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BY THE COMMITTEE CONSISTING OF

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## Abstract

This study aims to understand the behavior of a mixture of water and hydrogen peroxide with effects from a carbon nitride catalyst using classical molecular dynamics. Hydrogen peroxide's wide range of use drives the need for cheap and environmentally friendly production methods with high yields and simple processes. Our group has proven that hydrogen peroxide production occurs from water and oxygen in the presence of a carbon nitride, specifically  $C_5N_2$ . A simulation of a system containing five hundred hydrogen peroxide molecules applied two set of Lennard-Jones parameters for hydrogen peroxide, an adapted SPC/E model and a model for  $H_2O_2$  found in literature (Cussler, 2003), to determine which set better modeled hydrogen peroxide. The molecular dynamic study determined that SPC/E best models hydrogen peroxide based on a comparison of simulated densities to known/expected densities. Following the confirmation of the Lennard-Jones parameters for hydrogen peroxide, a molecular dynamic simulation was completed on a system containing a 50/50 wt% mixture of hydrogen peroxide and water in the presence of  $C_5N_2$ . The interaction of hydrogen peroxide and water was studied with the effects from two distinctive models for  $C_5N_2$ . The first model studied was a pristine surface, where the reaction has not occurred. The second  $C_5N_2$  model studied mimics the charges that would be present post reaction due to an O-H functional group proven to be bonded to the surface upon production of hydrogen peroxide. The density profile of each species as a function of distance from the surface of  $C_5N_2$  was calculated to understand the interactions of  $H_2O_2$  and  $H_2O$  with the catalyst surface. The behavior of hydrogen peroxide and water is most favorable at 500 K for the pristine and modified surfaces.



# Chapter 1: Hydrogen Peroxide

## 1.1 Introduction

Hydrogen Peroxide,  $H_2O_2$ , is one of the world's most useful chemicals due to its importance in a wide range of industries. In addition to being relatively stable at standard conditions and useful concentrations, the decomposition of hydrogen peroxide produces water and

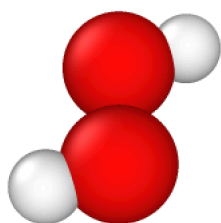


Figure 1: Representation of a single hydrogen peroxide molecule.

oxygen making for an environmentally “green” chemical that can behave as an oxidant, reducing agent, and as a reactant to produce peroxide compounds (Campos-Martin et al., 2006). Due to this broad range of applications, hydrogen peroxide is used in many different industrial processes. Hydrogen peroxide is most commonly known for its use in medicine for treatment of cuts and scrapes due to its ability to easily oxidize and neutralize bacteria, parasites, viruses, toxins, and yeast (Bellchem, 2018);

however, hydrogen peroxide's importance extends far beyond home health care with the largest industrial use being bleaching for the paper and pulp industry (American Chemistry, 2002), followed by sodium perborate and sodium percarbonate production (detergent bleachers), textile bleaching, and water purification (Essential Chemistry 2016).

Since hydrogen peroxide has such a wide range of uses, its importance in many different industrial processes continues to grow, contributing to an ever-growing need of hydrogen peroxide. The need for hydrogen peroxide has grown from 2.2 million tons in 2008 (Campos-Martin et al., 2006) to 7.2 million tons in 2018 (Gao et al., 2020). While global hydrogen peroxide needs continue to rise it is critical to have an environmentally friendly production method that can

achieve high yields with the ability to produce hydrogen peroxide on both large and small scales, in addition to being economically friendly. Approximately 95% of the world's supply of hydrogen peroxide is currently produced through a process known as anthraquinone oxidation. Although this production method achieves high yields, it has many drawbacks that drive the interest into alternative production methods. Electrochemical, photocatalytic, and direct synthesis are currently the most researched alternative production methods. All of these alternative production methods struggle to compete with the anthraquinone process due to limitations each experience.

Previous studies have proven the production of hydrogen peroxide using a carbon-based catalyst favors the two-electron oxygen reduction reaction to hydrogen peroxide (Yongyong, 2019). The use of carbon nitrides will replace toxic anthraquinone catalyst which is a benefit for the environment and will also result in a safer industrial process. The purpose of this study is to understand the movement of hydrogen peroxide and water to and from the surface of the catalyst. The results from this research provide an understanding of hydrogen peroxide's ability to move away from the catalyst surface which will provide a more complete understanding of the feasibility of using carbon nitrides, specifically  $C_5N_2$ , for the production of hydrogen peroxide.

### **1.2.1 Anthraquinone Oxidation**

A simplified version of the anthraquinone oxidation process is shown below in figure 2. The first required step in the anthraquinone process involves the catalyzed (nickel and palladium) hydrogenation of an anthraquinone (AQ) to anthrahydroquinone (AHQ). During the hydrogenation of AQ to AHQ, the aromatic rings present in the AQ are also subject to hydrogenation, leading to a degradation of the working solution, ultimately requiring a

regeneration process to promote the dehydrogenation of the destroyed aromatic compounds. The required hydrogenation step crucial to the anthraquinone process is the reduction of the carbonyl group on anthraquinone. This part of the process requires careful attention and control as the occurrence of side reactions that will destroy the anthraquinone catalyst increase at high conversions of AQ to AHQ (Campos-Martin et al., 2006). The requirement of maintaining approximately 60% conversion of AQ to AHQ, in addition to the degradation of working solution, results in large volumes of working solution to maintain significant production rates. Despite including a regenerative process, costly anthraquinone catalyst must be replenished in order to ensure the working solution is strong enough to promote the reaction. Finally, the catalyst required to dehydrogenate the cyclic rings present on the saturated anthraquinone will experience a decrease in activity over time. This will require the catalyst to be replaced adding to the already high cost involved in this process.

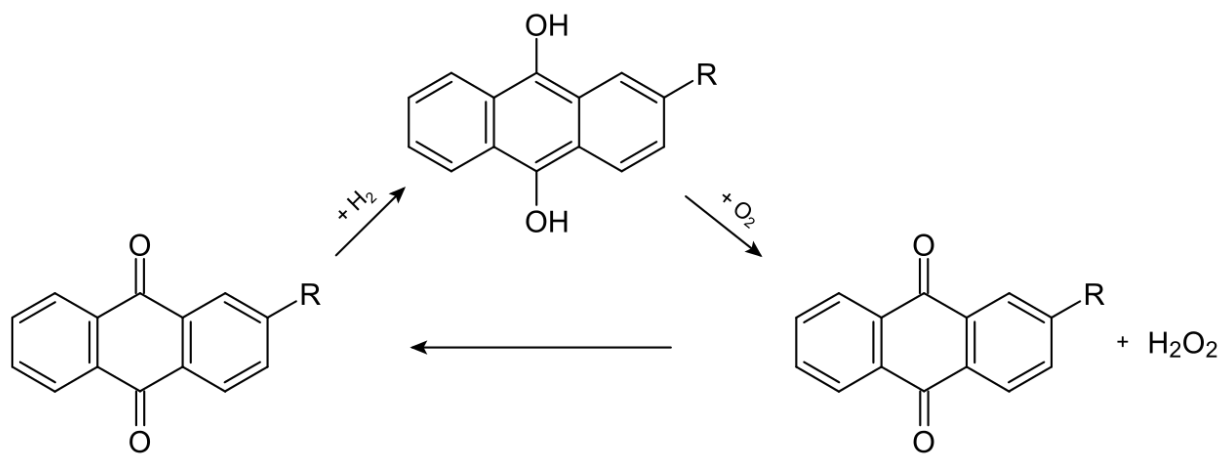


Figure 2: Schematic of a simplified anthraquinone process.

The final step in the production of hydrogen peroxide from the anthraquinone process is a free-radical oxidation step involving AQH and oxygen shown in figure 3 below. This reaction mechanism is uncatalyzed and takes place at minor conditions (Campos-Martin et al., 2006).

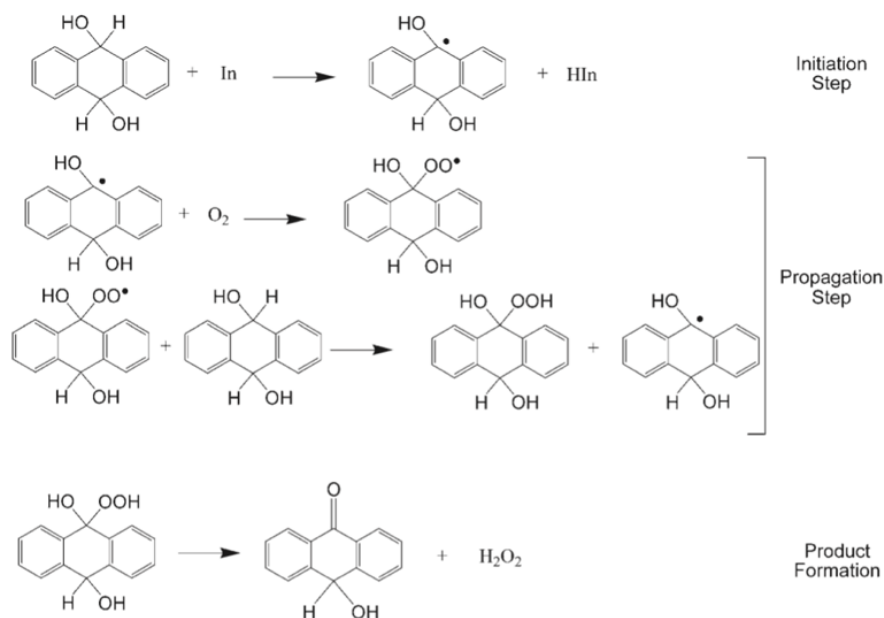


Figure 3: Schematic showing the free radical mechanism of AHQ and oxygen.

Upon completion of the reaction, separation of hydrogen peroxide from the working solution is necessary to obtain hydrogen peroxide in strengths required by industrial users of hydrogen peroxide. This separation consumes a substantial amount of energy.

The anthraquinone process has shortcomings, outlined above, that promote research into alternative production methods. The limitations include a rather complex separation method to purify hydrogen peroxide to commercial concentrations, side reactions requiring regenerative processes, costly anthraquinone catalysts, and expensive dehydrogenation catalysts that must be replaced over time. Due to all of these limitations, the anthraquinone process is only economically favorable for industrial production on a scale of 40,000 tons/year (Samata, 2008). This requires

that most consumers transport hydrogen peroxide to their facilities, an additional limitation resulting in increased purchasing cost.

### 1.2.2 Electrochemical Synthesis

The first alternative production method of hydrogen peroxide discussed is electrochemical synthesis from either water at the anode or oxygen at the cathode. Figure 4 shown below demonstrates this process (Perry et al., 2019).

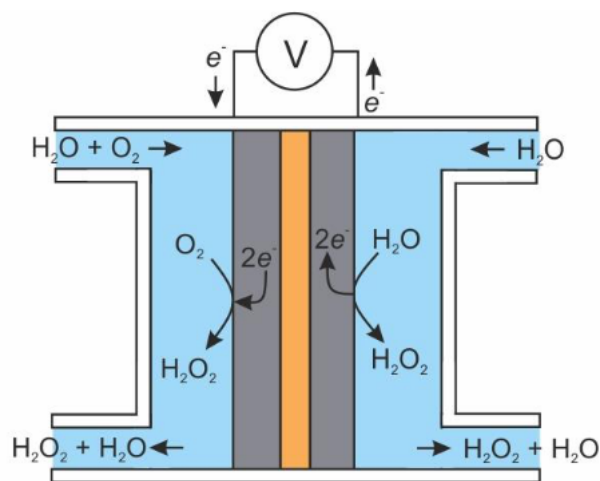


Figure 4: Schematic showing the electrochemical synthesis of hydrogen peroxide from oxygen and water.

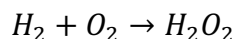
Electrochemical synthesis of hydrogen peroxide is environmentally kind; however, the yield of hydrogen peroxide is a major limitation. The production of hydrogen peroxide from water at the anode is less favorable than the four-electron oxidation of hydrogen peroxide to oxygen, resulting in less production of hydrogen peroxide than what would be favorable for industrial processes. The reduction of oxygen to hydrogen peroxide at the cathode is less favorable than the reduction of

hydrogen peroxide to water, leading to lower conversion similar to the oxidation of hydrogen peroxide to oxygen (Perry et al., 2019).

Although electrochemical synthesis of hydrogen peroxide is an environmentally friendly and relatively simple process (Lim et al., 2019), the competing reactions result in low yields. The competing reactions is a major limitation involved in the production of hydrogen peroxide that C<sub>5</sub>N<sub>2</sub> will solve.

#### **1.2.4 Direct Synthesis**

The production of hydrogen peroxide from direct synthesis uses only molecular hydrogen and oxygen catalyzed by a noble metal catalyst such as palladium (Garcia-Serna et al., 2014). The following equation governs this reaction.



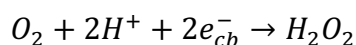
Due to the presence of oxygen and hydrogen at elevated pressures, this method of hydrogen peroxide production presents a significant explosion hazard; consequently, the process requires a large amount of dilute gases, such as nitrogen or carbon dioxide along with a liquid working solution to increase the safety and efficiency of this process (Flaherty, 2018). Although palladium is active for the direct synthesis of hydrogen peroxide, the catalyst is also active for the decomposition of oxygen bonds, leading to increased water formation over hydrogen peroxide. Finally, the production of hydrogen peroxide from direct synthesis results in only about a 1 wt% solution, while industrial uses generally require a minimum of 10% (Garcia-Serna et al., 2014).



The requirement of a dilute solution, along with the fact hydrogen peroxide production through direct synthesis requires an expensive catalyst, provides an opportunity for new methods that do not have these characteristics. Our group proved  $C_5N_2$  can produce hydrogen peroxide with oxygen and water as reactants. This removes the presence of oxygen and hydrogen at elevated pressure, removing the explosion hazard present in direct synthesis. In addition, the production of hydrogen peroxide from  $C_5N_2$  does not require a noble metal catalyst which will decrease the production cost for the process. The results presented in this study provide the information needed to understand if production of hydrogen peroxide using  $C_5N_2$  experiences similar limitations based on the behavior of water and hydrogen peroxide.

### 1.2.3 Photocatalytic Synthesis

Another alternative to the anthraquinone process is the use of semiconductors, such  $TiO_2$ , in a photocatalytic reaction. The reaction below has been proposed for this production method.



The reaction, although environmentally friendly, has incredibly low yields. This production method results in a product containing micromolar amounts of hydrogen peroxide. A study found the addition of up to 50 micromolar of  $Cu^{II}$  will increase the production up to 20 times. However, even with this increase in hydrogen peroxide production, the amount produced is currently not able to compete with other production methods (Compos-Martin et al., 2006). Similar to the issue with direct synthesis, scaling photocatalytic synthesis into a process that will produce significant

amounts of hydrogen peroxide proves very challenging due to the low yield involved in the process. Carbon nitrides hope to improve upon this by offering an alternative production method with high yields. This research aims to understand if the behavior of hydrogen peroxide and water with  $C_5N_2$  will limit additional reactions or increase the difficulty of separating hydrogen peroxide from the catalyst surface.

