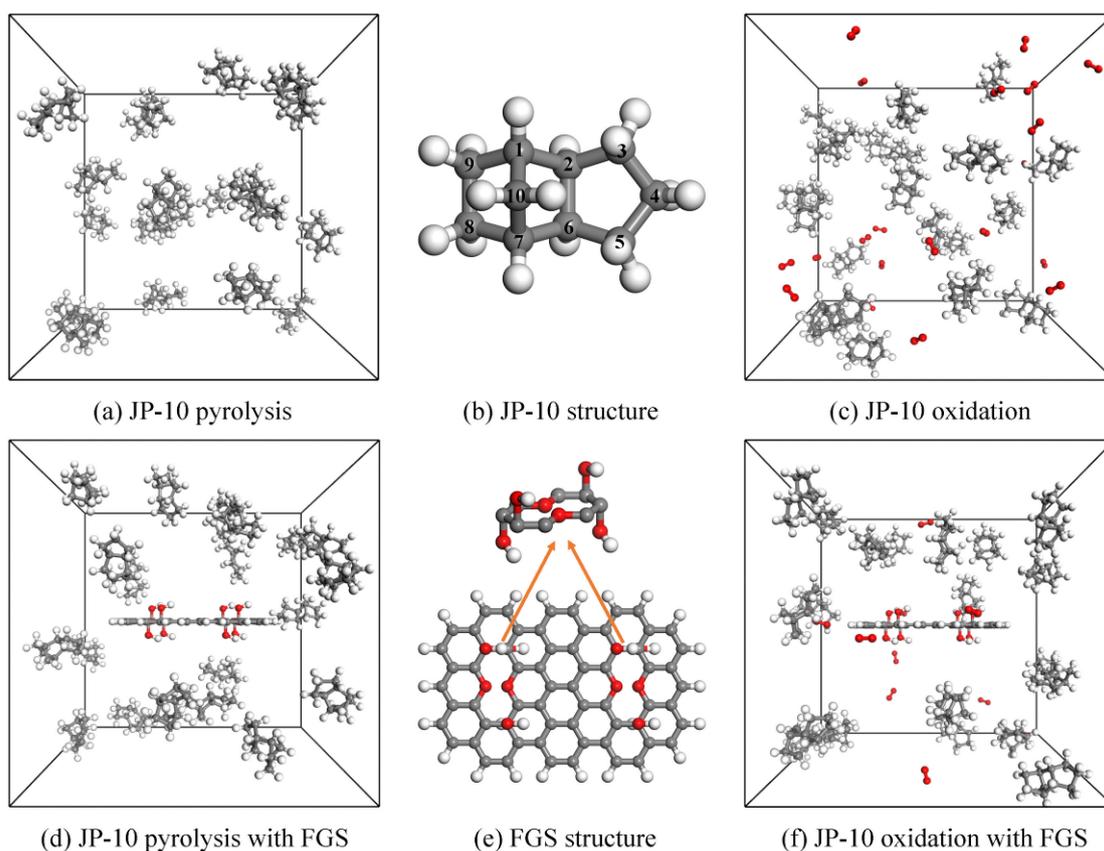
Fig. 1. System configurations for pyrolysis and oxidation of JP-10 and their mixture with FGS: (a) JP-10 pyrolysis, (b) JP-10 structure, (c) JP-10 oxidation, (d) JP-10 pyrolysis with FGS, (e) FGS structure and (f) JP-10 oxidation with FGS. C, H and O atoms are represented in grey, white and red, respectively.

The canonical ensemble (NVT) is employed for all the ReaxFF MD simulations and the system temperature is controlled by the Nosé-Hoover thermostat with a damping constant of 100 fs. The time step used in this study is 0.1 fs. To start with, energy minimization procedure by conjugate gradient algorithm is carried out for every system to eliminate the artificial effects on the initial geometric configuration. Then the system is equilibrated at the starting temperature 300 K for 50 ps. After the equilibrium, temperature is linearly raised to 2300 K during a time period of 1000 ps (heating rate: 2 K/ps), and finally kept constant at 2300 K for another 1000 ps (heating strategy shown in Fig. 3). Simulation results are outputted every 100 fs. A 0.2 bond order cutoff is adopted for species analysis to recognize the molecules/radicals forming during the simulation because a low cutoff value could benefit the capture of all the reactions including those with very short-lived species [40, 46]. All the visualizations of ReaxFF MD simulation results are produced using Visual Molecular Dynamics (VMD) software [50].

2.2. Nudged elastic band (NEB) calculation

Nudged elastic band (NEB) is a method for finding the transition state and calculating the energy barrier of a specific reaction between known reactants and products. A series of intermediate replicas are inserted and the spring force is applied between those replicas in order to find the minimum energy path. The NEB calculation is basically a simultaneous minimization procedure performed via damped dynamics. This method was developed by Henkelman and co-workers [51, 52], and has now been widely used in computational chemistry. All the NEB calculations are conducted by the NEB module in LAMMPS. The initial and final structures of all the studied

158 reactions are fully relaxed. Two or three intermediate replicas are generated depending on the

159 complexity of each reaction. The spring constant for connecting each replica is 1 kcal/(mol·Å).

