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### Interactions of Carbon Dioxide on Nickel Surface: A Reactive Molecular Dynamics Study of Plasma- Catalysis

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# Interactions of Carbon Dioxide on Nickel Surface: A Reactive Molecular Dynamics Study of Plasma-Catalysis

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## Abstract

The adsorption probability and reaction behavior of CO<sub>2</sub> on nickel catalyst surfaces are investigated employing reactive molecular dynamics (MD) simulations using the ReaxFF potential. Such catalyst is used in the dry reforming reaction where greenhouse gases, carbon dioxide and methane, react producing synthesis gas, a potential clean energy source. However, this reaction is strongly endothermic due to the reactants' thermodynamic stability and requires a significant amount of energy. The selectivity and energy efficiency can be improved by combining a nonthermal plasma with a catalyst. Further insight into the underlying mechanisms of this process is needed to increase its applicability. Through reactive molecular dynamics simulations, it is possible to obtain a complete description of the reactions at the atomic scale. In this research, single impacts of carbon dioxide were performed on a clean Ni(111) surface and a Ni(111) surface partially covered with methyl groups at a temperature of 400 K. CO<sub>2</sub> remained kinetically stable on both surfaces after impact.

## I. Introduction

In the dry reforming reaction (DRR), two of the most harmful greenhouse gases, carbon dioxide and methane, react to produce synthesis gas (a mixture of CO and H<sub>2</sub>). This process is gaining increasing interest worldwide due to global climate change and an increase in energy consumption.<sup>1</sup> It can also be considered to fit the "cradle-to-cradle" concept since it aims to convert waste into new raw materials for the chemical industry. The synthesis gas can be used to produce clean energy, hydrogen, ammonia, methanol, and synthetic hydrocarbon fuels.<sup>2</sup> Usually, this reaction is catalyzed by nickel, and it is strongly endothermic due to the reactants' thermodynamic stability, requiring a significant amount of energy for their dissociation. A promising method to improve this reaction is the combination of catalysis and plasma, named plasma catalysis.<sup>3</sup>

Catalysis is already a mature field in chemistry, and this technology is utilized in about 80% of industrial processes.<sup>3</sup> Catalysis is defined as the process in which the reaction rate is increased without changing the overall standard Gibbs energy change. The rate increases due to the decrease in the activation barrier by stabilizing the transition state and the regeneration of catalyst after each reaction cycle. Due to the high stability of carbon dioxide and methane, the dry reforming reaction using just thermal catalysis is more efficient at a temperature greater than 1000 K.<sup>4</sup>

A plasma or gas discharge is a partially ionized gas consisting of free electrons, ions, photons, neutral molecules, radicals, and excited species. A plasma is created when an electric field of sufficient magnitude is applied to a gas, making free electrons collide with heavier gas particles and generating a rich mix of reactive species.<sup>5</sup> These species can interact with each other creating a reactive environment. In this paper, the focus will be

on low-temperature plasma, which a key characteristic is a far-from-equilibrium state at relatively low temperatures, typically in the range 300 - 1000 K.<sup>4</sup> This allows the combination of reactivity, far-from-equilibrium state, and low-temperature operations, enabling plasma to be used for many complex applications, including catalysis. However, plasma lacks selectivity in terms of product formation. For DRR, typical products formed are syngas, higher hydrocarbons, oxygenates, such as methanol, ethanol, formaldehyde, acetaldehyde, and carboxylic acids.<sup>3</sup>

The selectivity and energy efficiency of dry reforming reaction can be improved by combining the plasma with a catalyst. The plasma can activate the inert molecules, such as CO<sub>2</sub> and CH<sub>4</sub>, and induce reactions at reduced temperatures, while the catalyst can increase the selectivity towards specific reaction products.<sup>2</sup> The effect of combining the plasma with the catalyst was up to 50% higher than the sum of their individual effects, and this phenomenon is often termed synergy. This occurs because plasma and catalyst have independent effects and display some interdependence, as the plasma affects catalyst properties and its activity, and vice-versa.<sup>5</sup>

The plasma can enhance the formation of smaller catalyst nanoparticles, which results in a larger surface area and higher catalytic activity. This dispersion also increases the catalyst lifetime since it reduces coke formation on the surface. Also, the plasma can cause modifications to the catalyst structure.<sup>4</sup> For example, during DRR, some oxygen can adsorb on the catalyst, creating an oxide surface. Plasma can induce NiO reduction to a metallic surface (Ni), which has a higher catalytic activity.<sup>6</sup> Additionally, the plasma can induce reactions at a lower temperature at the catalyst surface since the active species formed on plasma have more energy when compared with the initial stable gas molecules.

