Reactive dynamics simulations of thermal decomposition of Methane to synthesize Graphene and Hydrogen gas

Sourav Das

Project Report for MSE581

Summary: There is a growing trend in graphene and CNTs synthesis research from hydrocarbon compounds. Methane is one of the easily available hydrocarbons in industry. In this report, the methane decomposition mechanism has been studied at high temperatures to synthesize graphene particles and Hydrogen gas. The Reactive Dynamics (RD) force field has been used in Lammps to simulate the methane decomposition and formation of Carbon and Hydrogen molecules on the nickel particle, which is at a lower temperature than methane. This report includes the methane molecule's decomposition rate, different intermediate compounds, and the effectiveness of this process for graphene and hydrogen synthesis. It has been discussed how this study will be helpful for future research on graphene synthesis.

1. Introduction

There is a great deal of interest in creating graphene structures from different material sources as opposed to the traditional top-down graphite-to-graphene synthesis. We are familiar with the recent trend of using graphene in different electronic sensors. There is an exponential increase in the study to produce graphene alongside hydrogen from different hydrocarbon compounds. Protocols such as pyrolysis reported transforming hydrocarbon substances such as polymer gaseous compounds into conducting carbon-based substances. One such hydrocarbon is Methane, which can be used as a raw material to produce fine graphene particles with the addition of heat. In this process, Methane is heated above 2300K in an inert atmosphere (in the

absence of oxygen), and when the hot methane gas comes in contact with a nickel rod which is at room temperature, graphene particles deposited on the nickel surface, and hydrogen is liberated as a valuable by-product. Experimentally, it was found that Nickel helps to break the C-H hydrogen bond and acts as a good catalyst in the reaction. The decomposition of the Methane, the movement of the activated hydrocarbon species to the growing graphene's edge, and the addition of the activated carbon species to the growing end are the three processes that the nickel particle catalyst catalyzes during graphene growth. [1] Depending on the growth conditions, these processes may be rate-limiting; nonetheless, experimental data indicates that Methane decomposition is the limiting step for low-temperature graphene growth. During this thermal conversion process, the compound goes through different steps during the transition from a sp3 - to sp2 -hybridized state. [2][3] This project aims to understand different aspects of the thermal decomposition of methane gas in the presence of Nickel as a catalyst.

2. Objective

The main objective of the project is to gain valuable and detailed insights into the thermal decomposition of methane (CH_4) at high temperatures (2500 °C) in the presence of low-temperature (500 °C) nickel metal. It will also explore how an increase in temperature helps the adsorption of carbon molecules on the Nickel surface. As a valuable by-product of this process, Hydrogen generation and its absorption on nickel surfaces can also be studied, hence, as it is known that CH4 decomposes through different steps. This will help to gain insight into the preferred decomposition pathways for methane species on nickel, to help guide the choice of optimum temperature of the feedstock species for controlling graphene growth. ReaxFF reactive force field potential has been used to explore how many different types of molecules formed

during the Methane decomposition process. This project will also help us to understand the limitations of molecular study.

3. Methodologies

A Cubic box has been created 75Å x 75Å x 75Å with 500 Methane molecules, and 360 Nickel molecules are created in Lammps. An orthogonal FCC Nickel crystal with dimensions 20Å x 10Å x 20Å and 360 Nickel has been created with a lattice constant of 3.52 Å. The simulations (energy minimization and reactive dynamics) shown here utilize the literature's ReaxFF reactive force field potential from earlier literature [2,6]. The total system energy in the ReaxFF force field depends on several partial energies: Coulombic interaction, van der Waals interaction, hydrogen bonding, lone pairs, undercoordination, over coordination, torsion angle, conjugation, and valence energy. [4,5,6]