3. Results and discussions

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

162   The time evolution of the number of JP-10 molecules for all the four systems is shown in Fig. 2.

163 Both pyrolysis and oxidation of JP-10 are enhanced in the presence of FGS, resulting in the earlier

164 decomposition of JP-10 at a lower temperature. Also, the average reaction rate of JP-10 is faster with

165 the addition of FGS in both cases. The enhancement is further confirmed by the change in relative

166 potential energy between JP-10 pyrolysis/oxidation with FGS and JP-10 pyrolysis/oxidation as

167 shown in Fig. 3. These two lines have a similar trend, which increases to a peak firstly and then

168 keeps decreasing. The increase in the difference of relative potential energy means that the heat

169 absorption is accelerated in the systems with FGS. After about 1000 ps, the potential energy of the

170 systems with FGS reaches their peak values and starts to drop down proceeding to the heat release

171 stage but the potential energy of the systems without FGS is still climbing. As a result, the change in

172 relative potential energy subsequently decreases. This also suggests that the reaction of both

173 pyrolysis and oxidation are advanced and enhanced in the presence of FGS. In order to gain deeper

174 insight into the enhancement, the detailed initial decomposition pathway of every single JP-10

175 molecule is tracked by analysing the evolution of species together with the visualization of

176 trajectories. The results are summarized in Tables 1 and 2.

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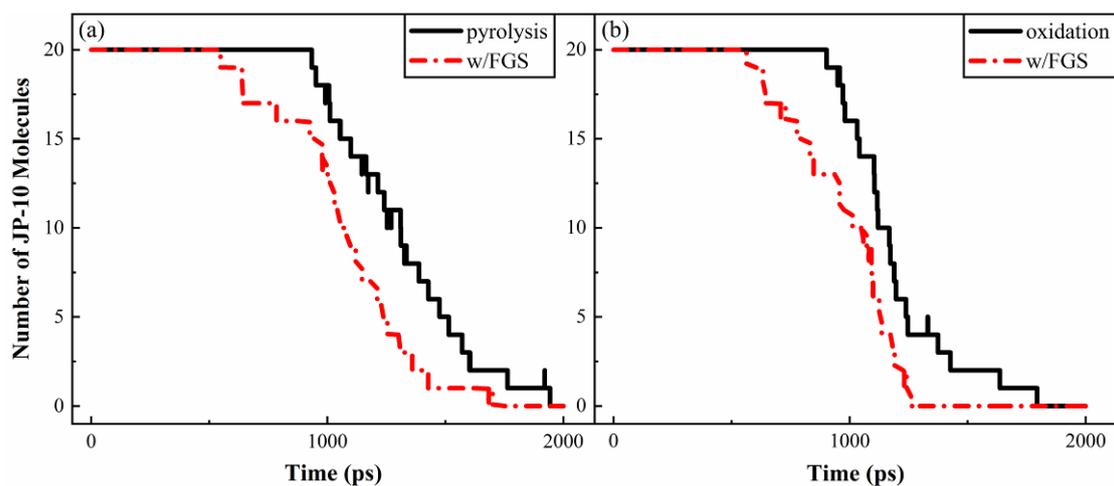
Fig. 2. Time evolution of JP-10 molecule number during NVT MD simulations of: (a) JP-10

pyrolysis and its mixture with FGS and (b) JP-10 oxidation and its mixture with FGS.

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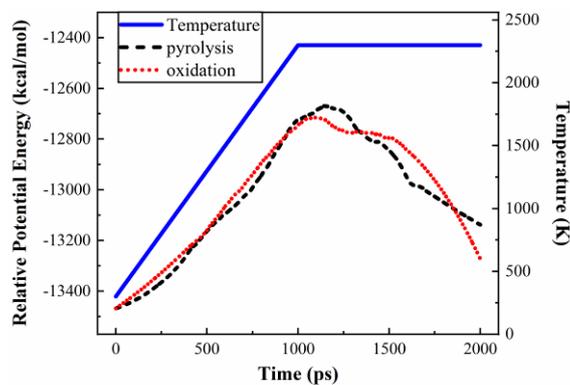
Fig. 3. Heating strategy and time evolution of relative potential energy between JP-10

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.