The activation energy is lower since the difference between the activated species and transition states is reduced, and less energy is required for the reaction to happen.<sup>2</sup>

The catalyst can affect plasma properties by enhancing the electric field distribution near the surface. Consequently, the same applied power yields higher electron energy, increasing the ionization and dissociation of gas molecules, making the plasma more energy efficient. The presence of catalyst also affects the composition of plasma species. When a species is adsorbed on the catalyst surface, it will no longer be available to interact with other species on the plasma, contributing to increased selectivity toward targeted products.<sup>5</sup>

Plasma catalysis is already a highly successful approach for the small-scale fabrication of expensive materials, including carbon nanotubes and inorganic nanowires. However, plasma catalysis is still an expensive process for large-scale applications due to the high investment in specialized equipment and energy needed to generate and maintain a plasma.<sup>3</sup> Moreover, additional energy costs associated with the plasma generation may be offset by the benefits offered by the synergistic plasma-catalytic processes, including operation at reduced temperature, selectivity toward forming value-added products, reducing catalyst poisoning, and a speedy switch-on time.<sup>4</sup>

The interactions between plasma and catalyst and their effects demonstrate the complexity of plasma catalysis. Due to the inherent complexity, the basic processes taking place in plasma catalysis are not well understood. Further insight into the underlying physical and chemical processes is crucial for a complete comprehension of the process and increase applicability in large-scale processes. Through reactive molecular dynamics simulations using ReaxFF potentials is possible to obtain a better understanding of the reactions at the atomic scale.<sup>1</sup>

## II. Methods

### 2.1 Molecular Dynamics

In a MD simulation, the trajectories of all atoms in the system are followed through space and time by integrating the equations of motion. Forces between the atoms are derived from a suitable interatomic potential. The potential used in this work is the Ni/C/O/H Reactive Force Field (ReaxFF) potential developed and validated by Shin and co-workers.<sup>7</sup> ReaxFF is based on the bond order/bond distance relationship.<sup>1</sup>

The total system energy is divided over partial energy terms related to pair interactions, lone electron pairs, atomic under- and over coordination, valence and torsion angles, conjugation, hydrogen bonding, and van der Waals and Coulomb interactions. The van der Waals and Coulomb interactions are calculated between every pair of atoms so that ReaxFF describes covalent bonds and nonbonded interactions between all atoms. Charge distributions are calculated with the electron equilibrated method, which is based on the geometry and connectivity of the system.<sup>8</sup>

Molecular dynamics simulations are intended to capture the system's dynamics at the atomic scale. The focus is on the short timescale dynamic phenomena, such as adsorption and desorption on nickel catalyst surface to improve the insight in dry reforming reaction system using plasma catalysis.<sup>2</sup>

### 2.2 Simulation Method

In this study, the simulations were performed with the Ni(111) surface, which is the most stable and the most abundant surface facet in typical nickel catalysts.<sup>6</sup> The Ni(111) slab used in this work consists of 300 atoms equally divided over six layers, as illustrated in Figure 1.

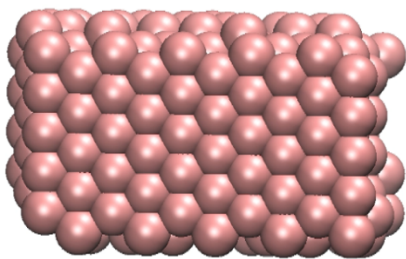


Figure 1: Top view of Ni(111) slab

Simulations were also performed using a Ni(111) surface with twelve methyl adsorbates to study the effects of plasma catalysis, as illustrated in figure 2.