The velocity Verlet integrator with a time step of 0.25 fs has been used in this temperature-programmed RD simulation because its simplified nature in calculating the particle position at the next time steps depends on acceleration and velocity at the current time steps. After 50 ps, the system temperature reached 2500 K. The temperature was originally set to 500 K and rose steadily at 20 K/ps for each time step, considering the nickel temperature fix at 500 K. A Berendsen thermostat with a damping constant of 100 fs for temperature regulation has been utilized. The Berendsen thermostat provides simulations' stability, and the degree of temperature control testifies to the parameters' suitability for handling these specific systems. Each simulation started with a Boltzmann distribution of particle velocities at 500 K. During the

simulation, the methane molecules break down into individual Carbon and hydrogen molecules and occasionally desorb (e.g., H_2) on the Nickel surface. We used a bond-order cutoff of 0.30 to evaluate the connection and examined the reactive dynamics trajectory to identify the molecular species at each step to get information about these reactive processes. Each chemical species population was tracked to understand how each catalytic system evolved.

We considered a higher elevated temperature (2500K) compared to the experimental condition to increase the probability of methane breakdown. Periodic Boundary condition with the real unit and charge atom style has been used. Ovito was used for the visualization of the system.

The decomposition of methane with temperature follows an Arrhenius dependency, as shown by an earlier study [2]. The rate of decomposition of Methane Molecule

$$\frac{dN}{dt} = -N_a R_a + N_s R_d,$$

Considering the desorption rate (Rd) from the particle surface is negligible, neglecting the second term. The probability of chemisorption on the particle surface increases with the increase in particle collision with the surface, which depends on average molecular velocity, which eventually depends on Temperature $(\sqrt{T})$. [2]

4. Result

The initial and final distribution of the molecule has been shown in the figure1 and 2, respectively. The nickel compound is represented as yellow molecules, blue is Carbon molecules, and red is hydrogen molecules. The random distribution of Methane molecules in the gaseous phase at 2500K temperature is shown in figure 2.
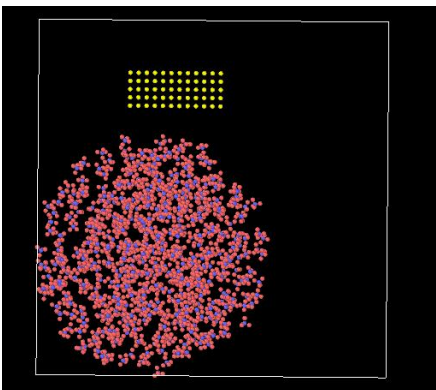
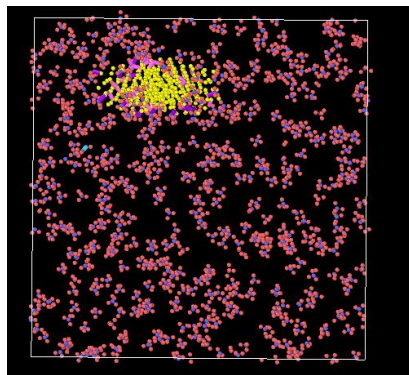Figure 1: Molecular Distribution at the initial state   Figure 2: Molecular Distribution after 100 ps

The temperature and the total energy profiles show initial fluctuation in Figures 3 and 4, respectively, during energy minimization steps due to the relaxation of configuration. Figure 5 shows the nickel-carbon bond around the Nickel particle, implying a high density of adsorbed hydrocarbon molecules around the nickel particle after 50 ps. This adsorbed hydrocarbon molecule signifies the large decomposition of CH_4 around nickel particles, which justified the decrease in the total no of methane molecules in the system, as shown in Figure 6.
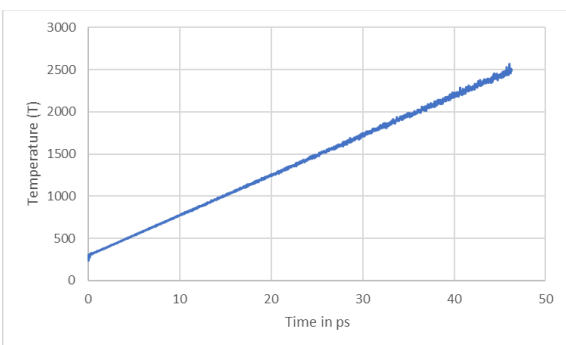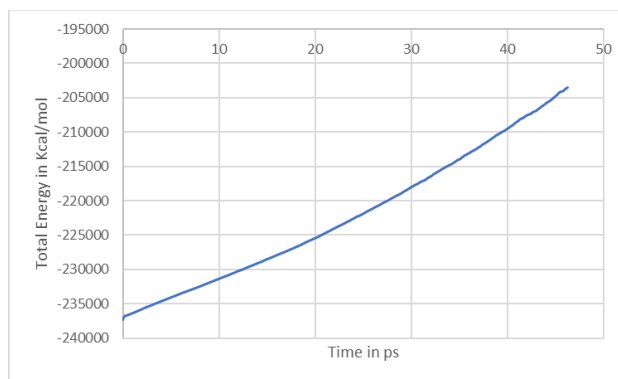