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Table 1. Detailed initial decomposition pathways of every single JP-10 molecule in the systems of: (a) JP-10 pyrolysis and (b) JP-10 pyrolysis with FGS.
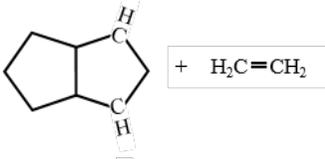
No.	(a) Decomposition Reaction	Time (ps)	No.	(a) Decomposition Reaction	Time (ps)
1	+ $H_2C{=}CH_2$	934.3	11		1311.9
2	+ $H_2C{=}CH_2$	951.9	12		1335.3
3	+ H_2C CH_2	1007.3	13		1388.7
4	+ H_2C CH_2	1011.1	14		1428.1
5	+ $H_2C{=}CH_2$	1056	15		1475.7
6	+ $H_2C{=}CH_2$	1099.8	16		1515
7	+ H_2C CH_2	1164.9	17		1570.9
8	+ $HC{=}CH_2$	1214.7	18		1604.9
9	+ H_2C CH_2	1241.8	19		1763.8
10	+ $H_2C{=}C{=}CH_2$	1310.4	20		1943.5
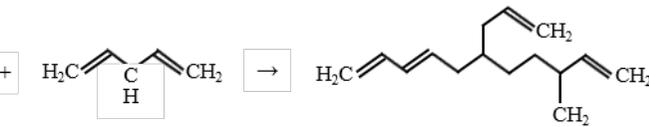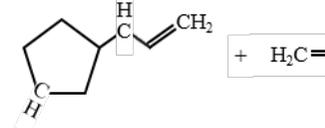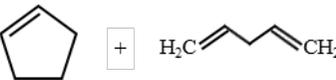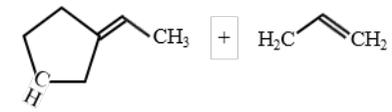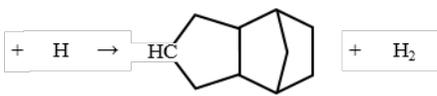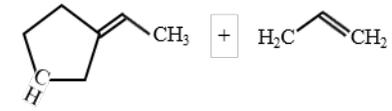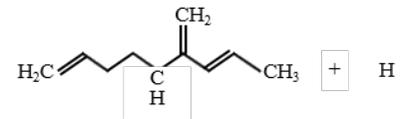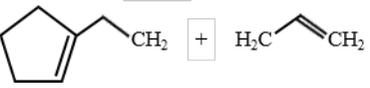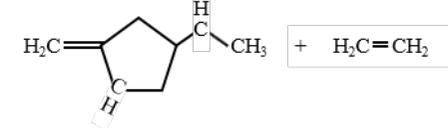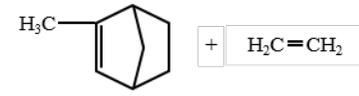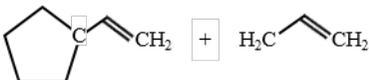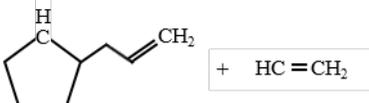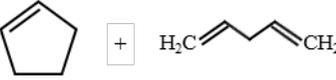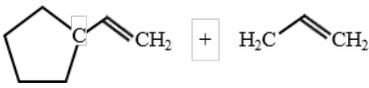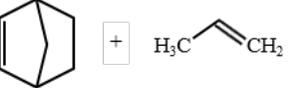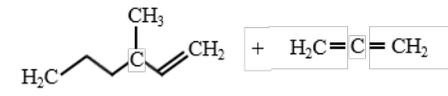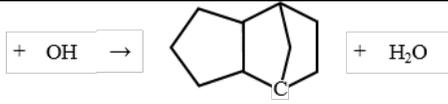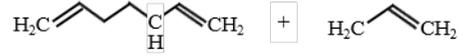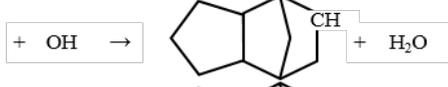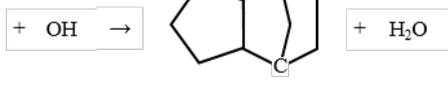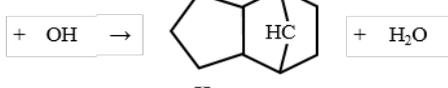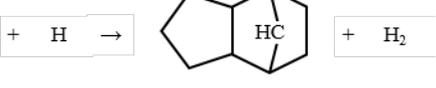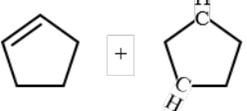
No.	(b) Decomposition Reaction	Time (ps)	No.	(b) Decomposition Reaction	Time (ps)
1	+ OH → [structure] + H$_2$O	547.7	11	H$_2$C⎓⎓CH⎓⎓CH$_2$ + H$_2$C⎓CH$_2$	1081.9
2	+ OH → [structure] CH + H$_2$O	638.6	12	HC [structure] + H	1120.5
3	+ OH → [structure] + H$_2$O	642.4	13	[structure] + [structure]	1147
4	+ OH → [structure] HC + H$_2$O	785.5	14	+ H → [structure] HC + H$_2$	1211.3
5	[structure] + [structure]	925.5	15	[structure] + H$_3$C⎓⎓CH$_2$	1229
6	[structure] + H$_3$C⎓⎓CH$_2$	978.3	16	[structure] + H$_2$C=CH$_2$	1255
7	H$_3$C⎓CH⎓⎓CH$_2$ + H$_2$C⎓⎓CH$_2$	996.5	17	CH$_2$ H$_2$C⎓CH$_2$ + H$_3$C⎓CH⎓⎓CH$_2$	1307.7
8	CH$_2$ H$_3$C⎓CH$_2$ + H$_2$C⎓⎓CH$_2$	1011.3	18	[structure] + H	1359.5
9	[structure] + [structure]	1030.5	19	H$_2$C⎓CH⎓CH$_2$ + H$_3$C⎓⎓CH$_2$	1427.3
10	CH$_3$ H$_3$C⎓C⎓⎓CH$_2$ + H$_2$C⎓⎓CH$_2$	1052.9	20	H$_2$C⎓⎓CH$_2$ + H$_2$C⎓CH$_2$	1700.8

Table 2. Detailed initial decomposition pathways of every single JP-10 molecule in the systems of: (a) JP-10 oxidation and (b) JP-10 oxidation with FGS.