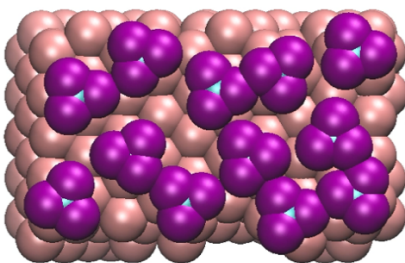


Figure 2: Top view of Ni(111) slab with 12 adsorbed methyl radicals

All surfaces were first equilibrated at 400 K using the Bussi thermostat with a coupling constant of 100 fs, followed by a relaxation in the microcanonical ensemble. In this ensemble, also referred to as the NVE ensemble, the system's total energy ( $E$ ) is conserved. Furthermore, the number of particles ( $N$ ) in this isolated system and the volume ( $V$ ) are kept fixed. To simulate a semi-infinite surface, periodic boundary conditions are applied in the  $\{x,y\}$  directions.

Single  $\text{CO}_2$  impacts were performed at 400 K, a typical temperature for low-temperature plasma. Every single impact was performed for a total simulation time of 5 ps. The carbon dioxide was added to the system at a  $z$  position of 10 Å above the top layer of the nickel surface and with initial random  $\{x,y\}$  coordinates. The incident molecule was

randomly rotated about the central carbon atom, and its z-velocity was set to the root-mean-square velocity corresponding to the substrate temperature of 400 K. Impacts on the catalyst surface with 12 adsorbed methyl radicals were performed to further study the reactions after adsorption and mimic experimental conditions. When the radical impacts on the surface, it can be absorbed, reflected, or decomposed. The impacts were repeated 500 times for each surface to obtain a statistically reasonable result.

The simulations were performed on the large-scale atomic/molecular massively parallel simulator (LAMMPS), a classical molecular dynamics code that models ensembles of particles in a liquid, solid, or gaseous state. In the most general sense, LAMMPS integrates Newton's equations of motion for a collection of interacting particles and uses neighbor lists to keep track of nearby particles. The lists are optimized for systems with repulsive particles at short distances so that the local density of particles never becomes too large.<sup>9</sup>

The LAMMPS is executed by reading commands from an input script (appendix 1), one line at a time. The input file directs LAMMPS to read the data file, which contains basic information about the size of the simulation, the initial atomic coordinates, and molecular topology. The input file and data files were written using a python script (appendix 2) which generated initial random  $\{x,y\}$  coordinates for carbon dioxide and calculated its velocity magnitude at 400 K. The LAMMPS was coupled with python, enabling a python script to automatize the process to run LAMMPS from the command line.

Four files are written after each simulation: log, dump, and species. The thermodynamic information is printed periodically on the log file, every 100 timesteps, including temperature, pressure, kinetic energy, potential energy, and total energy. Since



the goal of these molecular dynamic simulations was to get information about the dynamics of the system, this information was used just to verify if the system is in the expected temperature. The dump file provided the charge and x, y, z coordinates for each atom every 400 timesteps, and this file was used to create the trajectories to visualize the system dynamics. The species file shows the chemical species information computed by the ReaxFF at every 100 timesteps. The statistical analysis was performed using a python script (appendix 3) to analyze the species files and determine the reflected and adsorbed molecules (that reacted or not) and the reaction and sticking probability.

### III. Results

Table 1 – Results of single impacts of CO<sub>2</sub> on a clean surface

Total impacts	500
Reflected molecules	500
Adsorbed molecules	0
Reaction probability	0 %
Sticking probability	0 %

Table 2 – Results of single impacts of CO<sub>2</sub> on the surface with 12 adsorbed methyl

Total impacts	500
Reflected molecules	500
Adsorbed molecules	0
Reaction probability	0 %
Sticking probability	0 %
Free radicals	H

### IV. Discussion

In this study, molecular dynamics were used to study carbon dioxide interactions on a clean Ni(111) surface and a Ni(111) surface with adsorbed methyl radicals. There are

two types of adsorptions on a surface: physisorption and chemisorption. In physisorption, the gas molecules accumulate on the surface due to weak intermolecular forces, usually van der Waals forces. Chemisorption is strongly bound adsorption, where a chemical bond is formed between the gas molecules and the surface.<sup>10</sup> In this study, adsorption refers to chemisorption, and the sticking probability refers to the probability that molecules impacted on the surface will adsorb chemically.