All of the current production methods have limitations that need to be addressed, especially as hydrogen peroxide consumption continues to increase. Carbon nitrides, such as  $C_5N_2$ , have shown to be able to produce hydrogen peroxide in a cheaper and more environmentally friendly process. This study aims to understand the behavior of hydrogen peroxide and water mixture with  $C_5N_2$  in order to challenge some of the current production methods by improving upon their limitations. The feasibility of using carbon nitride catalysts as an alternative to current production methods for hydrogen peroxide production depends on the characteristics of the system following the reaction. The interactions of water and hydrogen peroxide will determine if using  $C_5N_2$  as a catalyst for the production of hydrogen peroxide will experience the same limitations currently hindering existing production methods. This study provides a better understanding of the possibility of using carbon nitrides as a new production method for hydrogen peroxide.

## Chapter 2: Model and Simulation Details

The simulations performed in this study used Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) utilizing OU Supercomputing Center for Education and Research (OSCER). LAMMPS has the ability to model collections of particles in liquid, solid, or gaseous state in two or three dimensions through a means of time integration of Newton's equation of motion. LAMMPS calculates the forces for the intermolecular and bonded interactions through time at a user specified timestep.

Packmol created all of the initial systems studied from an individual molecule's XYZ files. Visual Molecular Dynamics (VMD) took the initial system file created by Packmol, containing the coordinates for each atom in the system, and assigned partial charges, bonds and angles, to each atom. In addition, VMD formatted the file to be used in LAMMPS calculations.

The simulations presented in this study use periodic boundaries in the X, Y, and Z direction to remove the effects from imaginary walls and end effects that would be present without the repeating simulation cell. LAMMPS calculates the intermolecular forces between molecules with the equation for "12/6 Lennard-Jones potentials." LAMMPS requires the Lennard-Jones parameters,  $\epsilon$  and  $\sigma$ , for each pair of molecules be defined in the input file for the simulation. The  $\epsilon$  parameter, in units of kcal/mol, characterizes the energy between two non-bonded atoms and  $\sigma$ , in units of Å, defines the bond distance of the Van der Waals forces. The following equation is used, along with LJ parameters, to determine the energy as a result from the Van der Waals forces.

$$E_{vdw} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \text{ for } r < r_c$$

The unknown Lennard-Jones parameters were calculated using the Lorentz-Berthelot rules as follows (Sklogwiki):

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$$

LAMMPS calculates the coulombic interactions at each timestep using the “coul/cut” command which is based on user specified charge information using the following equation where  $r_c$  is the cutoff distance.

$$E_{coul} = \frac{C q_i q_j}{\epsilon r} \text{ for } r < r_c$$

LAMMPS calculates the energy resulting from the bonds between two atoms at each timestep using the equation for harmonic style shown below where  $r_o$  is the equilibrium bond distance.

$$E_{bonded} = K(r - r_o)^2$$

In addition to the energy contributed to the system from the bonded interaction between two atoms, the energy contribution from the angles in the system are also calculated using

LAMMPS harmonic function following the equation below, where  $\theta_c$  is the equilibrium angle position.

$$E_{angle} = K(\theta - \theta_c)$$

Each of the systems studied will be simulated using a particle-particle particle mesh (PPPM) solver which ensures coulombic interactions are calculated across the periodic boundaries, with an allowed error of 1.0e-5. All of the simulations presented in this study reset O-H bonds in both hydrogen peroxide and water to equilibrium length and angle values at each timestep using the “Shake” command with the LAMMPS desired tolerance of 1.0e-4. All simulations presented in this study employed an NPT ensemble, which requires specifying temperature and pressure. This allowed the volume of the system to vary with the interactions of the molecules to reach equilibrium at the specified temperature and pressure. The calculations performed to analyze the behavior of every system used the trajectory files generated by LAMMPS containing the position of each atom in the system. Once the simulations were finished, an R script graphed the densities and temperatures versus time using ggplot to determine when the system reached a steady state. A detailed explanation of the analysis completed for each system is discussed below.

## **2.1 Confirmation of Lennard-Jones Parameters**

The simulations used a system containing five hundred hydrogen peroxide molecules to determine if an adapted SPC/E model or a model for hydrogen peroxide available from literature by E.L Cussler and co-workers more accurately described hydrogen peroxide (Cussler, 2003). The

simulations used an NPT ensemble at 1 atm and 250 K, 300 K, 350 K, 400 K, 450 K, 500 K, and 750 K along with an initial timestep of 0.5 fs and a cutoff distance for the LJ interactions of 10 Å. The analysis for these simulations includes determining steady state was achieved based on the changes in temperature and density over time. An R script prepared the density and temperature profiles as a function of time from data output by LAMMPS. Once the system reached a steady state, the average simulated density was calculated using the last 2 ns of simulation in intervals of 50 fs. This value was compared to known/estimated values to determine the accuracy of the thermodynamic parameters used in the simulation.

## **2.2 C<sub>5</sub>N<sub>2</sub> with Hydrogen Peroxide and Water**

A 50/50 wt% solution of hydrogen peroxide and water containing 1780 H<sub>2</sub>O<sub>2</sub> and 2310 H<sub>2</sub>O was studied with the effects of C<sub>5</sub>N<sub>2</sub> at 350 K, 500 K, and 750 K. There are three distinct charges present throughout the catalyst defined by each atoms position in the C<sub>5</sub>N<sub>2</sub> sheet as shown in figure 5 below. Previous molecular dynamic simulations performed by our group confirmed the values of the charges for the nitrogen atoms and carbon atoms attached to the nitrogen atoms. Once these values were determined, a calculation proved the charge of the remaining carbons were 0.550 based on what was required to make the carbon nitride net neutral.

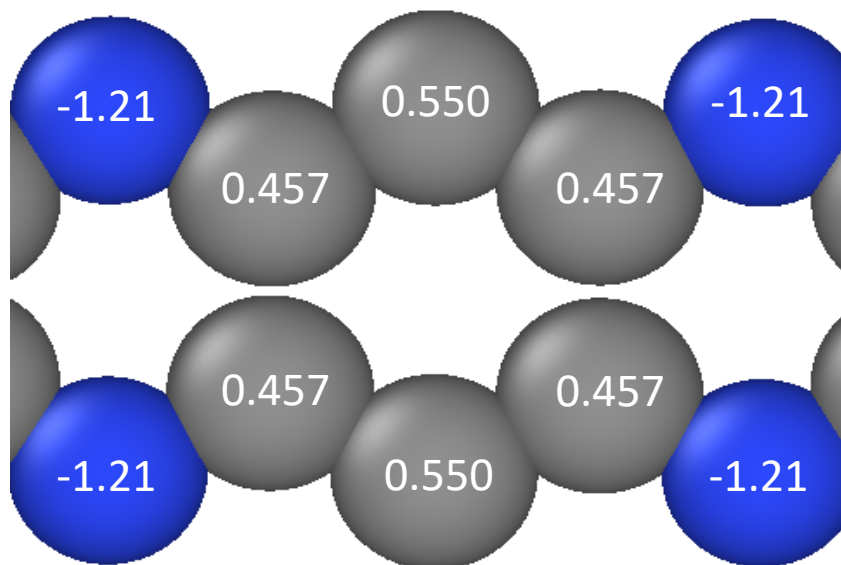


Figure 5: Carbon nitride partial charges used for the pristine surface simulations. The nitrogen atoms are show in purple and the carbon atoms are show in gray.

The simulations began at a timestep of 0.5 fs to allow the initial system to relax before increasing the timestep for all simulations. Once it appeared the system was approaching equilibrium, the timestep increased to 2.0 fs to expand the simulated time of the calculations. All of the simulations ran for a minimum of 15 ns allowing the system to reach a steady state based on the changes in density and temperature profiles. The system continued to run for at least 2 ns at equilibrium to collect data for the calculation of the density of each species throughout the solution. This ensured the calculations for the density profiles used only data from the system at equilibrium, removing the effects from the configuration of the initial system.

## 2.3 Modified $C_5N_2$ with Hydrogen Peroxide and Water

Our group proved that as hydrogen peroxide is produced on  $C_5N_2$  an O-H group will stay bonded to the location where the reaction takes place. The bonded O-H alters the charge distribution through  $C_5N_2$  which changes the distribution of molecules away from the surface of the catalyst. Figure 6 below demonstrates the locations, shown in red, where the charges have been modified to reflect this occurrence. There is an even distribution of modified locations across the catalyst surface to keep the interactions with the solution evenly spread.

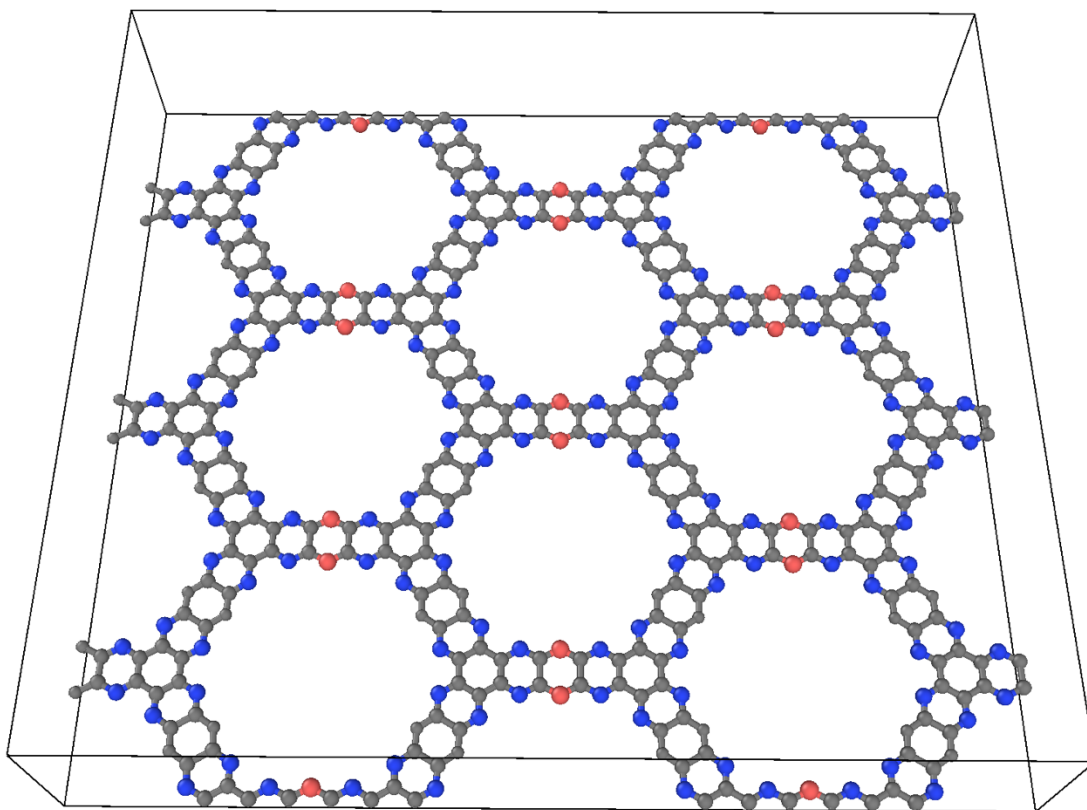


Figure 6: Representation of the modified surface used in simulations. The modified locations that will mimic the charges on the surface post reaction are shown in red, nitrogen atoms are shown in blue, and carbon atoms are shown in gray.



Charge information for the O-H functional group and carbon nitride were taken from literature and shown on their respective atoms below in figure 7 (Wang et al., 2017). The charges and Lennard-Jones parameters used in this study are presented below in Table 1.

Table 1: Graphene and O-H functional group parameters used in the simulations with the modified  $C_5N_2$  surface.

Species	Bond	$\sigma$ (Å)	$\epsilon$ (kcal/mol)	$q$ (e)
C	C-C	0.355	0.293	0.000
C	C-O	0.355	0.150	0.150
H	H-O	0.040	0.192	0.435
O	C-O	0.315	0.636	-0.585

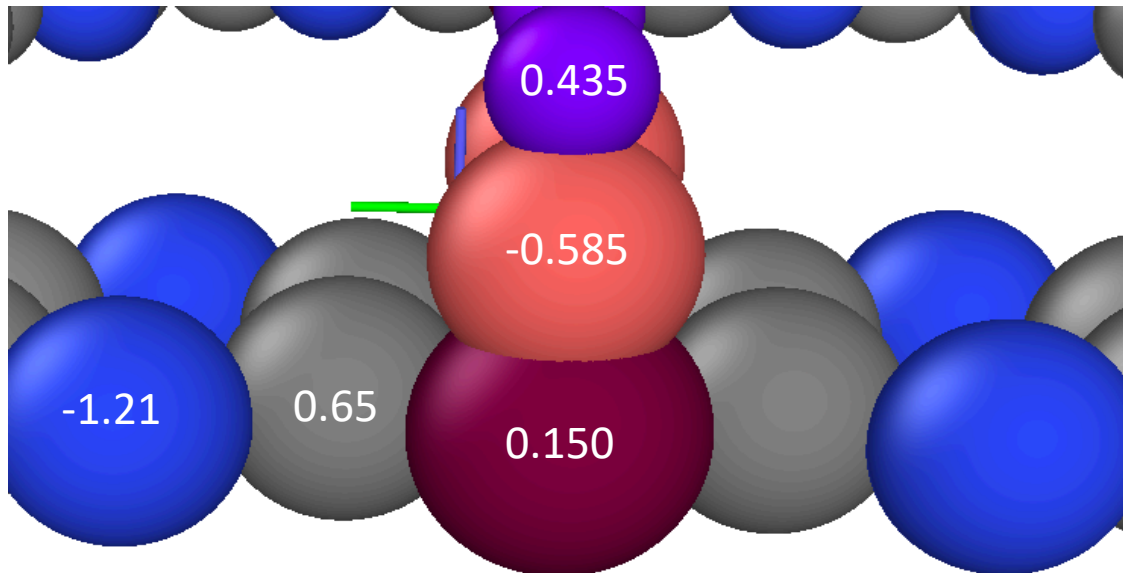


Figure 7: The charges for the O-H group, carbon, and nitrogen on  $C_5N_2$  that will be present as a result of the reaction. The nitrogen atoms are shown in blue, carbon in gray/maroon, oxygen in pink, and hydrogen in purple.

The sum of the charges belonging to oxygen, hydrogen, and carbon replicated the effect from the O-H bond on the solution of hydrogen peroxide and water. The simulations used the sum of charges shown in figure 8 below to replicate the system post reaction.

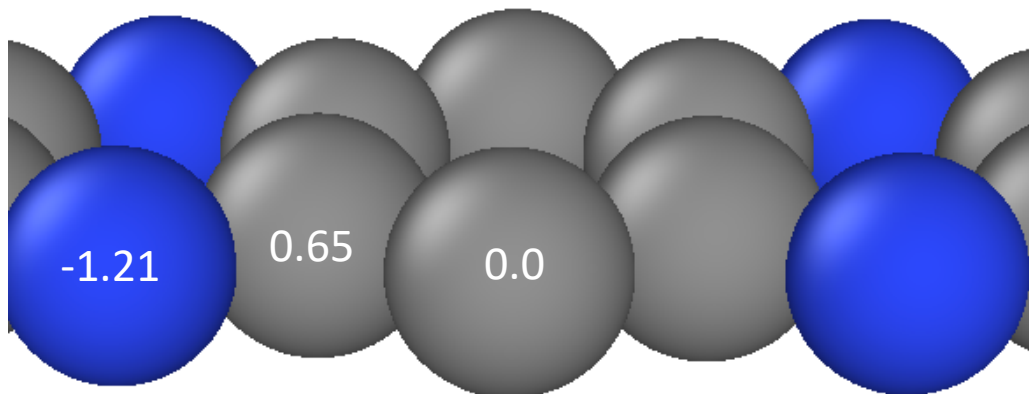


Figure 8: The charges on carbon nitride used in the simulations for the modified surface to mimic the charges of the O-H functional group present on the surface once the reaction has occurred. The nitrogen atoms on the catalyst surface are shown in blue while the carbon atoms are shown in gray.