No.	(a) Decomposition Reaction	Time (ps)	No.	(a) Decomposition Reaction	Time (ps)
1		902.4	11		1168
2		958	12		1173.5
3		971.8	13		1189.2
4		980.5	14		1196.3
5		1032.2	15		1239.1
6		1041.6	16		1246.7
7		1104	17		1375.1
8		1105.2	18		1427.1
9		1117.2	19		1636.9
10		1120.6	20		1794.6

No.	(b) Decomposition Reaction	Time (ps)	No.	(b) Decomposition Reaction	Time (ps)
1	+ OH → (HOCH$_2$, H$_2$C– structure)	563.2	11	(structure) + H$_3$C–CH=CH$_2$	1072
2	+ OH → (CH structure) + H$_2$O	633.5	12	(structure) + H$_3$C—CH$_2$	1092.7
3	+ OH → (HOCH$_2$ H C structure)	643.5	13	H$_3$C–CH=C(H)–...=CH$_2$ + H	1093.6
4	+ OH → (structure) + H$_2$O	729	14	(structure) + H$_2$C=CH–...=CH$_2$	1099.3
5	+ O$_2$ → HC (structure) + HO$_2$	777.2	15	(structure) + (structure)	1125.3
6	H$_2$C=...CH$_2$ structure + H$_2$C=CH$_2$	832.2	16	+ H → (structure) + H$_2$	1136
7	+ HO$_2$ → (structure) + H$_2$O$_2$	848.2	17	(structure) + H$_3$C–CH=CH$_2$	1181.8
8	(H, CH$_3$ structure) + H$_3$C–CH=CH$_2$	957.4	18	(H, C structure) + H$_2$	1190.1
9	(H structure) + H$_2$C=CH$_2$	957.6	19	H$_3$C–CH=C(H)–CH$_2$ + H$_2$C=...=CH$_2$	1241.3
10	(structure) + H	1012.1	20	(structure)–CH=CH$_2$ + H$_2$C=CH–CH$_2$	1260.6

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 [46, 53]. Especially, Chenoweth et al. [46] carried out a comprehensive comparison of the JP-10 decomposition products between various experimental [1, 7-9, 54, 55] 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 C_2H_6 and $C_{10}H_8$ (napthalene) are not observed in the present research. Both Chenoweth et al.'s [46] and this study capture some decomposition products like C_3H_5 (allyl radical) and C_5H_8 (1,4-pentadiene), which were not found in those experiments, but were obtained in several recent experimental studies [6, 12, 14]. In addition to the comparison with experimental results, Chenoweth et al. [46] 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 for JP-10 as in experiments [39]. Detailed uncertainty analysis including comprehensive and extensive comparison between QM/experimental and ReaxFF data included in the ReaxFF training set, and validation of the quality of the present ReaxFF force field for studying the JP-10 chemistry are provided in Ref. [39]. 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.

3.1.2. Effects of FGS addition on JP-10 pyrolysis

The initial step of decomposition for every single JP-10 molecule in the systems of JP-10 pyrolysis and its mixture with FGS is presented in Table 1 and the corresponding time of occurrence is given. The JP-10 pyrolysis has been well studied by both experiment [12-14] and numerical modelling [17, 19, 20, 46] 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 [39] results, for normal pyrolysis, the JP-10 molecules mainly decompose into various smaller hydrocarbons by some dominant

209 pathways (i.e. C_8 & C_2, C_5 & C_5, C_7 & C_3 or $C_{10}H_{15}$ & H), whereas with FGS, the decomposition of

210 the first 4 JP-10 molecules begins with the dehydrogenation by the OH group on FGS forming H_2O

211 and the initiation of these 4 JP-10 molecules all occurs earlier than the first JP-10 decomposition

212 without FGS. After the initial dehydrogenation, it is also found that the secondary decomposition

213 into smaller hydrocarbons of these 4 $C_{10}H_{15}$ radicals happens at 883.8 ps, 893.4 ps, 959.6 ps and 995

214 ps, respectively, which is more efficient than those JP-10 molecules in normal pyrolysis reactions.

215 Additionally, the dehydrogenation of JP-10 without FGS (R13, R14 and R17 in Table 1a) is only

216 observed at a high temperature (2300 K), which also agrees well with the previous results [39].

217 There are in total 8 OH functional groups on the FGS. The results show that 6 of them are

218 consumed and the remaining 2 are retained at the end of the simulation. Hence, further to the first 4

219 OH groups, the complete reactions of the 5th and 6th OH group during the whole simulation time are

220 analysed as well and they are summarized in Table 3. As can be seen, the two series of reactions both

221 start from the separation of OH from the FGS. Then the OH quickly reacts with a hydrocarbon

222 radical forming an oxygenated hydrocarbon. Subsequently, the oxygenated hydrocarbon either reacts

223 with another hydrocarbon or directly decomposes to produce a smaller oxygenated hydrocarbon.

224 Next, this smaller oxygenated hydrocarbon goes through various reactions or decompositions

225 generating H_2O or CO eventually. It can be expected that the last 2 OH groups could also take part in

226 similar intermediate reactions to enhance the pyrolysis reaction, provided that the simulation time is

227 long enough.

228 **Table 3.** Complete reactions of the 5th and 6th OH group during the whole simulation time of JP-10

229 pyrolysis with FGS.