During simulations on both surfaces, in certain timesteps was observed some adsorption or dissociation of carbon dioxide. However, the adsorption was not sufficiently strong on the catalyst. The species immediately desorbed into the gas phase and was not chemically modified.

As expected, no reaction or dissociations were observed for CO<sub>2</sub> on a clean catalyst surface at 400K since the catalyzed dry reforming reaction is usually carried at high temperature due to the thermodynamic stability of reactants. These simulations were performed as a control.

To simulate the effect of plasma, methyl radicals generated by fragmentation of methane were adsorbed on the catalyst surface. The methane requires less energy (868.4 kJ/mol) to dissociate due to electron impact than carbon dioxide (1109.6 kJ/mol), so in a plasma-catalysis system is more probable first to dissociate the methane.<sup>5</sup>

In general, there are three high-symmetry adsorption sites on the Ni(111) crystal surface shown in figure 3. The atop site resides above a surface atom, a 3-fold hollow site labeled fcc, and one bridge site, which lies halfway between the neighbor atoms.<sup>11</sup>

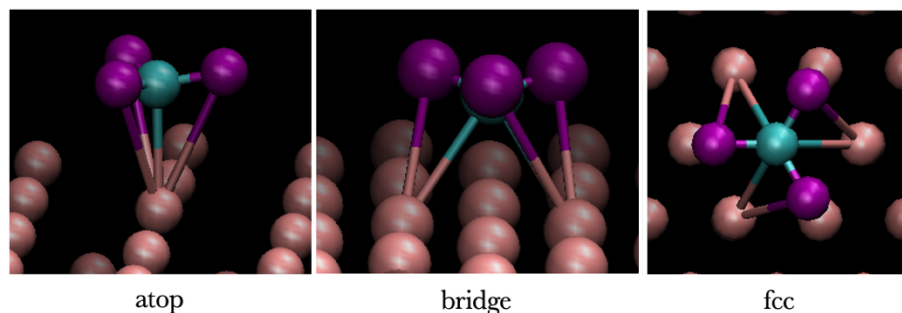


Figure 3: Adsorption site Ni(111)

Studies showed that the adsorption fcc site is preferred since the binding energy is more negative (-197 kJ/mol) than a bridge (-171 kJ/mol) and top (-169 kJ/mol).<sup>11</sup> The position of 11 of methyl were at fcc site and one at top site, which agrees with the studies showing that the fcc position is more stable. The symmetry also agrees with previous studies, and all the methyl radicals had  $C_{3v}$  symmetry.

The surface with methyl radicals adsorbed on the surface is only one of the various possibilities in the system since methane can have sequential hydrogen abstraction forming methylene ( $\text{CH}_2^*$ ), Methylidyne ( $\text{CH}^*$ ), and atomic C and H.<sup>6</sup> Since the results were similar to the simulations with a clean surface and the carbon dioxide remained stable, this suggests that other adsorbed molecular fragments should be investigated. Future work should include simulations with surfaces containing methylene, methylidyne, carbon, and hydrogen to investigate which surface condition will improve the interactions of carbon dioxide and can be a probable mechanism in dry reforming plasma catalysis.

## V. Conclusions

Both surfaces presented similar results with no probability of reaction or chemisorption of carbon dioxide. The simulations performed to mimic plasma catalysis were one of the several possibilities that could occur. These results indicate that probably the methane molecules have more hydrogen abstractions. Future steps should include simulations with surfaces containing adsorbed species generated by sequential hydrogen abstraction from methane. The results suggest that this is not the most probable mechanism for the dry reforming reaction using plasma catalysis. However, it contributes to understanding the fundamental interactions of this complex system since this possibility of mechanism can be considered not probable.