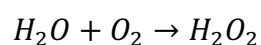
The simulations for the modified surface and pristine surface are similar. The simulations began at a timestep of 0.5 fs and allowed to relax before increasing the timestep to 2.0 fs at 0.02 ns. The simulations performed with the modified surface used an NPT ensemble at 350 K, 500 K, and 750 K. In addition, the simulations for the modified surface ran at steady state for at least 2 ns to collect data to calculate the density profile, similar to the simulations completed for the pristine surface.

All of the density profile calculations for pristine and modified  $C_5N_2$  were completed by taking the output files between 13 ns and 15 ns and counting the number of hydrogen peroxide and water molecules in 2 Å layers. The layer that hydrogen peroxide or water was grouped to was based on the molecule's oxygen atom(s). The grouping was done for hydrogen peroxide molecules

by calculating the average  $Z$  value between their oxygen atoms. This calculation shows the number of hydrogen peroxide and water molecules based on the distance from the catalyst surface. This will prove if hydrogen peroxide separates from the surface easily in addition to showing if water is attracted to the catalyst surface to promote additional reactions.

## Chapter 3: Hydrogen Peroxide Model Validation

The purpose of this research is to understand the interaction of a solution containing hydrogen peroxide and water with the effects of  $C_5N_2$ , a promising carbon nitride to be used in the production of hydrogen peroxide that has the potential to solve many of the current limitations of hydrogen peroxide synthesis. This study aims to not only prove whether separation of hydrogen peroxide from the carbon nitride is possible post-reaction, but also provide insight into the ability of water to migrate to the surface, increasing the conversion of water and oxygen to hydrogen peroxide, a limitation experienced by many of the alternative methods of hydrogen peroxide production. The principle reaction proven from previous molecular dynamic simulations is the synthesis of hydrogen peroxide by means of water and oxygen at standard pressure with only  $C_5N_2$  shown in figure 9 (Yongyong, 2019). The desired reaction is as follows:



Ideally, hydrogen peroxide will collect away from the catalyst surface and experience the greatest density furthest from the catalyst surface. This will result in easier separation and will not hinder movement of water to the surface for additional reactions. On the other hand, water will experience favorable behavior if it is found to be attracted to the catalyst surface in order to promote additional reactions.

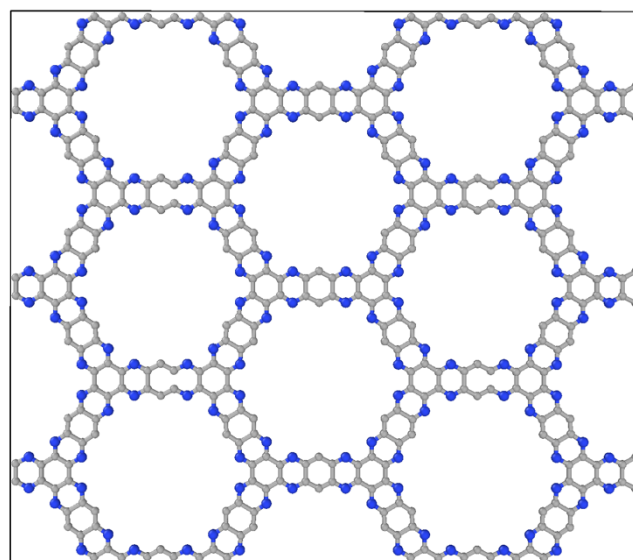


Figure 9: Single  $C_5N_2$  catalyst surface. The carbon atoms are shown in gray and the nitrogen atoms are shown in blue.

The reaction is proven to occur through the following two mechanisms from previous molecular dynamic studies (Yongyong, 2019).

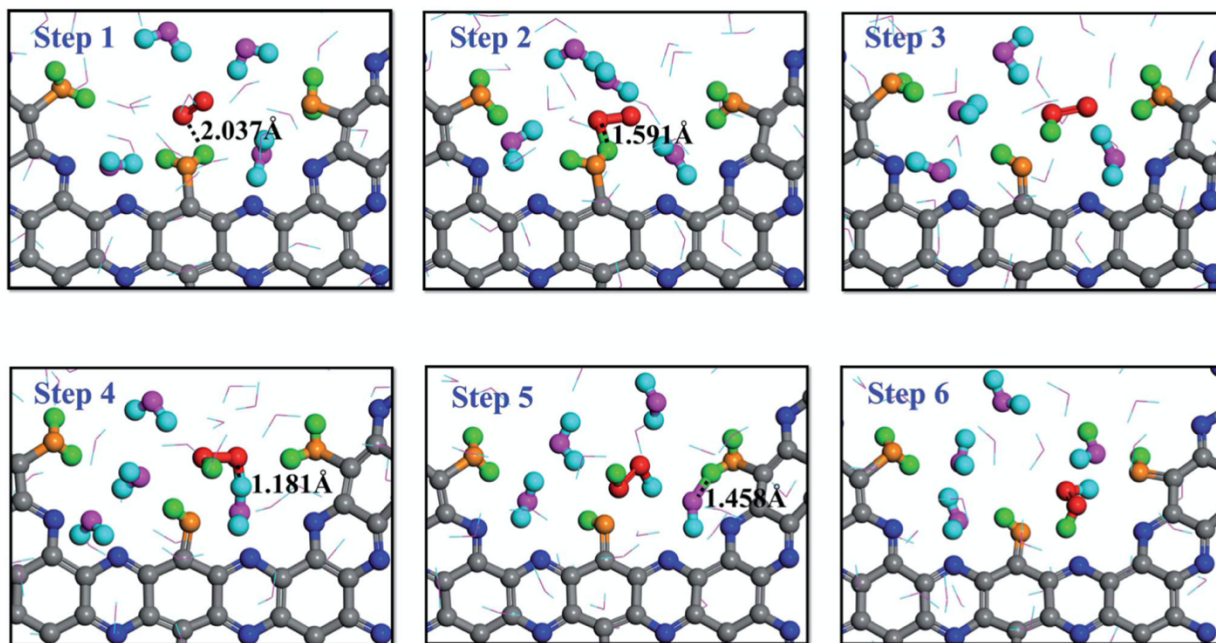


Figure 10: Carbon Nitride Catalyzed Reaction - Mechanism 1 Sourced from YongYong, 2019.

These snapshots demonstrate hydrogen peroxide is produced from the interaction of a water molecule bonded to the surface and an oxygen atom in the solution. The water that participates in the reaction remains attached to the catalyst surface as an O-H molecule. Hydrogen peroxide will be in the presence of water upon completion of the reaction. The carbon and nitrogen atoms belonging to the catalyst surface are shown in gray and blue, respectively. The oxygen atoms belonging to water are shown in orange with the hydrogen atoms shown in green. The oxygen molecules are red.

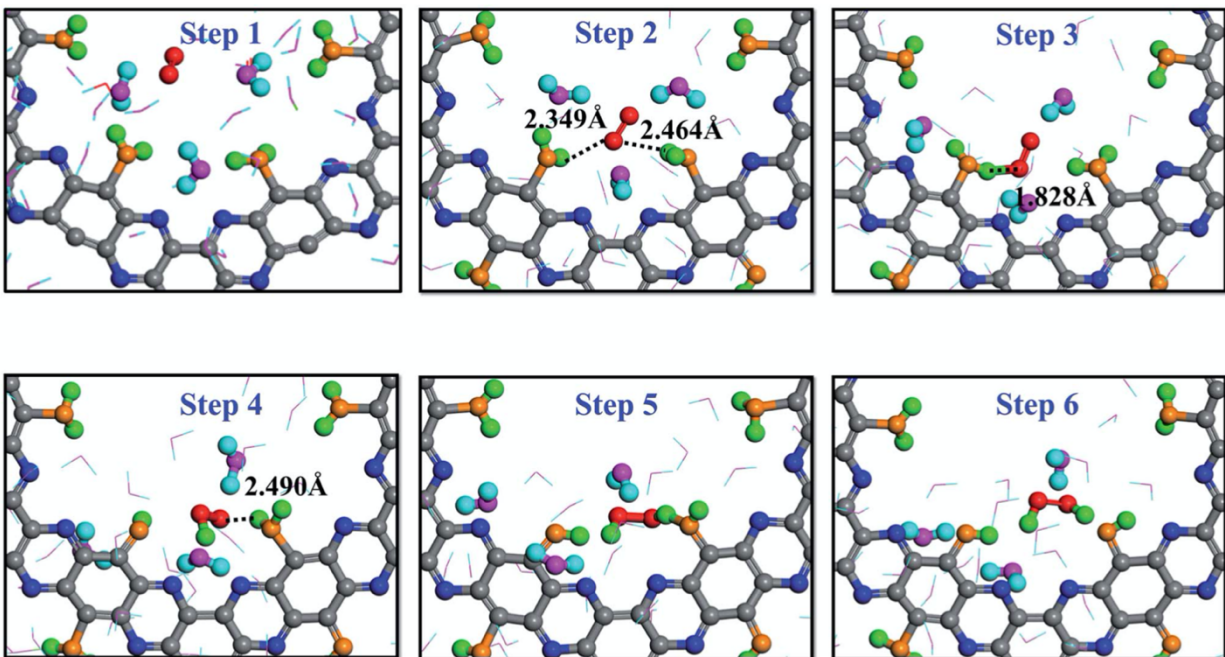


Figure 11: Carbon Nitride Catalyzed Reaction - Mechanism 2 Sourced from YongYong, 2019.

These snapshots demonstrate hydrogen peroxide is produced from the interaction of a water molecule bonded to the surface and an oxygen atom in the solution. The water that participates in the reaction remains attached to the catalyst surface as an O-H molecule. Hydrogen peroxide will be in the presence of water upon completion of the reaction. The carbon and nitrogen atoms belonging to the catalyst surface are shown in gray and blue, respectively. The oxygen atoms belonging to water are shown in orange with the hydrogen atoms shown in green. The oxygen molecules are red.

In each of the mechanisms shown in figure 10 and 11, hydrogen peroxide is produced from the interaction of oxygen with a water molecule attached to the surface separated from nitrogen atoms by a single carbon atom on each side. Upon production of hydrogen peroxide, the O-H group that is attached to the catalyst surface will remain attached. The simulations performed with the modified surface mimic the interactions of hydrogen peroxide and water with the surface once it has participated in reactions resulting in the O-H bonds. The following simulations prove which Lennard-Jones parameters more accurately define interactions of hydrogen peroxide which is required before studying the interactions of hydrogen peroxide and water with  $C_5N_2$ .



### 3.1 Hydrogen Peroxide Model Validations

Accurate Lennard-Jones parameters must be determined for hydrogen peroxide prior to studying the interaction between the mixture and  $C_5N_2$ . Previous molecular dynamic studies have used the SPC/E water model to describe hydrogen peroxide (Lv et al., 2016); however, the LJ parameters for hydrogen peroxide are defined in literature (Cussler, 2003). A simulation

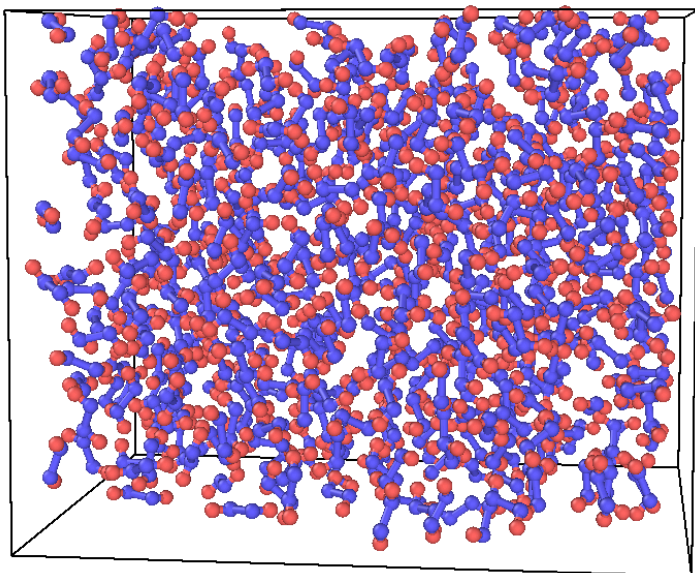


Figure 12: Initial system containing five hundred hydrogen peroxide molecules used in the simulations for the confirmation of LJ parameters. The oxygen atoms are shown in blue and the hydrogen atoms are shown in red.

below. The initial system for the simulations is shown in figure 12.

containing a system of five hundred hydrogen peroxide molecules proved which LJ parameter more accurately describe hydrogen peroxide. The average density of each simulation was calculated then used for a comparison to known and expected densities to determine if the LJ parameters used in the simulation accurately describe

both the bonded and non-bonded interactions within the system. The results for the system of pure hydrogen peroxide at 250 K, 300 K, 350 K, 400 K, 450 K, and 500 K are shown

### 3.2 SPC/E

The system of pure hydrogen peroxide reached equilibrium using the Lennard-Jones parameters that define water in SPC/E. The charge information used for the following simulations is shown below in Table 2 (Lv et al., 2016).

Table 2: Modified SPC/E parameters for hydrogen peroxide used in the simulations.

	<b>Charge (e)</b>	<b><math>\sigma</math> (Å)</b>	<b><math>\epsilon</math> (kcal/mol)</b>
<b>H-H</b>	0.4976	0.0	0.0
<b>O-O</b>	-0.4976	3.166	0.1554

This system ran for 30 ns then an analysis of the system determined the average density once it reached steady state. The densities and temperatures of each simulation are shown below in figure 13 and 14.