Sequence	Time (ps)	Reaction
		No. 5 OH
1	1631.5	OH leaves the FGS
2	1637.9	$OH + C_5H_5 \rightarrow C_5H_6O$
3	1771	$C_5H_6O + C_7H_{12} \rightarrow C_{10}H_{15} + C_2H_3O$
4	1916.1	$C_2H_3O \rightarrow C_2H_2 + OH$

5	1917.7	$OH + C_5H_8 \rightarrow C_5H_7 + H_2O$
		No. 6 OH
1	1947.3	OH leaves the FGS
2	1947.8	$OH + C_6H_{10} \rightarrow C_6H_{11}O$
3	1954.7	$C_6H_{11}O \rightarrow C_4H_7 + C_2H_4O$
4	1967.7	$H + C_2H_4O \rightarrow H_2 + C_2H_3O$
5	1976.2	$C_2H_3O \rightarrow C_2H_3 + CO$

230

231   Combing the above two paragraphs, the catalytic reaction steps for JP-10 pyrolysis on FGS can

232   be summarized as follow (Fig. 4): (1) OHs leave the FGS; (2) OHs initiate the pyrolysis reaction by

233   reacting with JP-10 forming $C_{10}H_{15}$ and H_2O; (3) more OHs leave the FGS; (4) OHs take part in

234   various intermediate reactions involving oxygenated hydrocarbons. It is indicated that the OH

235   functional groups on the FGS can not only advance the initiation of JP-10 pyrolysis, but also

236   participate in various intermediate reactions to further enhance the pyrolysis reaction.
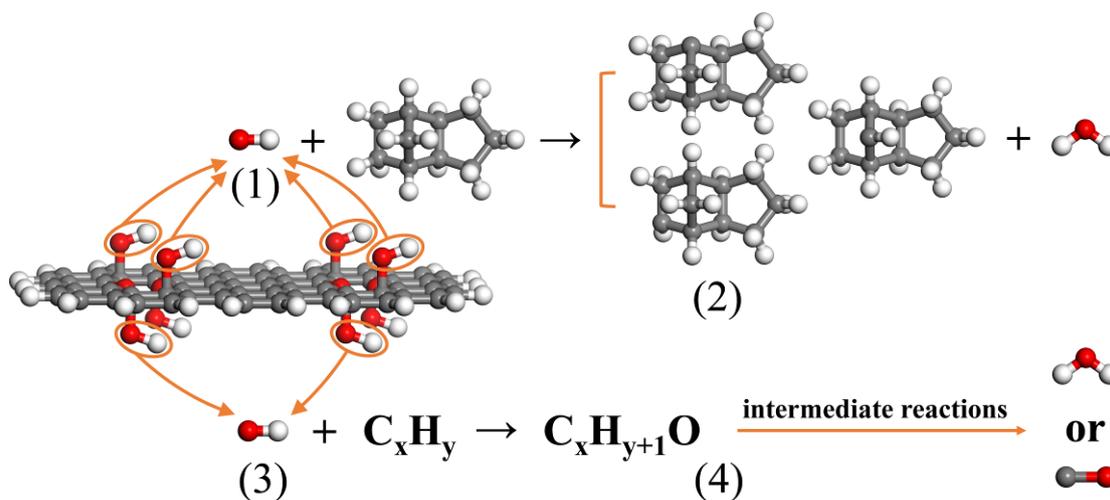
237

238   **Fig. 4.** Catalytic reaction steps for JP-10 pyrolysis on FGS: (1) OHs leave the FGS; (2) OHs initiate

239   the pyrolysis reaction by reacting with JP-10 forming $C_{10}H_{15}$ and H_2O; (3) more OHs leave the FGS;

240   (4) OHs take part in various intermediate reactions involving oxygenated hydrocarbons.

241   *3.1.3. Effects of FGS addition on JP-10 oxidation*

242   Table 2 presents the initial decomposition step for every single JP-10 molecule and its

243   corresponding time of occurrence in the systems of JP-10 oxidation and its mixture with FGS. The

244   analysis of effects of FGS addition rather than the simple JP-10 oxidation is emphasized in this

245   section. The results show that the initiation of normal JP-10 oxidation includes two main stages, i.e.

246   (1) decomposition of JP-10 and (2) reaction of JP-10 and other decomposed products with radicals

247   like O_2, O, H, OH, HO_2 and H_2O_2, which is in accordance with previous experimental [6] and

248   computational [5, 53] results. In contrast to JP-10 pyrolysis with FGS, the pathways are different

249   although the decomposition of the first 4 JP-10 molecules in the system of JP-10 oxidation with FGS

250   is still initiated by the reaction with OH. A new pathway is found, which involves the C-C bond

251   cleavage followed by OH attachment to one of those two C atoms (R1 and R3 in Table 2b). The

252   complete reactions that these two $C_{10}H_{16}OH$ molecules undergo during the simulation time are listed

253   in Table 4. They both firstly decompose into a smaller oxygenated hydrocarbon and then this

254   oxygenated hydrocarbon goes through a series of reactions to finally form CO and H_2O, respectively.

255   It is worth noting that a short exchange between intermediate products and FGS (R3 and R4 in Table

256   4 – No. 2 $C_{10}H_{16}OH$) is observed in the reactions of the second $C_{10}H_{16}OH$ molecule. The same as JP-

257   10 pyrolysis reactions, the initiation of the first 4 JP-10 molecules in the system of JP-10 oxidation

258   with FGS all proceed earlier than the first JP-10 decomposition without FGS and the

259   dehydrogenation of JP-10 without FGS (R12, R13, R15, R16 and R17 in Table 2a) only takes place

260   at a high temperature (2300 K).

261   **Table 4.** Complete reactions of two $C_{10}H_{16}OH$ molecules during the whole simulation time of JP-10

262   oxidation with FGS. The subscript of FGS represents the different forms of FGS containing different

263   numbers of C, H and/or O atoms.