Figure 3: Temperature vs Time profile   Figure 4: Total energy vs Time profile
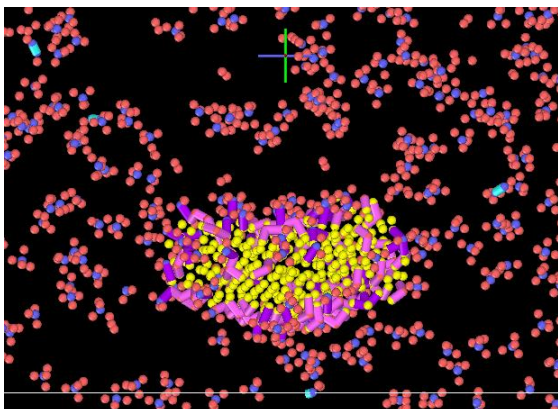
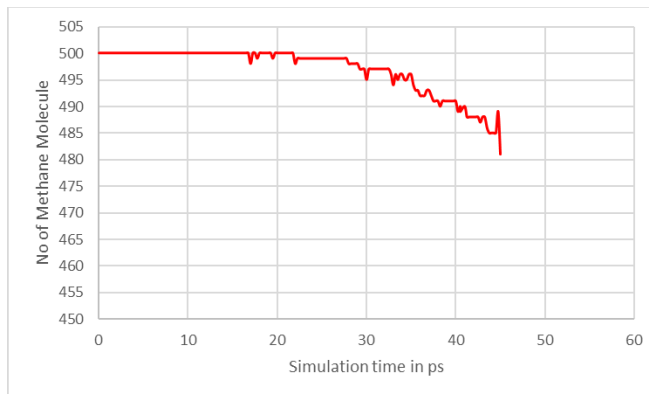Figure 5: Pink Colored Ni-C bond around Ni Particle
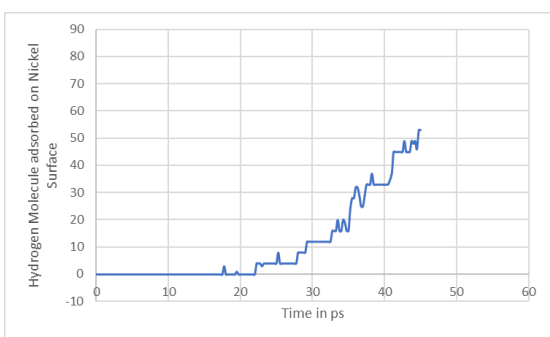

Figure 6: No of Methane Molecule with time

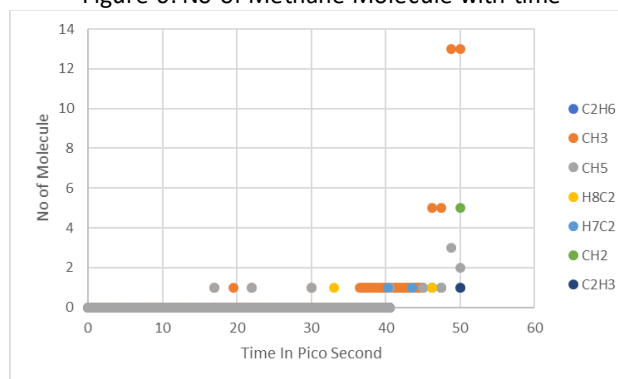Figure 7: Generation of Hydrogen Molecule with time