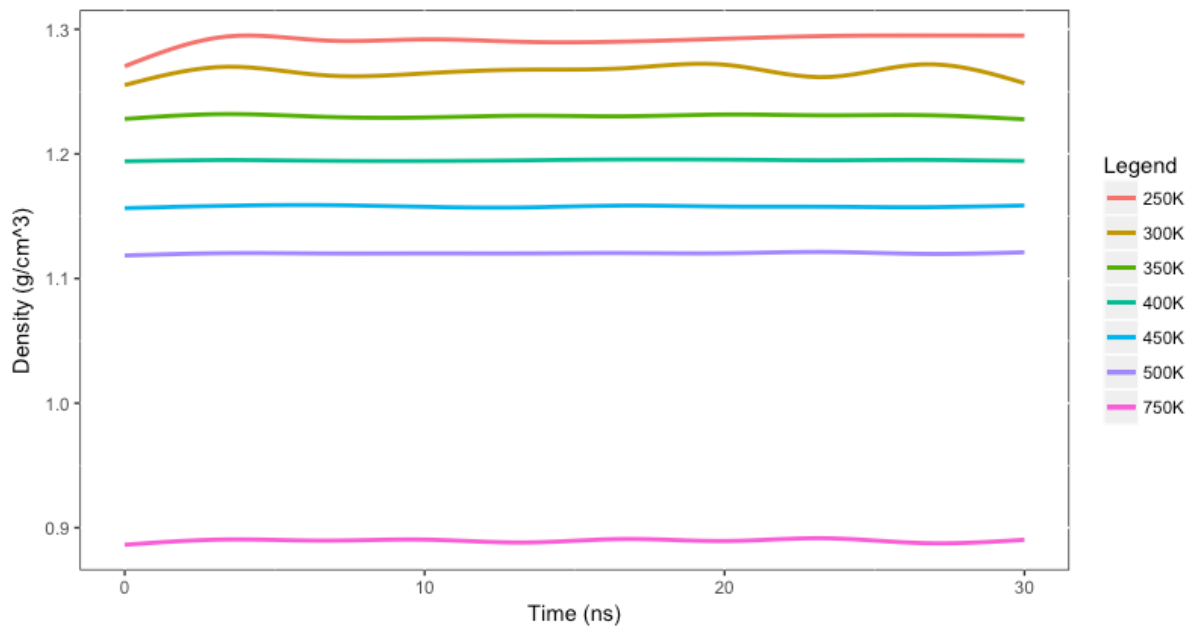


Figure 13: Density profile of simulated hydrogen peroxide using the SPC/E model.

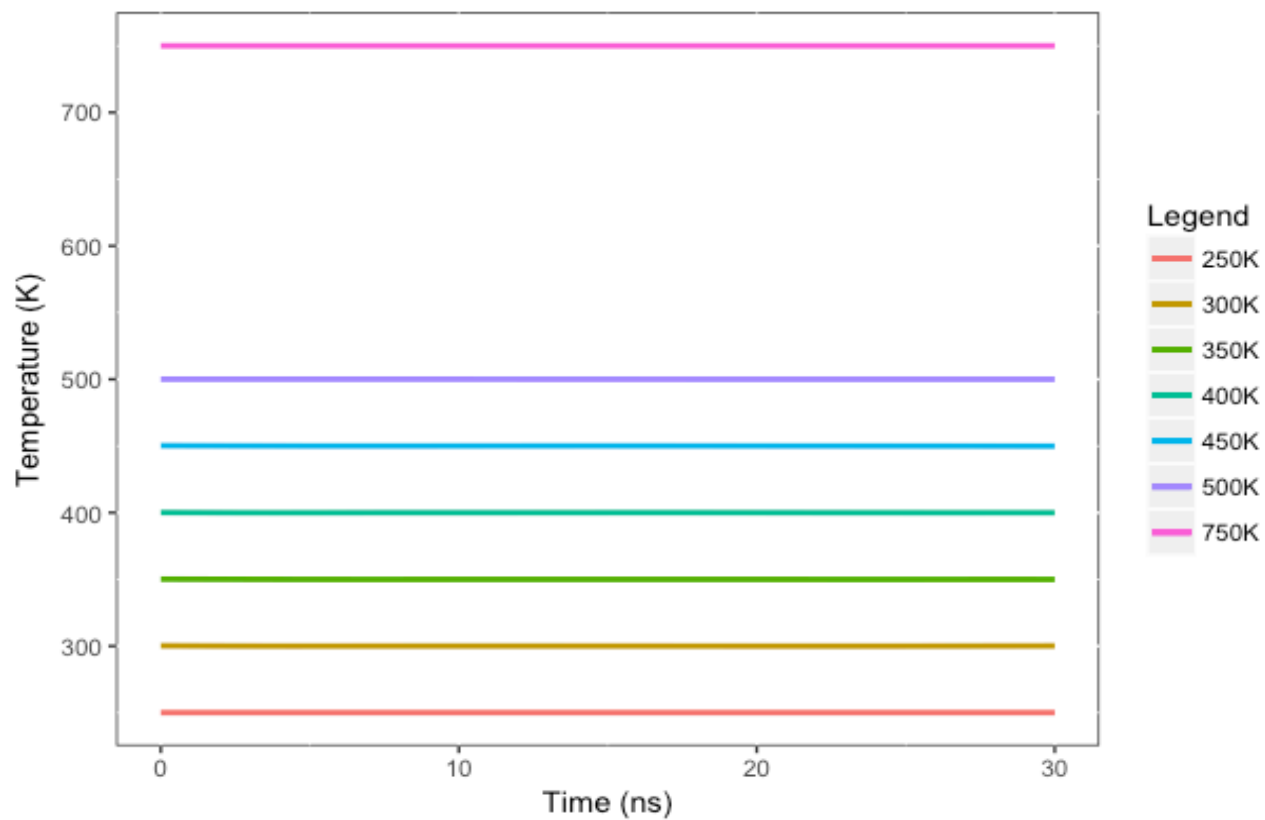


Figure 14: Temperature profile of simulated hydrogen peroxide using the SPC/E model.

The output files from LAMMPS between 28 and 30 ns in 50 fs increments allowed the average density of the system at steady state to be calculated. The temperature and density profiles prove the system reached a steady state prior to beginning the calculation for the average density. This will remove error due to the initial system attempting to reach equilibrium. The results for SPC/E model are summarized in the table below.

Table 3: Simulation results from adapted SPC/E model.

<b>Temperature, K</b>	<b>Density, g/cm<sup>3</sup></b>
250	1.2936
300	1.2630
350	1.2288
400	1.1948
450	1.1580
500	1.1206
750	0.8889

Performing the simulations at temperatures between 250 K and 750 K provided a large range of densities going from 1.2936 g/cm<sup>3</sup> to 0.889 g/cm<sup>3</sup>. The density of pure hydrogen peroxide is 1.45 g/cm<sup>3</sup> at 300 K; however, the density at higher temperature is not accurately known. The simulated density for this system at 300 K was 1.26 g/cm<sup>3</sup>, an error of 13%. The large decrease in density between 500 K and 750 K is due to vaporization.

### 3.1.3 H<sub>2</sub>O<sub>2</sub> Hydrogen Peroxide Parameters

Table 4 below summarizes the LJ parameters used in the following simulations (Cussler, 2003)

Table 4: Hydrogen Peroxide LJ parameters used in the simulations.

	Charge (e)	$\sigma$ (Å)	$\epsilon$ (kcal/mol)
<b>O-O</b>	-0.4976	2.0980	0.57489
<b>H-H</b>	0.4976	4.1960	0.0

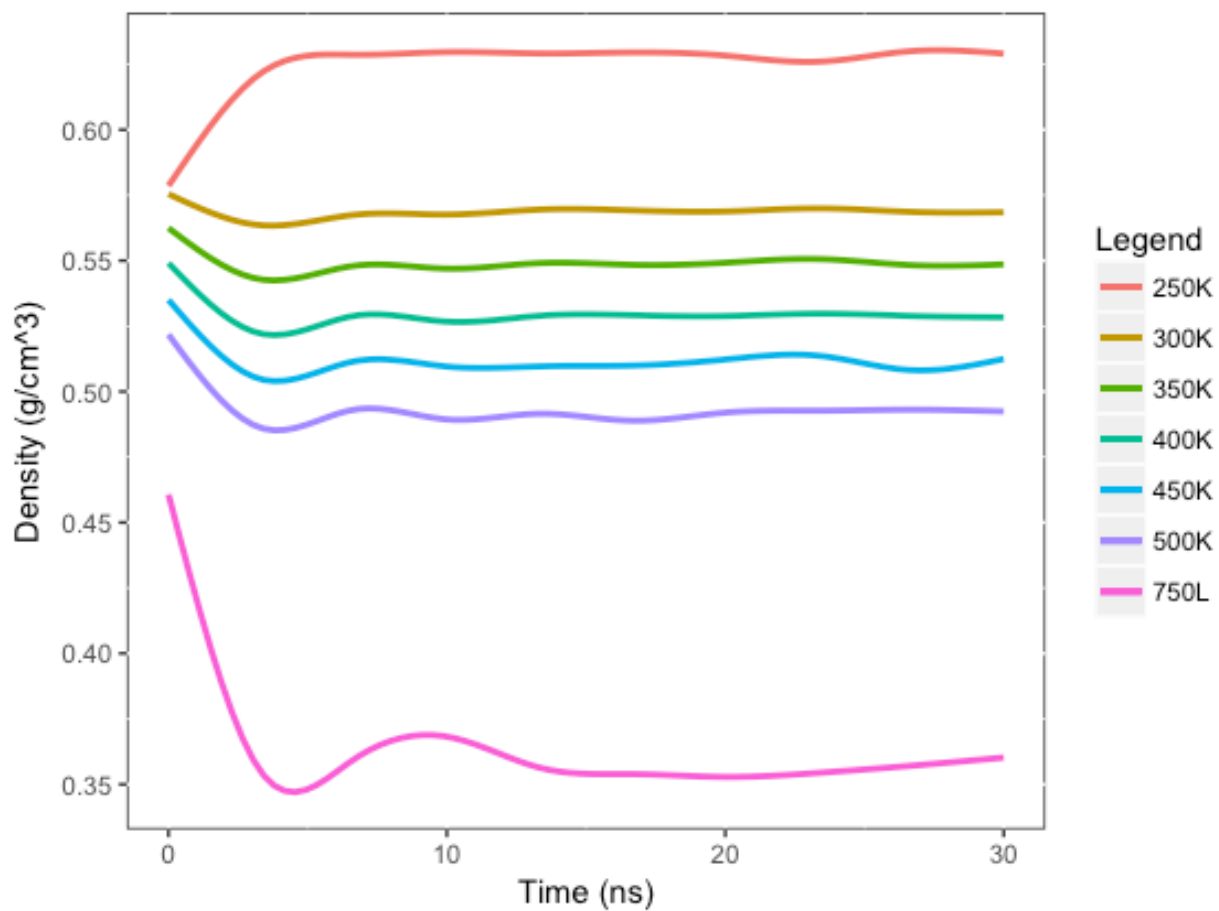


Figure 15: Density profile of simulated hydrogen peroxide H<sub>2</sub>O<sub>2</sub> model.

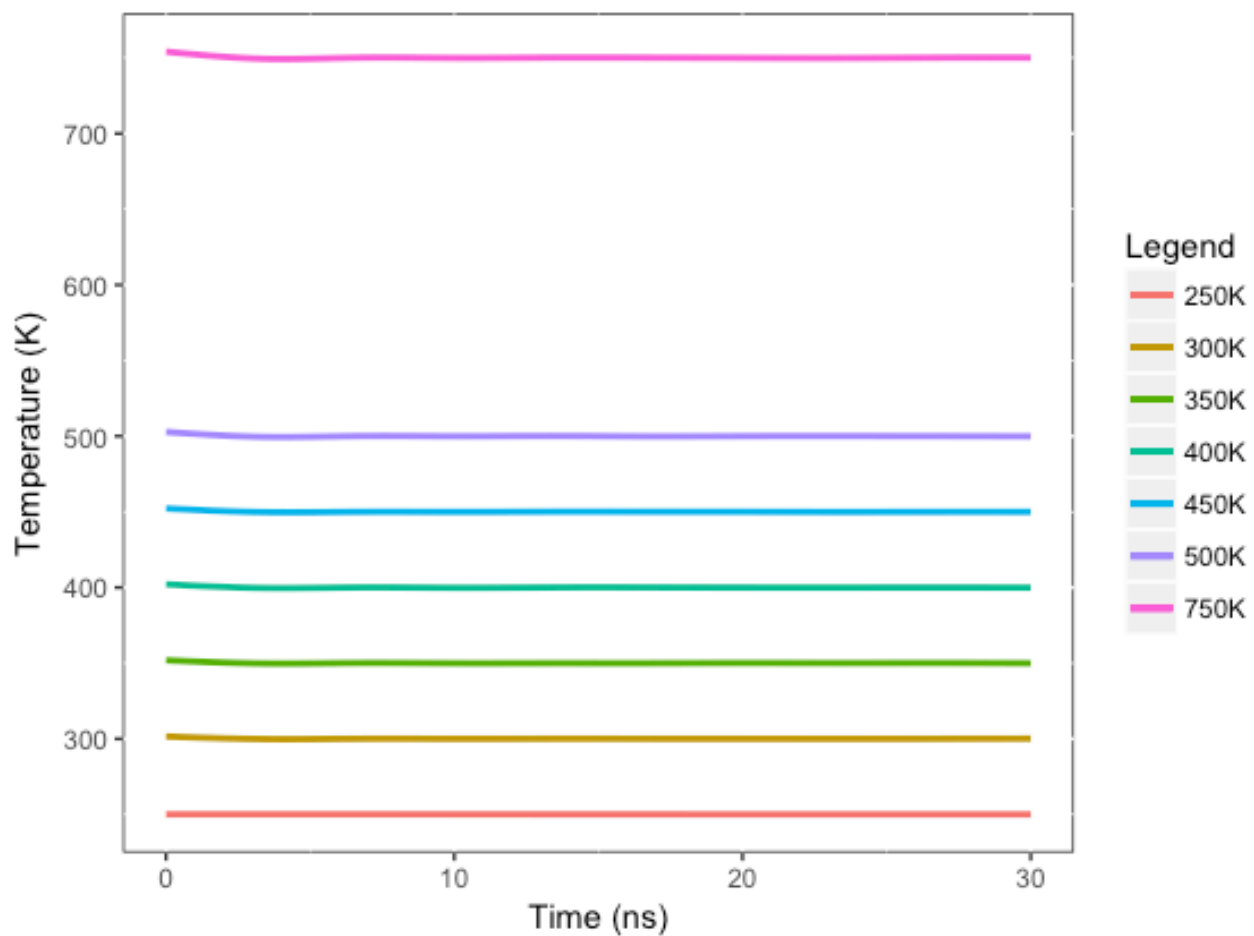


Figure 16: Temperature profile of simulated hydrogen peroxide using  $\text{H}_2\text{O}_2$  model.

Table 5: Simulation results from the hydrogen peroxide model.

<b>Temperature, K</b>	<b>Density, g/cm<sup>3</sup></b>
250	0.6299
300	0.5683
350	0.5483
400	0.5285
450	0.5104
500	0.4929
750	0.3597

The simulated density of the system using the LJ parameter for hydrogen peroxide is significantly lower than for SPC/E. Although the densities of aqueous hydrogen peroxide are not significantly studied, it is certain hydrogen peroxide has a higher density than water. Given that all of the simulated densities for hydrogen peroxide using the LJ parameter for hydrogen peroxide are significantly lower than water for all temperatures, these parameters cannot be considered to accurately define the system of pure hydrogen peroxide.

A comparison of the simulated densities from SPC/E and Hydrogen Peroxide's LJ parameters to each other and the known and expected density of hydrogen peroxide proved which set would more accurately define the non-bonded interactions for the following simulations. Figure 17 demonstrates the change in density at various concentrations of hydrogen peroxide (Density/Specific Gravity of Hydrogen Peroxide Solutions).