No. 1 $C_{10}H_{16}OH$ (1st JP-10 molecule)		
Sequence	Time (ps)	Reaction
1	674.2	$C_{10}H_{17}O \rightarrow C_2H_5O + C_8H_{12}$
2	961	$OH + C_2H_5O \rightarrow C_2H_6O_2$
3	1196.2	$C_2H_6O_2 \rightarrow CH_3 + CH_3O_2$
4	1328.2	$H + CH_3O_2 \rightarrow H_2 + CH_2O_2$
5	1594.9	$H + CH_2O_2 \rightarrow CH_3O_2$
6	1595.2	$CH_3O_2 \rightarrow H_2O + CHO$

7	1597.7	$C_2H_3 + CHO \rightarrow C_3H_4O$
8	1598.4	$C_3H_4O \rightarrow H + C_3H_3O$
9	1616.2	$C_3H_3O \rightarrow C_2H_3 + CO$

No. 2 $C_{10}H_{16}OH$ (3rd JP-10 molecule)

Sequence	Time (ps)	Reaction
1	1063.3	$C_{10}H_{17}O \rightarrow C_9H_{14}O + CH_3$
2	1117.2	$C_9H_{14}O \rightarrow C_6H_{10}O + C_3H_4$
3	1123.1	$C_6H_{10}O + FGS_1 \rightarrow FGS_2$
4	1124.7	$FGS_2 + C_{10}H_{14} \rightarrow FGS_1 + C_6H_{10}O + C_2H_4 + C_8H_{10}$
5	1353	$H + C_6H_{10}O \rightarrow C_6H_{11}O$
6	1353.1	$C_6H_{11}O \rightarrow C_6H_9 + H_2O$

264   With respect to the 8 OH functional groups on the FGS, 6 of them are consumed, leaving 1 OH

265   group and 1 attached O (lose the H) at the end of the simulation. The complete reactions of the 5th,

266   6th and 7th OH groups during the simulation time are shown in Table 5. Unlike those OHs in

267   pyrolysis reactions which react with hydrocarbon intermediates, the 5th and 6th OH groups are

268   attracted by an H radical directly generating H_2O and H_2, respectively, while the H is found to detach

269   from the 7th OH and then dehydrogenize a hydrocarbon producing H_2. This difference results from

270   the introduction of O_2 generating more OHs from HO_2 and H_2O_2 as well as some oxygenated

271   hydrocarbons which both react with hydrocarbon radicals. Besides, the O_2 itself can also compete

272   with OH's reaction with hydrocarbons. Due to these reasons, O-H bond cleavage of the OH group on

273   the FGS is only observed in the oxidation reactions. In addition, the H of OH can transfer between

274   different O atoms on the FGS. For example, at 1228.4 ps, an H of OH moves to a nearby O of ether

275   and transfers back to the original O of that OH later at 1512.6 ps. Similarly, in the two reactions of

276   No. 6 OH in Table 5, after losing the H, the O of OH shifts to another edge C atom of FGS and

277   finally leaves the FGS as CO. The remaining one OH group and one attached O could also be

278   involved in the intermediate reactions to further accelerate the JP-10 oxidation if the simulation is

279   continued.

**Table 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.

| Sequence	Time (ps)	Reaction
No. 5 OH		
1	1018.7	$H + FGS_1 \rightarrow FGS_2$
2	1018.8	$FGS_2 \rightarrow FGS_3 + H_2O$
No. 6 OH		
1	1030.5	$H + FGS_3 \rightarrow FGS_4 + H_2$
2	1986.6	CO leaves the FGS
No. 7 OH		
1	1755.3	$FGS_5 \rightarrow FGS_6 + H$
2	1759	$H + C_8H_{10} \rightarrow C_8H_9 + H_2$

To summarize, the catalytic reaction steps for JP-10 oxidation on FGS follow the procedure (Fig. 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 H_2O and H_2. 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.
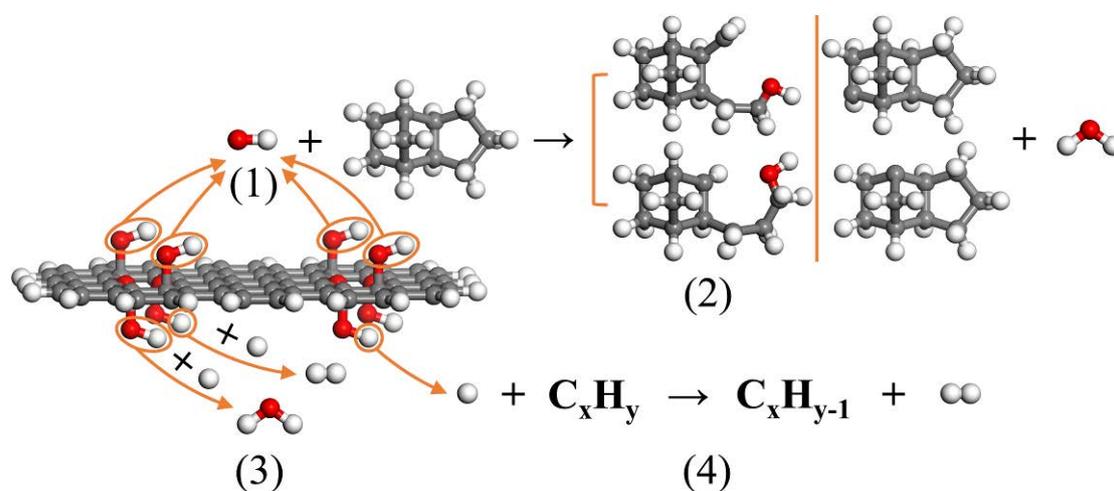

Fig. 5. Catalytic reaction steps for JP-10 oxidation on FGS: (1) OHs leave the FGS; (2) OHs initiate the oxidation reaction by reacting with JP-10 via different pathways; (3) OH or H of OH is abstracted

from or leaves the FGS; (4) OH or H take part in intermediate reactions involving the direct

formation of H_2O and H_2.