Figure 8: Population of intermediate Hydrogen Molecule during Methane Decomposition

Figure 7 and Figure 10 shows an increase in the total no of carbon and hydrogen molecule with time, which is justified by the increase in the decomposition of methane with temperature. Several intermediate compounds and by-products are formed during the Methane decomposition process, as shown in Figure 8. Figure 8 depicts the total population of different compounds and the intermediate with time.

With the increase in the temperature, the probability of methane molecules decreases within a cut-off radius due to decomposition, which is reflected in the decrease in peak height of radial distribution at the initial time and final time, as shown in Figures 11 and 12. The decrease in RDF of the Nickel-Nickel bond signifies the adsorption of other molecules on the nickel surface. Figure

9 clearly shows hydrocarbon adsorption around the nickel surface is the main reason for the smaller RDF in the case of nickel.
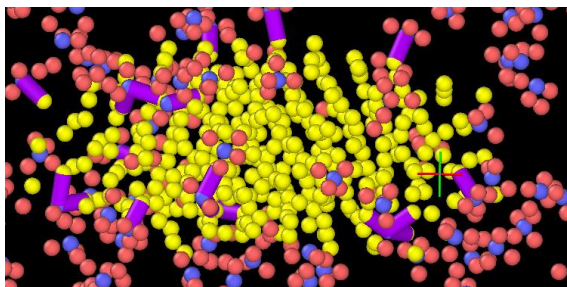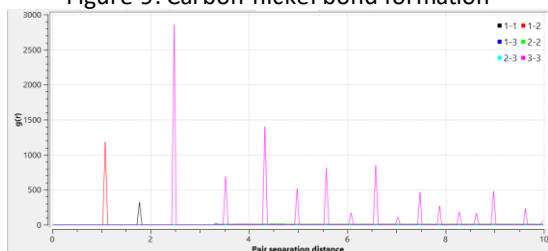

Figure 9: Carbon-nickel bond formation

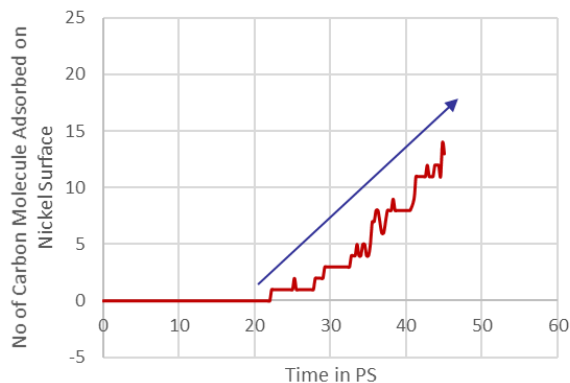
Figure 10: Generation of Carbon Molecule with time

Figure 11: Distribution of Radial distribution function at initial time
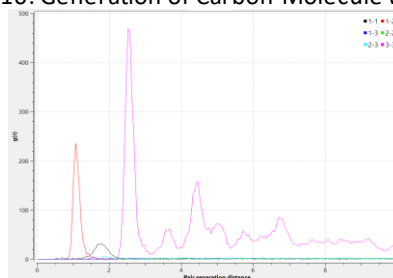
Figure 12: Distribution of Radial distribution function at final time

5. <u>Discussion</u>

Methane is one of the most used hydrocarbon molecules to study the bond energy of the carbon hydrogen bond. During the increase in heat, 1st CH_4 molecule started to fragment at T_A = 1347 K (21.875 ps) into CH_3 and H radicals. After this, CH_3 has been chemisorbed to the Ni surface and starts to break down as the rate of chemisorption increases with rising temperature. The reaction Mechanism of methane decomposition is described below.

$$CH_{4\ gas} \text{--> } CH_{3\ ad} \text{ --> } CH_{2\ ad} \text{ --> } CH_{ad} \text{ --> } C_{ad}$$