## Density of H2O2

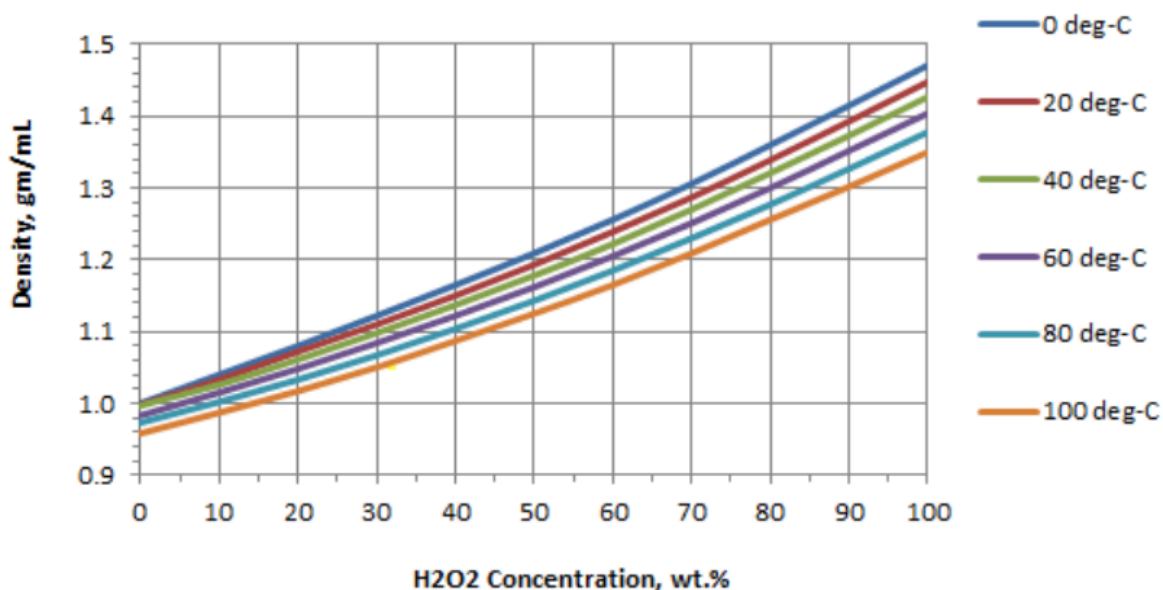


Figure 17: Density of hydrogen peroxide at various concentrations and temperatures

The simulated density was compared to the expected values at all temperatures using the figure above since the density of hydrogen peroxide is not well studied at various temperatures. It is clear that for all temperatures and concentrations of hydrogen peroxide, the density of hydrogen peroxide is greater than water. The simulated density of hydrogen peroxide molecules using SPC/E was much closer to the estimated value at all temperatures than the set of parameters defined for hydrogen peroxide. This comparison of simulated densities to known and expected densities proves hydrogen peroxide is more accurately modeled by using the adapted SPC/E water model rather than the LJ parameters for hydrogen peroxide.

## Chapter 4: C<sub>5</sub>N<sub>2</sub> with Hydrogen Peroxide and Water

The following simulations describe the behavior of hydrogen peroxide and water with interactions from C<sub>5</sub>N<sub>2</sub>. The initial system remained the same for all simulations and contained a 50/50 wt%

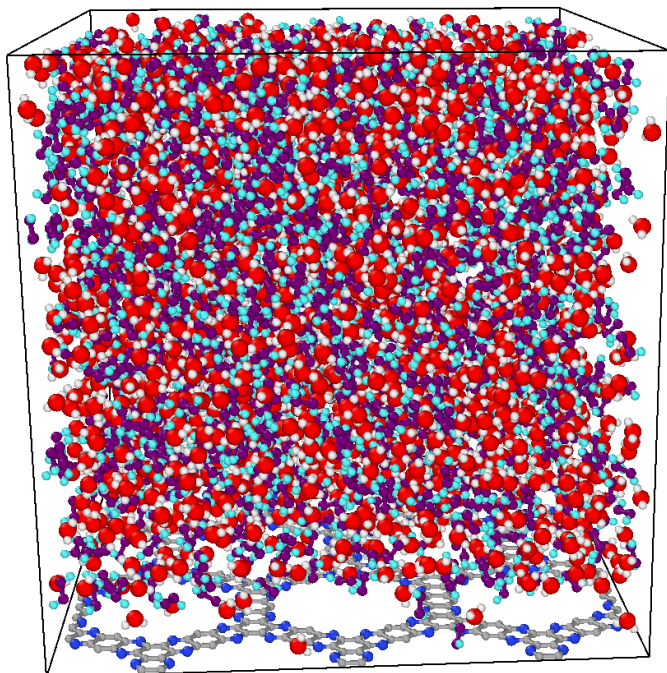


Figure 18: Initial system containing a 50/50 wt% solution of hydrogen peroxide and water with C<sub>5</sub>N<sub>2</sub> used in the simulations for modified and pristine surfaces. Carbon and nitrogen atoms belonging to C<sub>5</sub>N<sub>2</sub> are shown in gray and blue, respectively. Hydrogen belonging to water is shown in white while oxygen belonging to water is shown in red. Hydrogen peroxide is modeled with purple for the hydrogen atoms and teal for the oxygen atoms.

solution of hydrogen peroxide and water. The simulation cell which is shown in figure 18 is approximately 50 x 55 x 56 Å, where oxygen belonging to water is shown in red while hydrogen in water is white. The oxygen and hydrogen atoms belonging to hydrogen peroxide are defined with the purple and teal color, respectively. The SPC/E water model used to describe the non-bonded interactions of water and hydrogen peroxide are outlined in Table 6 below. The Lennard-Jones parameters for carbon nitrides was taken from literature (Lv et al., 2016).

Table 6: Lennard-Jones parameters for hydrogen peroxide, water, and graphene used for the simulations.

<b>Pair</b>	<b>Charge (e)</b>	<b><math>\sigma</math> (Å)</b>	<b><math>\epsilon</math> (kcal/mol)</b>
<b>C-C</b>	0.4570	3.55	0.07
	0.5496		
<b>N-N</b>	-1.2100	1.85	0.20
<b>O-O (Hydrogen Peroxide)</b>	-0.4976 <sup>1</sup>	3.17	0.16
<b>O-O (Water)</b>	-0.8476	3.17	0.16
<b>H-H (Hydrogen Peroxide)</b>	0.4976	0.0	0.0
<b>H-H (Water)</b>	0.4248	0.0	0.0

The chosen size of the system allowed a significant amount of C<sub>5</sub>N<sub>2</sub> and enough room in the z-direction to remove any effects due to the periodic boundaries on the layers closest to the catalyst surface. This allows the distribution of molecules closest to the surface to be affected by a single carbon nitride.

The trajectory files output by LAMMPS, containing the position of hydrogen peroxide and water, allowed the molecules to be grouped into 2 Å layers. The density of the top layer was corrected for the height of the simulation box being unevenly split into 2 Å.

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<sup>1</sup> Vibrational spectra and molecular dynamics of hydrogen peroxide molecules at quartz/water interfaces



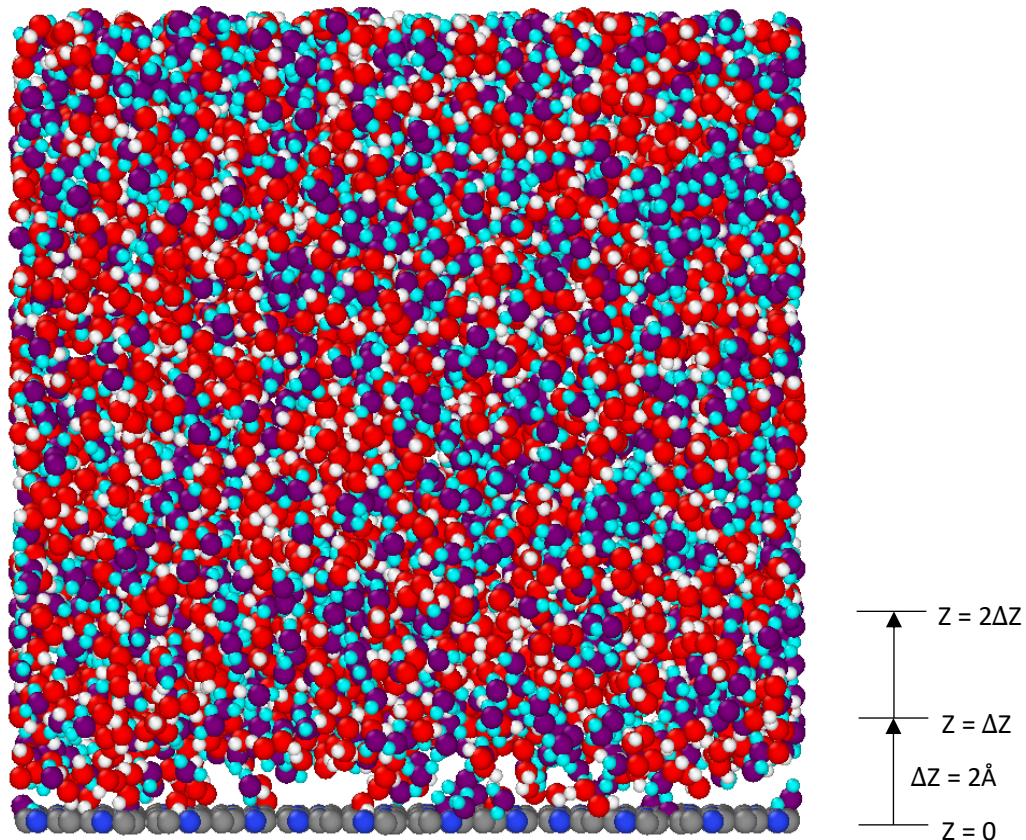


Figure 19: Visual representation showing the method used to calculate the density of hydrogen peroxide and water as a function of distance from the catalyst surface. Carbon and nitrogen atoms belonging to  $C_5N_2$  are shown in gray and blue, respectively. Hydrogen belonging to water is shown in white while oxygen belonging to water is shown in red. Hydrogen peroxide is modeled with purple for the hydrogen atoms and teal for the oxygen atoms.

The trajectory files output by LAMMPS every 2000 fs provided the data to calculate the average number of hydrogen peroxide and water molecules in each layer between 13 ns and 15 ns. The calculations for the following density profiles used this average number of hydrogen peroxide and water molecules in each layer to calculate the density as a function of distance from the catalyst surface. The temperature and density profiles as a function of time, shown in the following sections, prove the system reaches a steady state and analysis of the density profile is completed

only after the system reaches equilibrium. This will remove any errors in the density profile due to the movement of molecules while the system attempts to reach equilibrium

#### 4.1 C<sub>5</sub>N<sub>2</sub> with Hydrogen Peroxide and Water

The following calculations and simulations help to understand how water and hydrogen peroxide interact with pristine and modified carbon nitrides. The systems are simulated at 350 K (a), 500 K (b), and 750K (c). The temperature and density profiles, shown for each simulation, prove the system does reach a steady state and the calculations are not be affected by the changes in the initial system. This will provide a greater accuracy and understanding regarding the distribution of molecules throughout the solution as the distance from the surface increases.

(a) 350 K

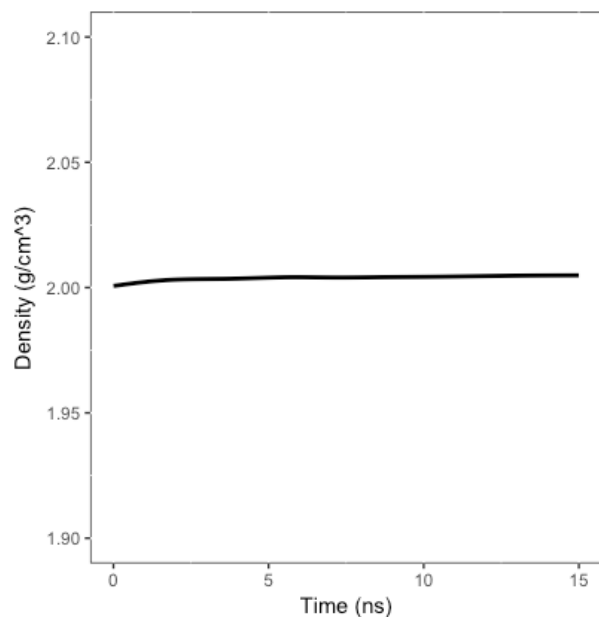


Figure 20: Pristine C<sub>5</sub>N<sub>2</sub> – Density profile at 350 K.

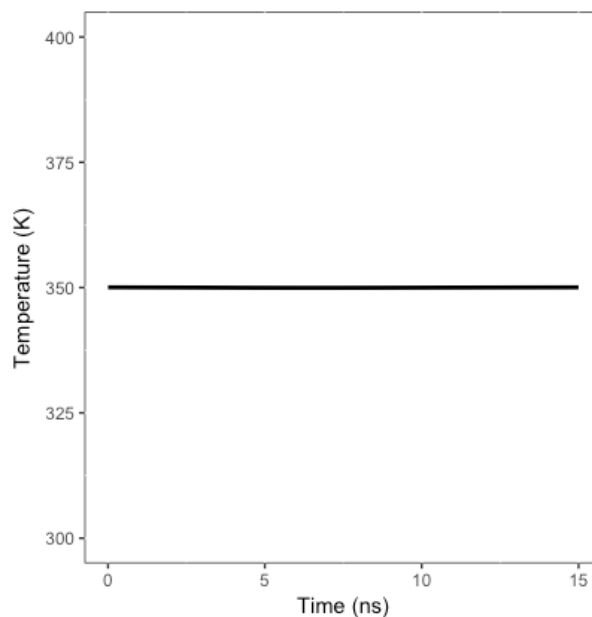


Figure 21: Pristine C<sub>5</sub>N<sub>2</sub> – Temperature profile at 350 K.

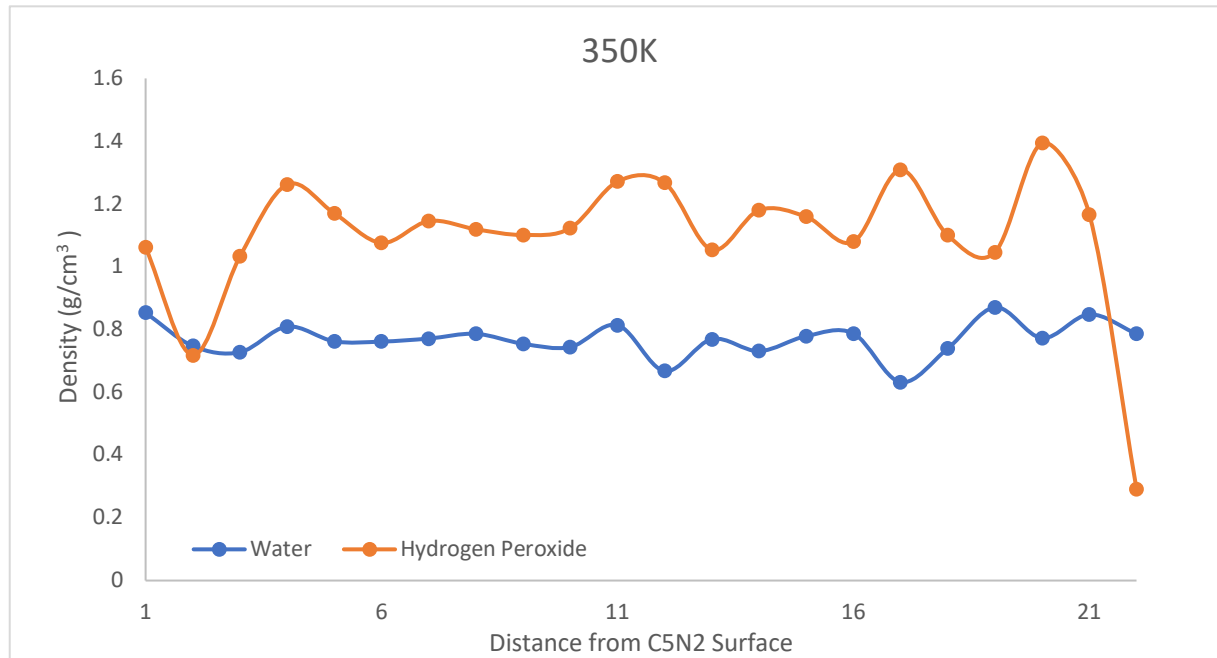


Figure 22: Pristine C<sub>5</sub>N<sub>2</sub> – Hydrogen peroxide and water density profiles as a function of distance from the catalyst surface at 350 K.