3.2. Transition state and energy barrier for key initiation reactions
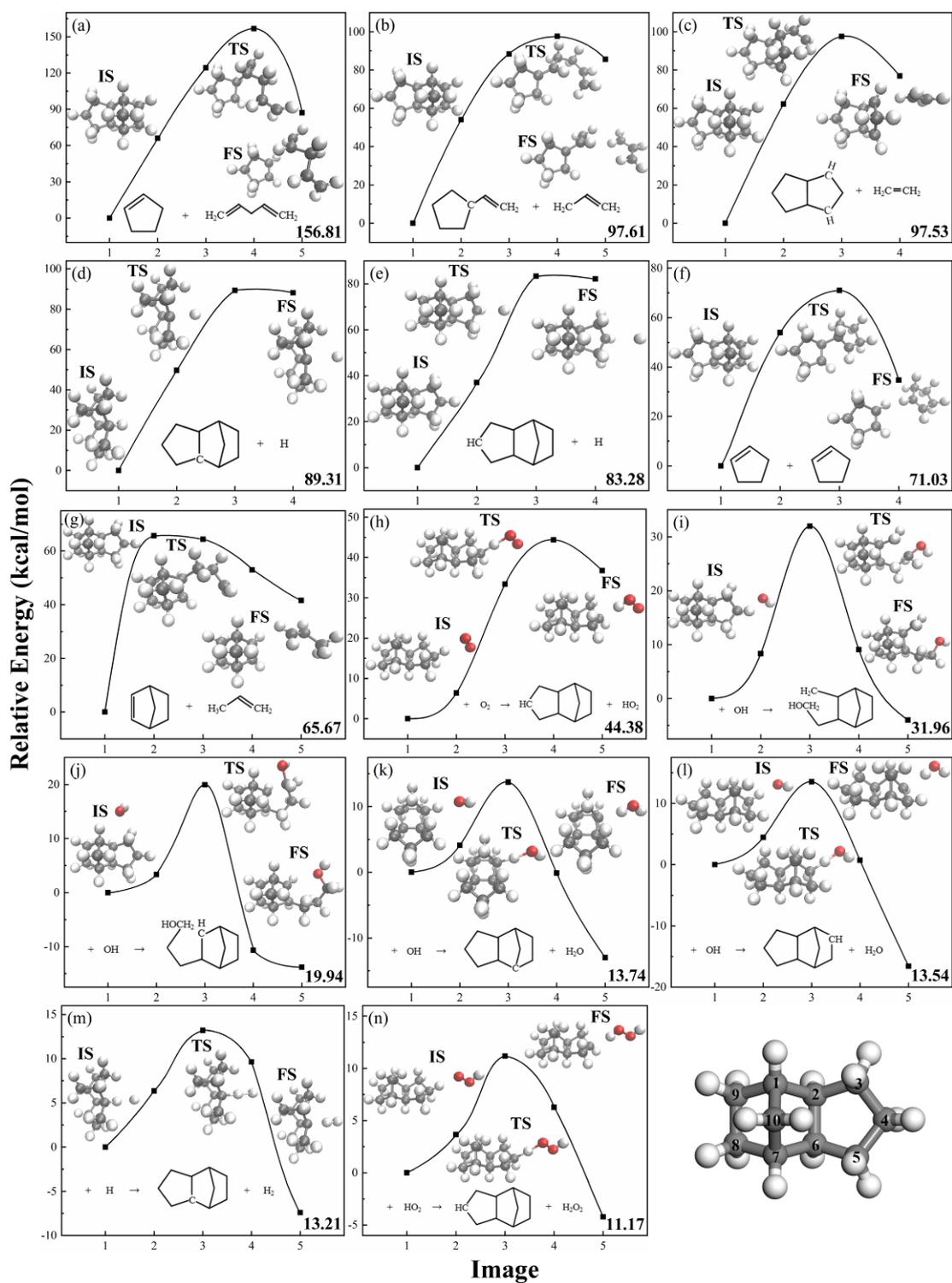
Fig. 6. Transition state and energy barrier for some frequently occurring and key JP-10

decomposition reactions from ReaxFF-NEB simulations. Figs. 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.