## VI. Acknowledgments

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## VIII. Supporting Information

### Appendix 1 – Example input file

```
# Ni(111) with 12 CH3 single CO2 impact normal to surface
units real
atom_style charge
processors 2 1 1
boundary p p f
read_data data.Ni-12CH3-CO2-1
balance 1.0 shift xyz 5 1.1
pair_style reax/c NULL enobonds yes
pair_coeff * * ffield.reaxPtNiCHO Ni C H O
neighbor 2 bin
neigh_modify every 1 delay 1 check no

group mobileNi id 1:250 301:348
group bpdNi id 101:250
group frozenNi id 251:300
group CO2 id 349:351
group mobile id 1:250 301:348 349:351

velocity frozenNi zero linear
velocity CO2 zero linear
velocity mobileNi create 400.0 18034064 mom yes dist gaussian

fix 1 frozenNi setforce 0.0 0.0 0.0
fix 2 bpdNi temp/csvr 400.0 400.0 100.0 76397251
fix 3 mobileNi nve
fix 4 all qeq/reax 1 0.0 10.0 1e-6 reax/c

timestep 0.25
compute mobileTemp mobile temp
thermo 100
thermo_style custom step temp c_mobileTemp press ke pe etotal
dump 1 all custom 400 dump.reax.fullNi-12CH3-CO2-1 id type q x y z
run 20000
velocity CO2 set 0.0 0.0 -0.0047613170032144185
unfix 3
fix 5 mobile nve
fix 6 all reax/c/species 1 10 100 Ni-12CH3-CO2-1.species &
    cutoff 1 1 1.0 &
    cutoff 1 2 0.3 &
    cutoff 1 3 0.3 &
    cutoff 1 4 0.3 &
    cutoff 2 2 0.3 &
    cutoff 2 3 0.3 &
    cutoff 2 4 0.3 &
    cutoff 3 3 0.3 &
    cutoff 3 4 0.3 &
    cutoff 4 4 0.3 &
    element Ni C H O

dump 2 all custom 400 dump.reax.Ni-12CH3-CO2-1 id type q x y z
run 20000
```