The density profiles of hydrogen peroxide and water were significantly different from each other at 350 K. The density of water near the surface remains relatively constant with a slight attraction at the surface indicated by a slightly higher density on layer 1 than throughout the bulk solution. The behavior of hydrogen peroxide near the surface experiences significant changes. The density of hydrogen peroxide at the surface itself is not significantly higher than through the bulk solution based on the density of the first layer; however, the density of hydrogen peroxide in the second layer significantly decreases. This proves that hydrogen peroxide is not strongly attracted to the surface at 350 K.

The sharp decrease in density of hydrogen peroxide and water at the top layer is due to the relaxed initial state and the interaction of both hydrogen peroxide and water with the catalyst surface in the periodic cell above. The trajectory of the system proves the hydrogen atoms

belonging to hydrogen peroxide and water immediately attach to the surface of  $C_5N_2$  at the nitrogen atoms. Since the initial system is enlarged in the  $Z$ -direction, the hydrogen atoms in the system with the opportunity to bond to the surface belong to the molecules above the catalyst, not in the periodic box below. This is due to the molecules being closer to the surface above the catalyst than below in the initial system. Oxygen from the periodic cell below the catalyst surface will experience repulsive forces due to the oxygen-oxygen interactions with the molecules bonded to the surface. This explains the lack of symmetry in the density profile of the two molecules.

(b) 500 K

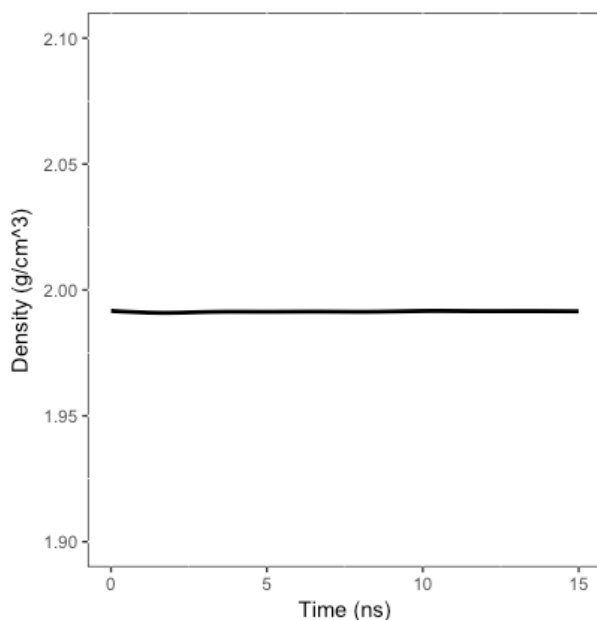


Figure 23: Pristine  $C_5N_2$  – Density profile at 500 K.

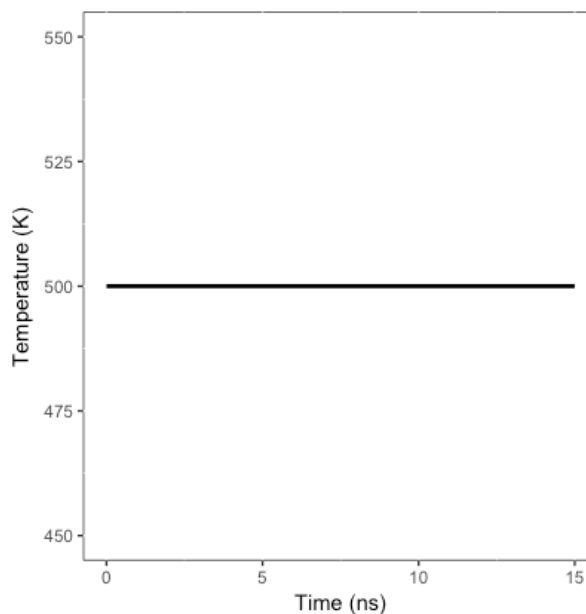


Figure 24: Pristine  $C_5N_2$  – Temperature profile at 500 K.

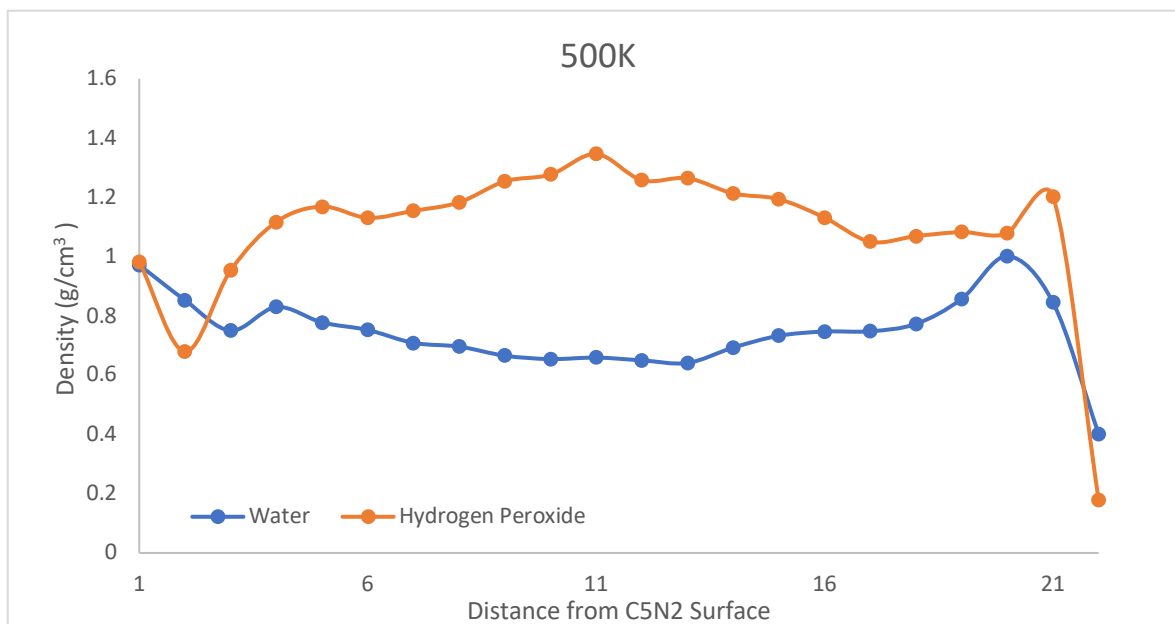


Figure 25: Pristine  $C_5N_2$  – Hydrogen peroxide and water density profiles as a function of distance from the catalyst surface at 500 K.

The behavior of water and hydrogen peroxide at 500 K is similar to the system at 350 K. It is important to note that the number of water molecules near the surface of the catalyst is greater at 500 K than for 350 K. This supports that water has an increased attraction to the catalyst surface at 500 K, which will allow additional reaction to occur. The density profile of hydrogen peroxide is favorable at 500 K. The amount of hydrogen peroxide slightly decreases at and near the surface from 350 K. In addition, the density of hydrogen peroxide gradually increases as the distance from the catalyst surface increases further proving hydrogen peroxide is repelled from the surface. This behavior of hydrogen peroxide and water will not only promote the reaction which will result in increased conversion of water to hydrogen peroxide but will also cause less difficult separation of hydrogen peroxide from the surface of the catalyst.

(c) 750 K

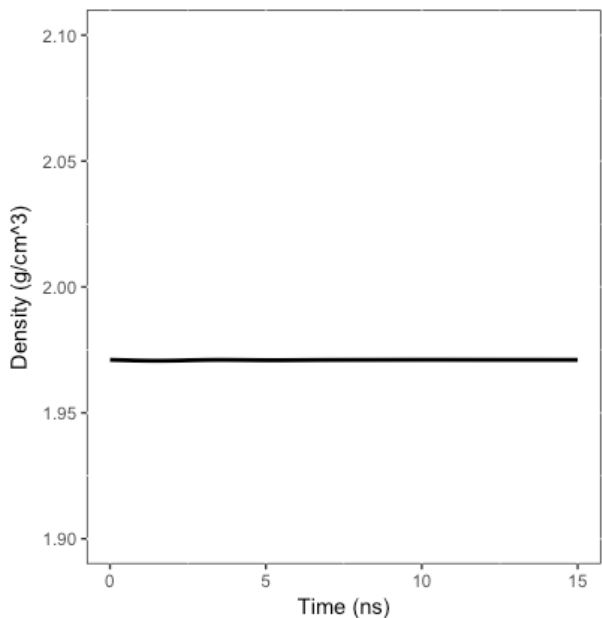


Figure 26: Pristine C<sub>5</sub>N<sub>2</sub> - Density profile at 750 K.

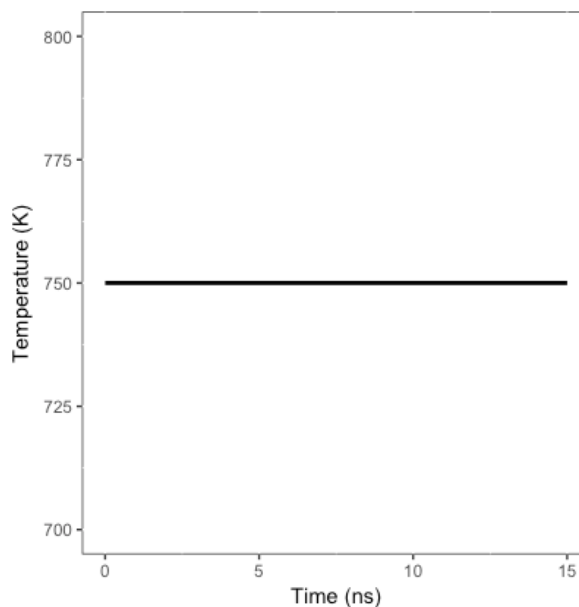


Figure 27: Pristine C<sub>5</sub>N<sub>2</sub> - Temperature profile at 750 K.

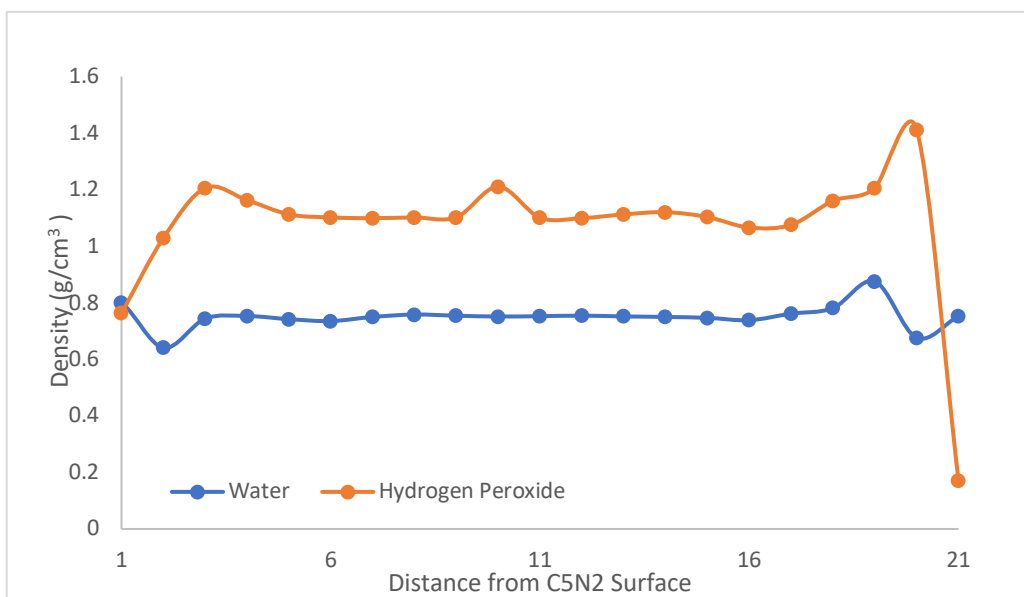


Figure 28: Pristine C<sub>5</sub>N<sub>2</sub> – Hydrogen peroxide and water density profiles as a function of distance from the catalyst surface at 750 K.

The behavior of the system at 750 K is not favorable based on the interaction of water and hydrogen peroxide with the catalyst surface. The density of hydrogen peroxide further decreases at the surface of the catalyst from 500 K. Furthermore, there is a significant increase of hydrogen peroxide in the second and third layers closest to the catalyst surface from 500 K while water also experiences a decrease near the surface. The increase in hydrogen peroxide near the surface indicates that at 750 K hydrogen peroxide will collect closer to the surface than for 350 K and 500 K. The decrease in density of water closer to the catalyst surface presents potential issues. Since water is required to interact with the surface of the catalyst to produce hydrogen peroxide, a strong attraction to the surface is favorable for increased hydrogen peroxide production.

The sharp decrease in amount of hydrogen peroxide and water molecules at the top layer can be attributed to the repulsive forces due to the bonds the hydrogen atoms have to the surface of the catalyst. The trajectory files demonstrate the hydrogen atoms immediately attach to nitrogen atoms on the surface of the catalyst for all temperatures. Since the molecules above the catalyst surface are closer than the molecules in the periodic system below, due to the relaxed initial state, they reach the surface faster. Figure 29 demonstrates the attraction of hydrogen peroxide and water to the nitrogen atoms on the surface of  $C_5N_2$ . It is important to note that in figure 29, all of the oxygen atoms face up from the surface resulting in a repulsive force on oxygen atoms belonging to water and hydrogen peroxide in the layer above and below the surface.