Fig. 6 depicts the transition state and energy barrier for some frequently occurring and key JP-10 decomposition reactions extracted from Tables 1 & 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 (Fig. 6a) has the highest energy barrier of 156.81 kcal/mol. This decomposition procedure follows the sequential cleavage of C-C bonds: C_8-$C_9 \rightarrow C_1$-$C_2 \rightarrow C_6$-C_7, which is the same as Chenoweth et al.'s results [46]. The sequence of C-C bond dissociation for the reaction producing allyl in Fig. 6b is C_1-$C_2 \rightarrow C_7$-$C_{10} \rightarrow C_8$-C_9 and the H attached to C_6 shifts to C_2 before the cleavage of C_7-C_{10} bond. These reaction steps are also found in DFT calculations [20]. Fig. 6c demonstrates the formation of ethylene resulting from the successive breaking of C-C bonds between C_1 & C_9 and C_7 and C_8. The C_2-C_6 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 [18] and ReaxFF MD [46] simulation results. These two reactions in Figs. 6b & c have very close energy barrier values. Figs. 6d & e illustrate the two scenarios of dehydrogenation of JP-10 at C_2 and C_4, respectively. Zhao et al. [14] computed the energy of C-H bond cleavage for every C position of JP-10 by DFT and found that the dehydrogenation at C_2, C_3, C_4 and C_9 are more preferable with the energy ranging from 92.73–97.04 kcal/mol. Three (C_2, C_3 and C_4) of these four dehydrogenations are observed in the present study and the calculated energy barrier for dehydrogenation at C_2 (89.31 kcal/mol) and C_4 (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 [6, 7, 12, 14, 17]. The C_1-C_2 bond is broken first followed by further fragmentation via C_6-C_7 separation. In this study (Fig. 6f), before the C_6 is separated from C_7, one H attached to C_{10} moves to C_1 producing two cyclopentenes eventually. Fig. 6g describes the formation

324 of 2-norbornene and propene from consecutive C_5-C_6 and C_2-C_3 bond scissions [6, 7, 17, 19], which

325 also involves the H transfer from C_4 to C_5 prior to the cleavage of C_2-C_3 bond.

326 Other species, i.e. O_2, OH, H and HO_2 are introduced in the JP-10 initiation reactions in Figs.

327 6h–n and the energy barriers of these reactions are all lower than the above unimolecular JP-10

328 decompositions as expected. Except for the two reactions in Figs. 6i & j, the remaining five all relate

329 to the dehydrogenation of JP-10 at various C positions. It can be seen that the dehydrogenation of JP-

330 10 by O_2 has the highest energy barrier of 44.38 kcal/mol among these reactions, followed by the

331 formation of two $C_{10}H_{16}OHs$ with OH attaching to C_4 and C_3, respectively. The OH is more likely to

332 attach to C_3 compared to C_4 because the energy barrier is much lower. Figs. 6k & l show the

333 dehydrogenation of JP-10 by the OH functional group on FGS at C_1 and C_8 producing H_2O and the

334 energy barriers for these two reactions are almost the same. It is indicated that JP-10 decomposition

335 initiated by OH is easier than by O_2. The H_2 formation via dehydrogenation of JP-10 by the H radical

336 in Fig. 6m has a similar energy barrier as those decompositions initiated by OH. As presented in

337 Table 5, the FGS can release the H of OH to participate in intermediate reactions, which could also

338 be helpful for JP-10 initiation. It can be expected to see the JP-10 reaction with H of OH on FGS if

339 the size of FGS is increased with more OH functional groups. The energy barrier of the

340 dehydrogenation of JP-10 by HO_2 generating H_2O_2 is slightly lower than those reactions in Figs. 6k–

341 m. However, it needs HO_2 as a precursor and the formation of HO_2 is not that straightforward and

342 easy as the release of OH or H from FGS. Based on the above analysis, it can be concluded that the

343 energy barrier for JP-10 decomposition reactions initiated by the OH or potential H of OH on FGS is

344 much lower that the unimolecular decomposition of JP-10 by the C-C or C-H bond scission. This

345 considerable reduction in the energy barrier makes the reactions of JP-10 with OH or H on FGS more

346 preferable than those cleavages of C-C or C-H bonds thereby changing and enhancing the JP-10

347 initiation.

348 **4. Conclusions**

The ReaxFF MD simulations are performed to investigate the initiation mechanisms of JP-10 pyrolysis and oxidation with FGS in comparison with normal JP-10 reactions. Moreover, the ReaxFF-NEB calculations are conducted to study the transition state and energy barrier for some key initiation reactions. The results show that both pyrolysis and oxidation of JP-10 are advanced and enhanced in the presence of FGS, leading to earlier decomposition of JP-10 at a lower temperature and a faster reaction rate. The detailed initiation reactions of pyrolysis and oxidation of JP-10 and their mixture with FGS are obtained to scrutinize the effect of FGS addition. Compared with pyrolysis of pure JP-10 mainly decomposing to various smaller hydrocarbons, the decomposition of JP-10 with FGS starts with the dehydrogenation by the OH functional groups on the FGS forming H_2O. Similarly, in the system of JP-10 oxidation with FGS, the decomposition of JP-10 is initiated by its reaction with OH. In addition to the H_2O formation, another pathway that involves the C-C bond cleavage followed by OH attachment to one of those two C atoms is observed. For both JP-10 pyrolysis and oxidation, as the reaction proceeds, more OH groups of FGS take part in various intermediate reactions involving oxygenated hydrocarbons or direct production of H_2O and H_2 as well. Moreover, the dehydrogenation of JP-10 without FGS only occurs at high temperatures. Therefore, it is the OH functional group on the FGS that not only advances the initiation of JP-10 but also participates in various intermediate reactions to further enhance the pyrolysis and oxidation of JP-10. A deeper insight into the enhancement resulting from the FGS is provided by the results of transition state and energy barrier for key initiation reactions. It is found that the JP-10 decomposition initiated by OH or H occurs at a lower energy barrier than unimolecular decomposition or through reaction with O_2. This makes the reactions of JP-10 with OH or H on the FGS preferable thereby changing and enhancing the JP-10 initiation. This research lays the scientific foundation for the potential use of FGS as a promising catalyst for JP-10 fuel systems.

377   **Declarations of interest:** none

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512