## Appendix 2 – Python script (summary) to generate input and data file

```
import math
import random
import os
import shutil
import glob
import numpy as np
import scipy
from scipy.stats import maxwell
from scipy.constants import R
from scipy.constants import k
from euclid import *

co2_temp = 400.0                # CO2 temperature (K)
slab_temp = 400.0              # slab temperature (K)

equil_time_ps = 5               # length of time to equilibrate slab
(in ps)
sim_time_ps = 5                 # length of time to simulate after CO2
initiation (in ps)
timestep_fs = 0.25             # timestep (in fs)

xmin = 0.000                   # simulation box dimensions
xmax = 21.58
ymin = 0.000
ymax = 12.46
zmin = -20.0
zmax = 1000

co2_z_offset = 10.0            # desired z distance of CO2 from slab
surface
slab_surface_z = 0             # z position of top slab layer
co2_z_pos = co2_z_offset - slab_surface_z

c_mass_kg = 0.012011
o_mass_kg = 0.016000

equil_steps = int(equil_time_ps*1000/timestep_fs)
sim_steps = int(sim_time_ps*1000/timestep_fs)

for x in range (1,501):

    # RANDOM NUMBER GENERATORS

    random.seed(x)
    velocity_seed = random.randint(1,99999999)
    tempcsvr_seed = random.randint(1,99999999)

    # PLACE CO2 MOLECULE

    # get alpha, beta, and gamma angles to rotate CO2 about C atom
    C_0 = Vector3(0, 0, 0)
    O1_0 = Vector3(-1.275, 0, 0)
    O2_0 = Vector3(1.275, 0, 0)

    alpha = random.uniform(0,2)
    rotate_x = Matrix4.new_rotatex(alpha*math.pi)
    C_Rx = rotate_x * C_0
    O1_Rx = rotate_x * O1_0
    O2_Rx = rotate_x * O2_0

    beta = random.uniform(0,2)
    rotate_y = Matrix4.new_rotatey(beta*math.pi)
    C_Rxy = rotate_y * C_Rx
    O1_Rxy = rotate_y * O1_Rx
    O2_Rxy = rotate_y * O2_Rx

    gamma = random.uniform(0,2)
    rotate_z = Matrix4.new_rotatez(gamma*math.pi)
    C_Rxyz = rotate_z * C_Rxy
    O1_Rxyz = rotate_z * O1_Rxy
    O2_Rxyz = rotate_z * O2_Rxy
```

```

# get random x and y coordinates for C atom in CO2
shift_x = random.uniform(xmin,xmax)
shift_y = random.uniform(ymin,ymax)
shift_z = co2_z_pos

shift = Vector3(shift_x, shift_y, shift_z)

C = C_Rxyz + shift
O1 = O1_Rxyz + shift
O2 = O2_Rxyz + shift

# wrap coordinates if they are outside periodic box
# RANDOM VELOCITIES

# CO2 velocity
# incoming normal to surface with vrms from Maxwell-Boltzmann distribution
co2_vx = 0.000000
co2_vy = 0.000000
co2_vz = -1*(math.sqrt((3*R*co2_temp)/(c_mass_kg + o_mass_kg +
o_mass_kg)))/100000

# MAKE NEW DIRECTORY

new_folder = "Ni-12CH3-CO2-" + str(x)
if not os.path.exists(new_folder):
    os.makedirs(new_folder)
os.chdir(new_folder)

# WRITE IN. AND DATA. FILES

with open('in.Ni-12CH3-CO2-' + str(x), 'w') as inWriter, open('data.Ni-12CH3-
CO2-' + str(x), 'w') as dataWriter, open('run.py', 'w') as runWriter:

    # write in. file with CO2 velocity and temp for chosen temperature, and
    random seeds
    os.chdir("../")

```

### Appendix 3 – Python script to perform statistical analyses of species files

```

import os
import readline
import fnmatch

surf = 111
temp = 400

Total = 0
Reflect = 0
Adsorb = 0
AdsorbNoRxn = 0
AdsorbRxn = 0
StickProb = 0
StickRxnProb = 0
RxnProb = 0

BrokenCO = 0
OneBrokenCO = 0
TwoBrokenCO = 0

AdsorbNoRxn = 0
AdsorbCO = 0
AdsorbC = 0
AdsorbO = 0
AdsorbO2 = 0

FreeCO = 0
FreeC = 0
FreeO = 0
FreeO2 = 0

```



```

for x in range(1,501):

    folder = "Ni-CO2-" + str(x)
    os.chdir(folder)

    file = open("Ni" + "-CO2-" + str(x) + ".species", 'r').readlines()
    num = file[-1].split()
    spec = file[-2].split()

    try: num1 = int(num[-1])
    except ValueError: pass
    try: num2 = int(num[-2])
    except ValueError: pass
    try: num3 = int(num[-3])
    except ValueError: pass
    try: num4 = int(num[-4])
    except ValueError: pass

    spec1 = str(spec[-1])
    spec2 = str(spec[-2])
    spec3 = str(spec[-3])
    spec4 = str(spec[-4])
    spec5 = str(spec[-5])

    Total = Total + 1

# STICKING PROBABILITY

    if fnmatch.fnmatch(spec1,"CO2") or fnmatch.fnmatch(spec2,"CO2"):
        Reflect = Reflect + 1

    elif fnmatch.fnmatch(spec1,"Ni*CO2") or fnmatch.fnmatch(spec2,"Ni*CO2"):
        AdsorbNoRxn = AdsorbNoRxn + 1

    else:
        AdsorbRxn = AdsorbRxn + 1

# ADSORBED SPECIES

    # CO

        if fnmatch.fnmatch(spec1,"Ni*CO") or fnmatch.fnmatch(spec2,"Ni*CO") or
fnmatch.fnmatch(spec3,"Ni*CO") or fnmatch.fnmatch(spec4,"Ni*CO"):
            AdsorbCO = AdsorbCO + 1
            OneBrokenCO = OneBrokenCO + 1

    # C

        if fnmatch.fnmatch(spec1,"Ni*C") or fnmatch.fnmatch(spec2,"Ni*C") or
fnmatch.fnmatch(spec3,"Ni*C") or fnmatch.fnmatch(spec4,"Ni*C"):
            AdsorbC = AdsorbC + 1
            TwoBrokenCO = TwoBrokenCO + 1

    # O2

        if fnmatch.fnmatch(spec1,"NiO2") or fnmatch.fnmatch(spec1,"Ni[0-9]O2"):
            AdsorbO2 = AdsorbO2 + 1

    # O

        if fnmatch.fnmatch(spec1,"NiO") or fnmatch.fnmatch(spec1,"Ni[0-9]O"):
            AdsorbH = AdsorbH + num1

        if fnmatch.fnmatch(spec2,"NiO") or fnmatch.fnmatch(spec2,"Ni[0-9]O"):
            AdsorbO = AdsorbO + num2

# FREE SPECIES

    # CO2

        if fnmatch.fnmatch(spec1,"CO") or fnmatch.fnmatch(spec2,"CO") or
fnmatch.fnmatch(spec3,"CO") or fnmatch.fnmatch(spec4,"CO"):
            FreeCO = FreeCO + 1