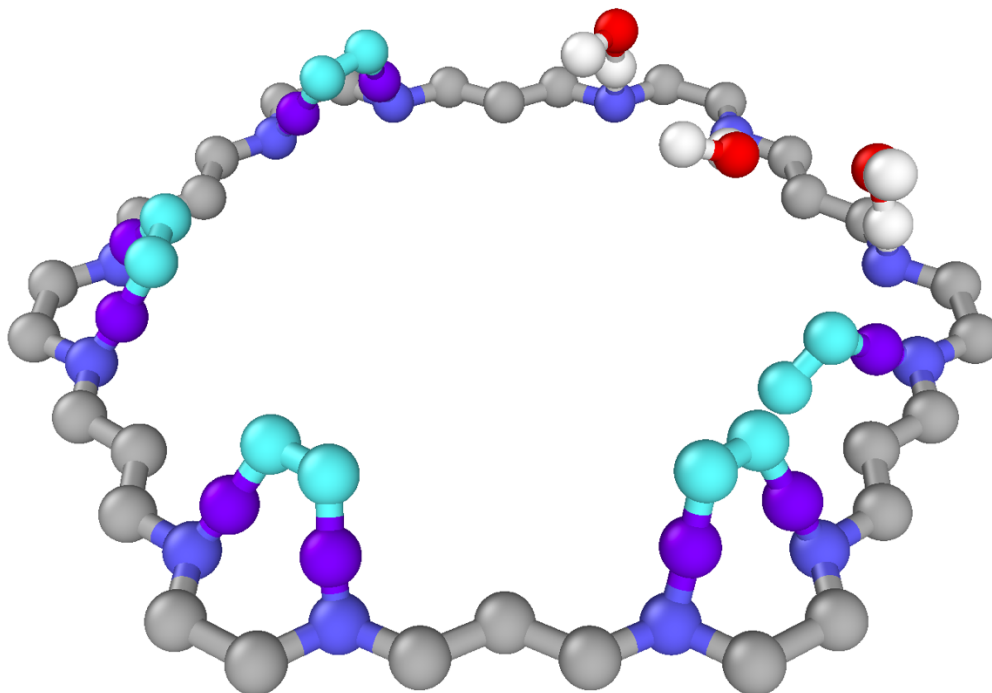


Figure 29: Interaction of hydrogen peroxide and water with the nitrogen atoms on the catalyst surface. These bonds occur immediately upon beginning the simulation. Carbon and nitrogen atoms belonging to  $C_5N_2$  are shown in gray and blue, respectively. Hydrogen belonging to water is shown in white while oxygen belonging to water is shown in red. Hydrogen peroxide is modeled with purple for the hydrogen atoms and teal for the oxygen atoms.

Although the hydrogen atoms of both water and hydrogen peroxide prove to immediately attach to the surface, hydrogen peroxide and water that are not bound to a nitrogen are still present on the surface. Figure 30 below shows hydrogen peroxide and water that are still attracted to the surface, all of which appear to be in acceptable locations for additional reactions, which are denoted by dashed lines.



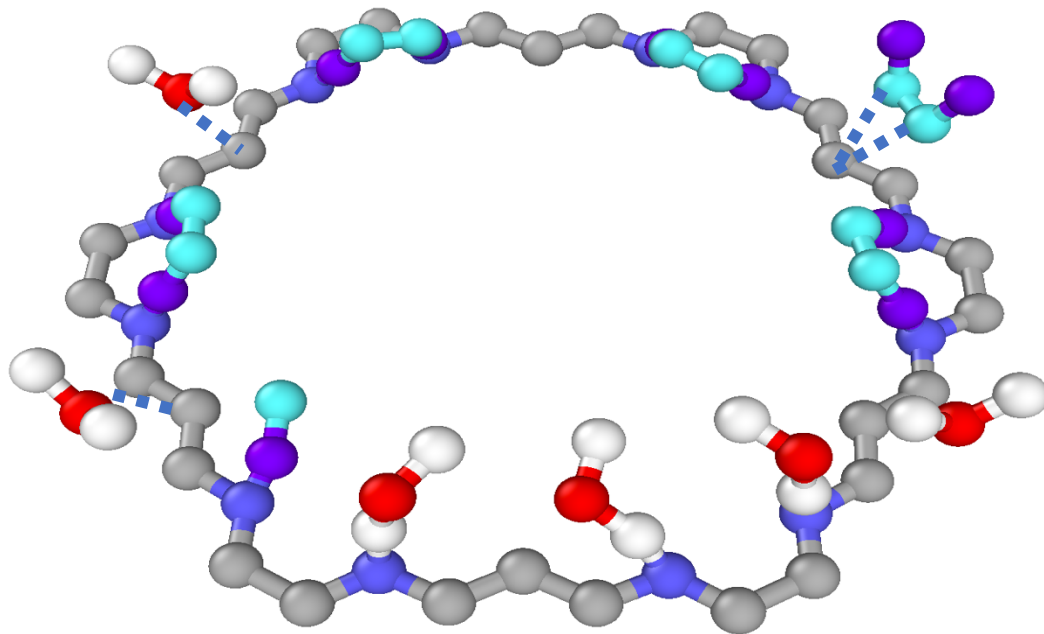


Figure 30: Hydrogen peroxide and water attraction to the catalyst surface despite the bonds formed with each species with the nitrogen atoms on  $C_5N_2$ . Carbon and nitrogen atoms belonging to  $C_5N_2$  are shown in gray and blue, respectively. Hydrogen belonging to water is shown in white while oxygen belonging to water is shown in red. Hydrogen peroxide is modeled with purple for the hydrogen atoms and teal for the oxygen atoms.

The density profiles at 350 K, 500 K, and 750 K exhibit similar characteristics on the top layers due to the coulombic interaction from the nature of the periodic boundary conditions. This is a result of a repulsive force on the molecules due to the hydrogen atoms attraction to the nitrogen atoms on the surface. The density profile of hydrogen peroxide on the surface of the catalyst experiences favorable conditions at both 350 K and 500 K. However, when the system is simulated at 750 K, it was observed that the amount of hydrogen peroxide near the surface significantly increases, despite the amount on the surface in the first layer decreasing. Water experiences the strongest attraction to the surface for 500 K. The observed trend of less hydrogen peroxide on the surface of the pristine catalyst at 500 K rather than 350 K, paired with the fact that the amount of water near the surface of the reaction is greatest at 500 K, suggest the system will not limit movement of water to the surface or experience an increase in difficulty of hydrogen peroxide

separation from the catalyst surface at 500 K. The system at 750 K is believed to drive water molecules further away from the surface of the catalyst due to the increase in hydrogen peroxide near the surface.

#### 4.2 Modified $C_5N_2$ with Hydrogen Peroxide and Water

(a) 350 K

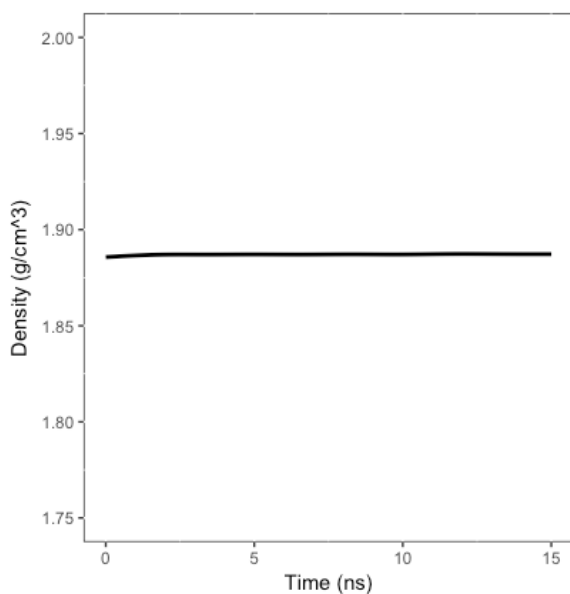


Figure 31: Modified  $C_5N_2$  – Density profile at 350 K.

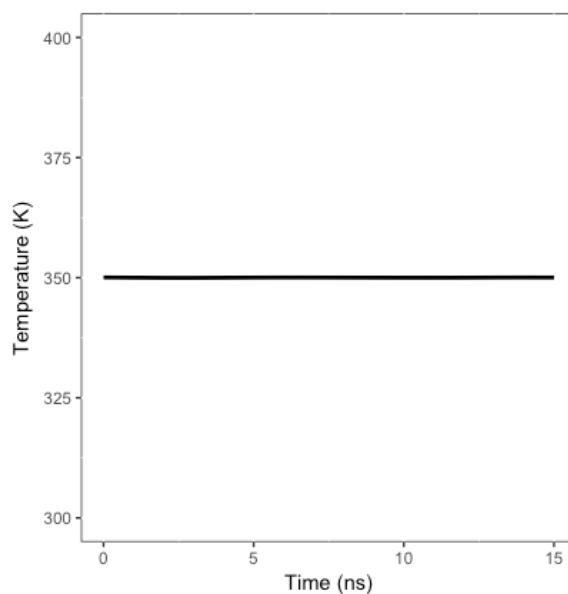


Figure 32: Modified  $C_5N_2$  – Temperature profile at 350 K.

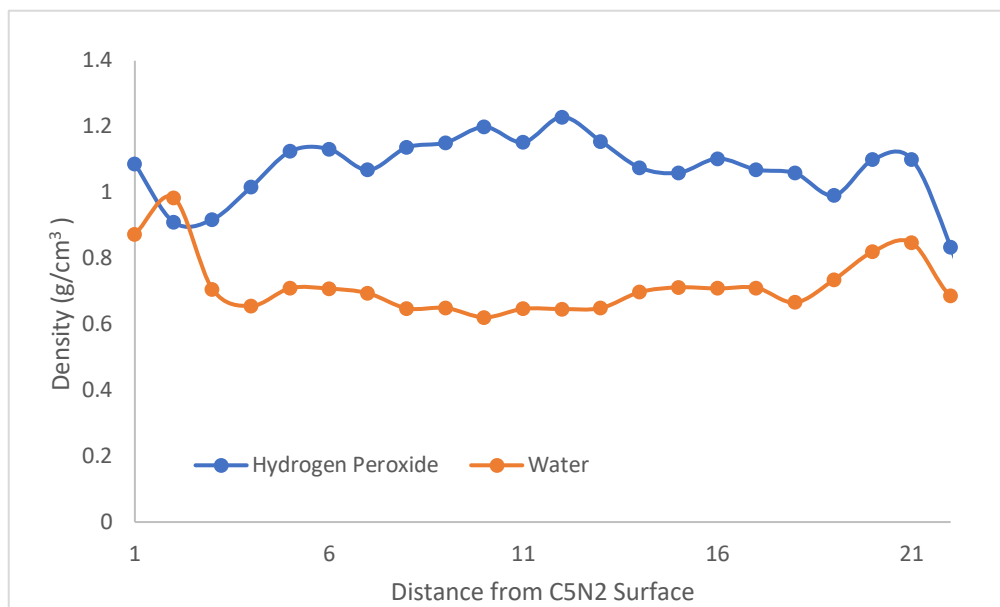


Figure 33: Modified C<sub>5</sub>N<sub>2</sub> – Hydrogen peroxide and water density profiles as a function of distance from the catalyst surface at 350 K.

The density profile of water is significantly greater closest to the surface of the catalyst than throughout the bulk solution which proves water is attracted to the surface at 350 K. This will increase conversion of water to hydrogen peroxide as movement to the surface is not hindered. In addition, the behavior of hydrogen peroxide near the surface is favorable for separation. In the first few layers, the density of hydrogen peroxide is less than the density through the bulk solution. The lower density near the surface of the catalyst will ease the separation of hydrogen peroxide from the catalyst surface.

(b) 500 K

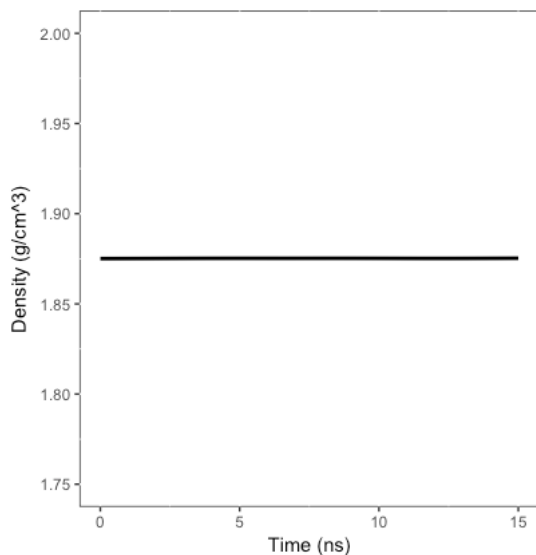


Figure 34: Modified C<sub>5</sub>N<sub>2</sub> –Density profile at 500 K

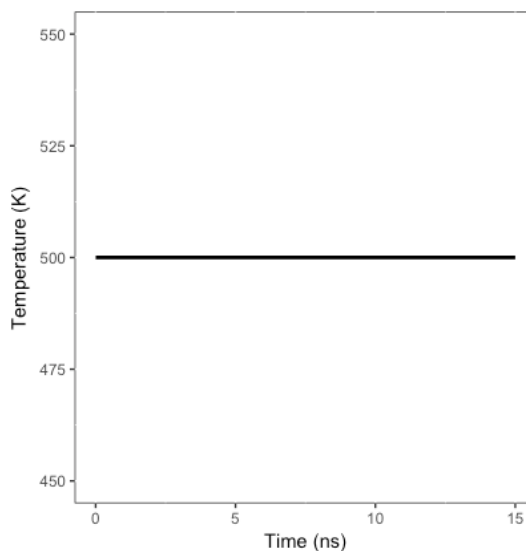


Figure 35: Modified C<sub>5</sub>N<sub>2</sub> – Temperature profile at 500 K

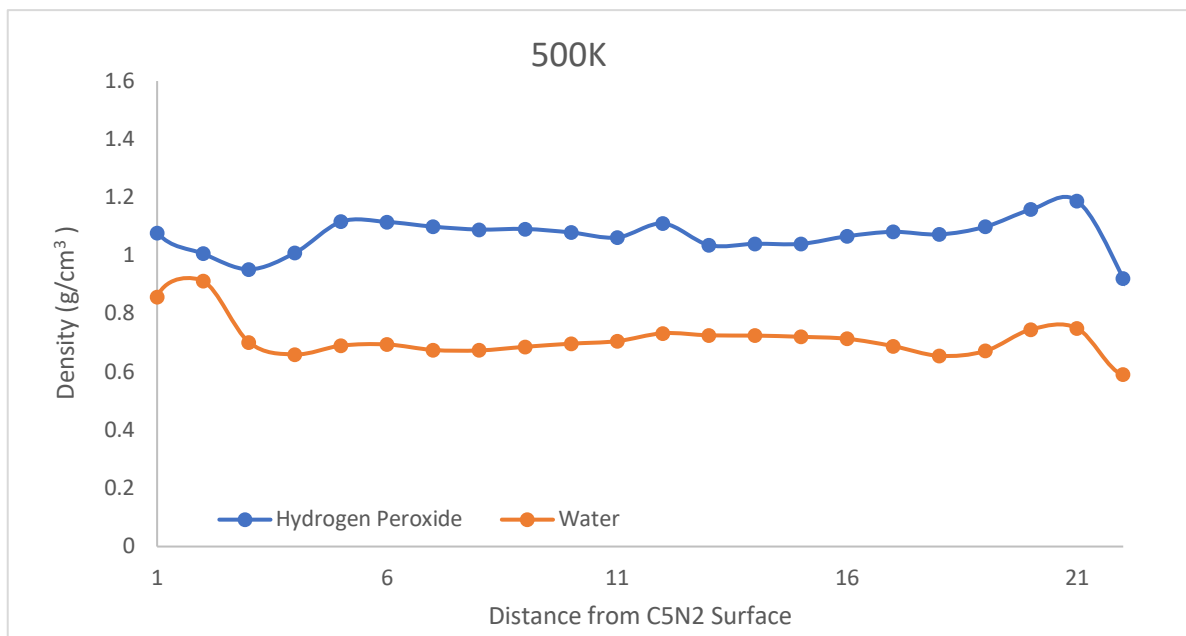


Figure 36: Modified C<sub>5</sub>N<sub>2</sub> - Hydrogen peroxide and water density profiles as a function of distance from the catalyst surface at 500 K.