(1)

$$CH_4 \rightarrow CH_3 + H$$

(2)

$$CH_{3(ad)} \rightarrow CH_2 + H$$

(3)

$$CH_{2(ad)} \rightarrow CH_{ad} + H$$

(4)

$$CH_{(ad)} \rightarrow C + H$$

(5)

$$C_{(ad)} + C_{(ad)} \rightarrow 2C_{(ad)}$$

(6)

$$CH_{3(ad)} \rightarrow CH_{3(gas)}$$

(7)

$$CH_{3(gas)} + CH_{3(gas)} \rightarrow C_2H_{6(gas)}$$

(8)

$$4H \rightarrow 2H_{2(gas)}$$

(9)
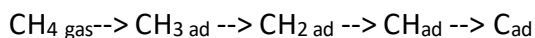
CH3 molecule first adsorbed onto the surface of nickel particle, and then 3 steps of dehydrogenation of the C-H bond occur (eq. 3-5) and forms either a C-C bond(eq.6) or higher order hydrocarbon (eq. 8). The rate of decomposition of CH_4 molecule is fairly high considering the high population of CH_3 molecule at the end of the simulation. During the simulation, it was observed that some isolated carbon atoms reacted to form a C_2 molecule (eq. 6) after 43.575 ps. But only a few of the generated C-C molecules survived after 50 ps. This is because most of the C-C molecules formed a bond with hydrogen to make higher-order hydrocarbons, such as C_2H_2, C_2H_4, and C_2H_6, form during the simulation. Figure 8 proves the population of this higher-order hydrocarbon. This formation of higher-order hydrocarbon is one of the big reasons of less stability of isolated C_2 molecules. Figure 8 also showcased some rare intermediate compounds for an instant (around 5 ps) which is not experimentally observed due to their unstable nature. Otherwise, this could be a tracking error due to the limited species tracking system in lammps.

On the formation of another valuable by-product, i.e., H_2, it has been observed that only 50 gaseous phase H_2 molecules formed after 50 ps. The first radical hydrogen molecule formed after 23 ps, just after the breakage of the CH_3 molecule around 1300 K temperature. The chemisorbed

CH_2 readily loses another hydrogen to form chemisorbed CH. However, this dehydrogenation of the CH molecule is very challenging and requires sufficient energy to break this bond. Concerning a similar study by Anirudhha et. al.[2], it can be assumed that besides the required thermal energy needed to break the CH bond and produce Carbon atoms, it also needs to be adsorbed on the nickel surface to stabilize individual atoms.

The presence of intermediate compound C_xH_x and higher order hydrocarbon compound(C_2H_6) highlight the stability of all those compounds. Another observable feature of methane decomposition is the rapid decomposition rate after 1600K. This exponential increase in decomposition with temperature proves the Arrhenius nature of the decomposition rates.

6. Conclusion and Future Prospects

This study aims to understand how reactive dynamics techniques can be used to study molecular decomposition. This project helps to understand the critical temperature range for methane decomposition.

It also helps to understand the mechanism behind methane decomposition and how nickel helps to accelerate the decomposition process. It provides insight into the hydrocarbon adsorption on nickel surface and graphene particle formation. This project understanding will help to design future manufacturing techniques for single-layer graphene formation and hydrogen generation. Furthermore, this model can serve as a base model to understand the effect of the adsorption of carbon particles on the nickel surface during graphene formation from long-chain polymer surfaces. This model will be further enhanced to understand the effect of other crystalline materials, such as Carbon and Copper, on Methane decomposition.

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Bibliography:

- R_a is the rate of adsorption on the particle surface

- N is the total Methane molecule

- N_s is the no of methane molecules desorbed from the Nickel surface

- N_a is the no of methane molecules adsorbed on the Nickel surface

- R_d is the desorption rate from the particle's surface.

- T is the Absolute Temperature

- T is Time
- C= Carbon, H= hydrogen, Ni=Nickel
- ad=Adsorbed