The behavior of hydrogen peroxide and water at 500 K is similar to the system at 350 K. The amount of water is greatest near the surface while the density of hydrogen peroxide is slightly less near the surface than throughout the bulk solution. It is important to note that the amount of hydrogen peroxide and water at the surface have both slightly decreased from 350 K which proves that at 500 K the separation of hydrogen peroxide from the surface will be easier at the expense of slightly less water at the surface to react.

(c) 750 K

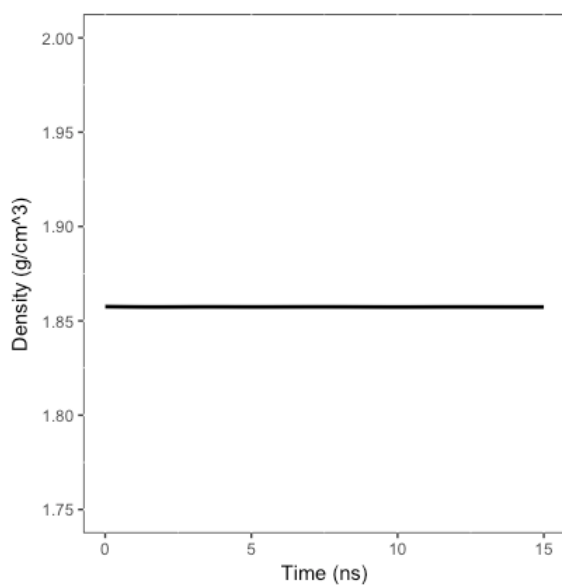


Figure 37: Modified  $C_5N_2$  – Density profile at 750 K.

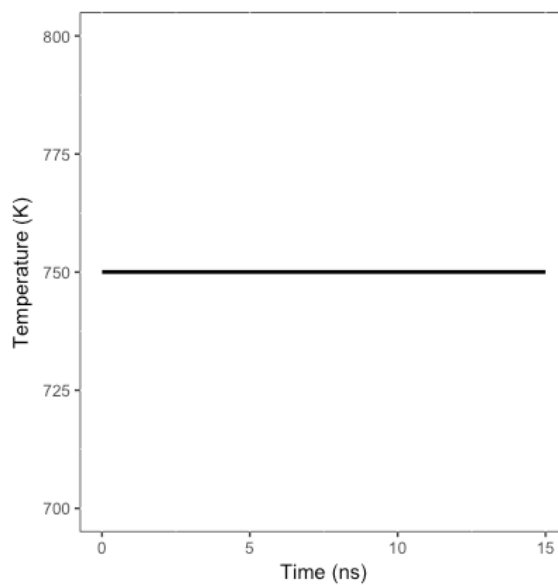


Figure 38: Modified  $C_5N_2$  – Temperature profile at 750 K.

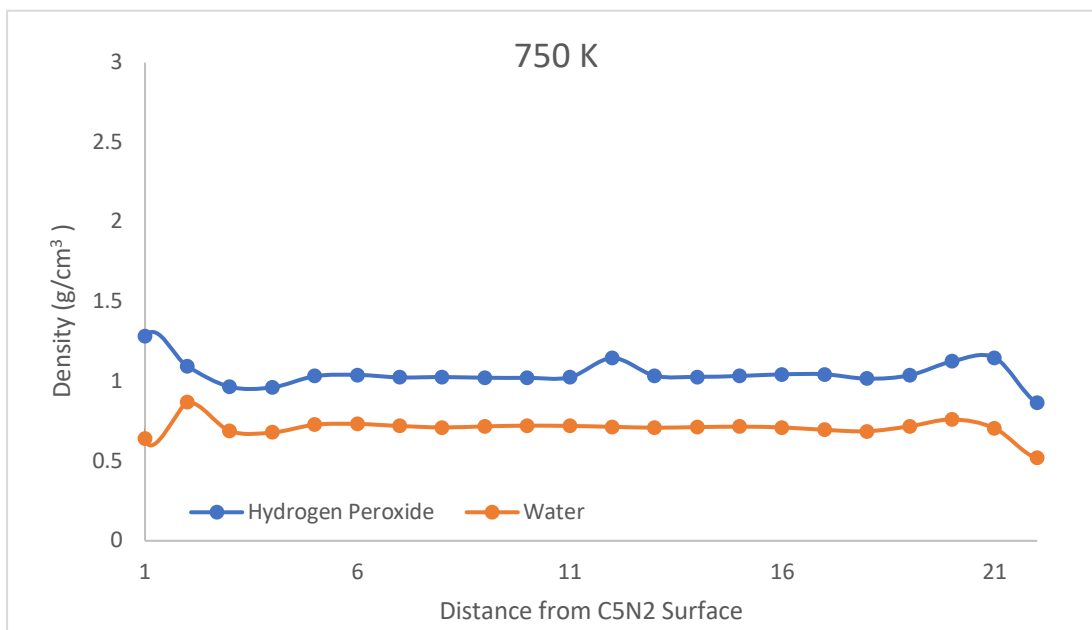


Figure 39: Modified C<sub>5</sub>N<sub>2</sub> – Hydrogen peroxide and water density profiles as a function of distance from the catalyst surface at 750 K.

The behavior of the system at 750 K is unfavorable for both the reaction and separation of hydrogen peroxide from the catalyst surface. The density profiles for hydrogen peroxide and water at 750 K strongly varies from the behavior of the system at 350 K and 500 K. The surface behavior of hydrogen peroxide and water are completely opposing. Hydrogen peroxide was observed to have a strong attraction to the surface while water collected away from the surface, which is opposite of the system at 350 K and 500 K. The attraction of hydrogen peroxide and decrease in density of water at the surface will result in difficult separation of hydrogen peroxide from the catalyst surface in addition to not allowing water to interact with the surface for additional reactions.

The modified C<sub>5</sub>N<sub>2</sub> exhibits different properties at 350 K, 500 K, and 750 K. The density profiles of the system at 750 K proves that at elevated temperatures, hydrogen peroxide will have

a stronger tendency to collect at the surface causing water to have a lower density near the surface. This behavior will not only increase the difficulty of separation but will also decrease the production of hydrogen peroxide. Finally, the mixture experiences favorable behavior at 350 K and 500 K. Water tends to significantly collect on the surface for both temperatures, but a slight decrease in density of hydrogen peroxide near the surface at 500 K from 350 K was observed. Since a strong attraction of water was still observed at 500 K, it suggests the reaction and separation will best be observed at 500 K

### **4.3 Conclusion**

The simulations performed on a 50/50 wt% solution of hydrogen peroxide and water provided insight into the behavior of the system at 350 K, 500 K, and 750 K, due to the interactions resulting from  $C_5N_2$ . The simulations studied the behavior of the system with both pristine and modified  $C_5N_2$ . The simulations help understand the feasibility of using carbon nitrides as an alternative production method. The current alternative production methods of hydrogen peroxide are hindered by low yields and difficult separation. A process that will challenge not only the anthraquinone process, but other alternative methods, will need to not experience these limitations. The charge distribution present on the pristine and modified  $C_5N_2$  surface promotes the coulombic attraction between the hydrogen atoms of water and hydrogen peroxide molecules which results in the hydrogen atoms immediately bonding to the nitrogen atoms on the surface. Hydrogen peroxide and water's attraction to the nitrogen on the surfaces of pristine and modified  $C_5N_2$  do not necessarily hinder the movement of molecules to the surface. The movement of water and hydrogen peroxide to the catalyst surface occurred at various temperatures. Since the nitrogen

atoms do not participate as an active site on the catalyst and the molecules attached to the surface do not repel water, the interaction required for the reaction can still occur.

The collection of hydrogen peroxide on the surface becomes prevalent over water for pristine and modified surfaces at 750 K. This not only hinders further reactions but increases the difficulty of separating hydrogen peroxide from the surface of the catalyst. Although it was observed that at 350 K for the modified surface there was a slightly stronger attraction of water near the surface, the following reasons prove 500 K is best for the reactions. The pristine surface has the most favorable density profile near the surface for water at 500 K. In addition, the density profile of hydrogen peroxide at the pristine surface decreases as temperature increases, further supporting the conclusion that 500 K is better for the reaction than 350 K. The density profile of hydrogen peroxide with the pristine surface at 500 K gradually increases as the distance from the catalyst surface increases which proves favorable for the separation of hydrogen peroxide. In addition, the density profile of hydrogen peroxide for the modified surface slightly decreases with the density profile of water from 350 K to 500 K. Although the density of water also slightly decreases at 500 K a strong attraction of water to the surface was still observed, indicating that water is still significantly present for additional reactions.

The following density profile, shown in figure 40, demonstrates the behavior of both pristine and modified catalyst surfaces with hydrogen peroxide at 500 K. It is clear hydrogen peroxide tends to collect further away from the surface of the pristine catalyst at 500 K. Although this will decrease the ability to separate hydrogen peroxide from the catalyst surface as the reaction occurs, it is not expected to significantly alter the yield, as water still collects significantly on the modified surface as shown in figure 41. In conclusion, hydrogen peroxide experiences favorable behavior for both pristine and modified  $C_5N_2$  at 500 K, despite demonstrating slightly more



attraction to the surface as the reaction affects the catalyst surface. Water experiences a slight decrease in density at the surface for modified  $C_5N_2$ ; however, the effect is small and a strong attraction to the surface is still observed.

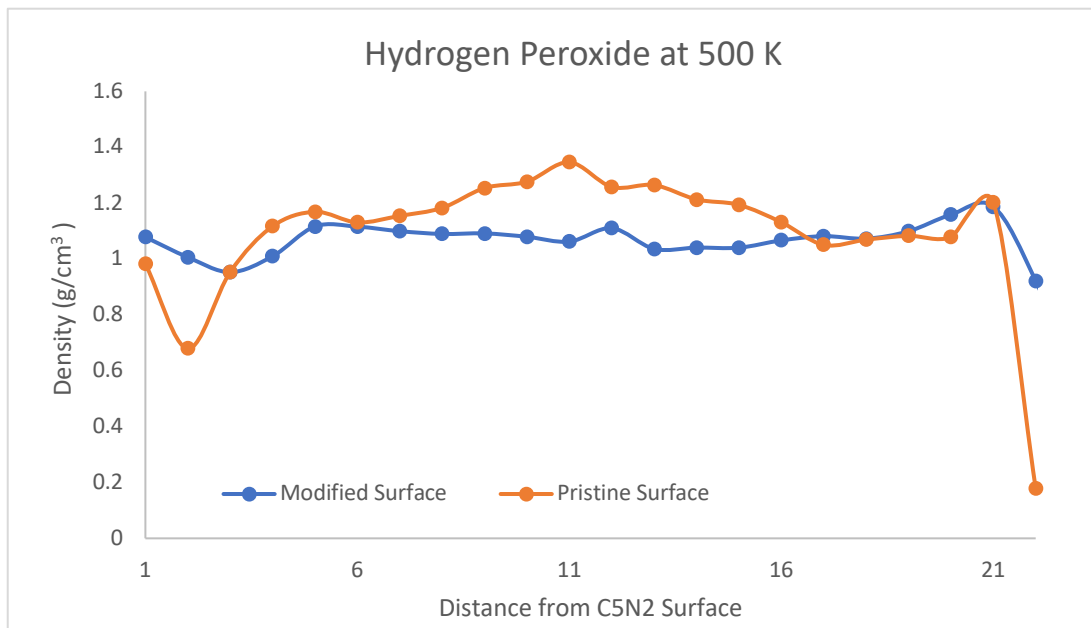


Figure 40: Hydrogen peroxide density profiles as a function of distance from the catalyst surface at 500 K for pristine and modified surfaces.

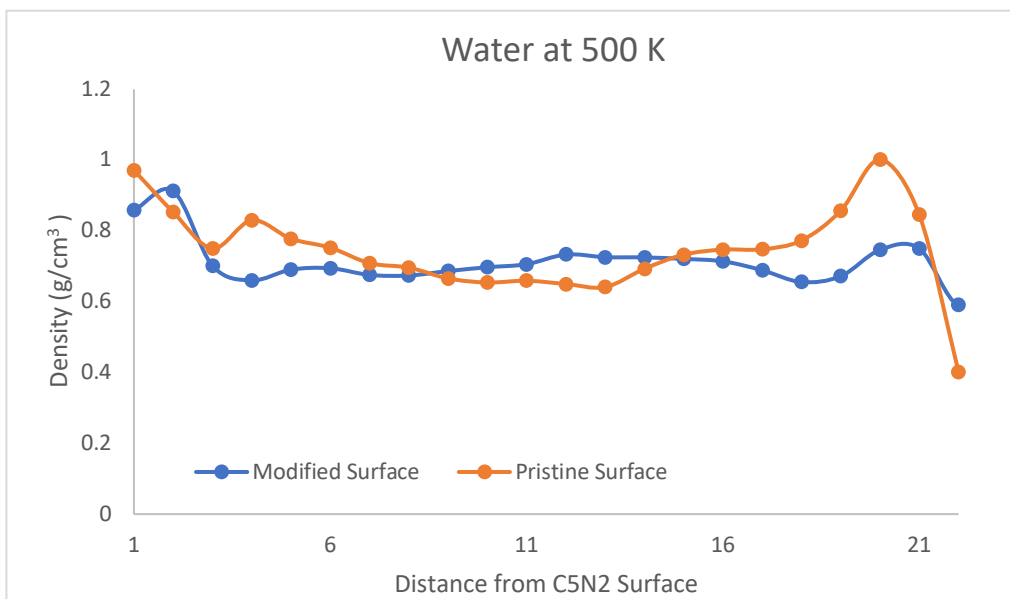


Figure 41: Water density profiles as a function of distance from the catalyst surface at 500 K for pristine and modified surfaces.

#### 4.4 Outlook

This study aimed to understand the interaction of hydrogen peroxide and water with effects from C<sub>5</sub>N<sub>2</sub> modifying the charges of the active sites to account for the O-H molecules that will be present on the surface post reaction. The calculations show that the modified sites have an unfavorable effect on the behavior of hydrogen peroxide and water. Changing the number of modified sites can provide a more comprehensive understanding of these effects and possible limitations that could arise as more reactions occur. Although the reaction has been studied and proven to occur on the carbon atoms separated from a nitrogen atom by a carbon atom on each side, the mixture studied is randomly packed. When the reaction occurs, hydrogen peroxide will be closer to the surface than the initial system used in this study. Studying systems where hydrogen

peroxide is placed at the pores of the catalyst or near the active sites will provide a better understanding of the mixture directly after a reaction occurs.

The Lennard-Jones parameters for hydrogen peroxide can be studied more thoroughly, specifically at various concentrations, to ensure the adapted SPC/E model was the most accurate for modeling hydrogen peroxide. In addition to confirming these parameters, performing the calculations at additional ratios of hydrogen peroxide to water could provide insight into how much hydrogen peroxide can be produced before any significant effects from these molecules will occur, especially at elevated temperatures.

The carbon nitride studied in these calculations was  $C_5N_2$ . Changing the amount of nitrogen in the catalyst could have desirable effects on the behavior of the mixture. The number of nitrogen atoms present in the catalyst would alter the charges throughout the catalyst surface which will significantly change the behavior of the solution. Studying the interaction of hydrogen peroxide and water with various amount of nitrogen atoms on the surface of the catalyst would provide a better understand of the catalyst.

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