```

```

        OneBrokenCO = OneBrokenCO + 1

    # C
    if fnmatch.fnmatch(spec1,"C") or fnmatch.fnmatch(spec2,"C") or
fnmatch.fnmatch(spec3,"C") or fnmatch.fnmatch(spec4,"C"):
        FreeC = FreeC + 1
        TwoBrokenCO = TwoBrokenCO + 1

    # O2
    if fnmatch.fnmatch(spec1,"O2") or fnmatch.fnmatch(spec2,"O2") or
fnmatch.fnmatch(spec3,"O2") or fnmatch.fnmatch(spec4,"O2"):
        FreeO2 = FreeH2 + 1

    # O
    if fnmatch.fnmatch(spec1,"O"):
        FreeH = FreeH + num1

    if fnmatch.fnmatch(spec2,"O"):
        FreeH = FreeH + num2

    os.chdir("../")

Adsorb = AdsorbNoRxn + AdsorbRxn

StickProb = float(100.000*Adsorb/Total)
StickProbOut = format(StickProb, '.3f')

RxnProb = float(100.000*AdsorbRxn/Total)
RxnProbOut = format(RxnProb, '.3f')

if Adsorb != 0:
    StickRxnProb = float(100.000*AdsorbRxn/Adsorb)
    StickRxnProbOut = format(StickRxnProb, '.3f')

    BrokenCO = OneBrokenCO + 2*TwoBrokenCO
    BrokenCOper = float(1.000*BrokenCO/Adsorb)
    BrokenCOperOut = format(BrokenCOper, '.3f')

    TotalC = Total
    TotalO = 2*Total

    FracNoBrokenCO = float(100.000*AdsorbNoRxn/Adsorb)
    FracNoBrokenCOOut = format(FracNoBrokenCO, '.3f')

    FracOneBrokenCO = float(100.000*OneBrokenCO/Adsorb)
    FracOneBrokenCOOut = format(FracOneBrokenCO, '.3f')

    FracTwoBrokenCO = float(100.000*TwoBrokenCO/Adsorb)
    FracTwoBrokenCOOut = format(FracTwoBrokenCO, '.3f')

    TotalFrac = FracNoBrokenCO + FracOneBrokenCO + FracTwoBrokenCO
    TotalFracOut = format(TotalFrac, '.3f')

# WRITE OUT FILE

outfile = open("Ni" + str(surf) + "-CO2_" + str(temp) + "K.stats", 'w')

outfile.write("\nTotal Radical Impacts = " + str(Total) + "\n")
outfile.write("Reflected Radicals = " + str(Reflect) + "\n")
outfile.write("Adsorbed Radicals = " + str(Adsorb) + "\n")
outfile.write("  No Reaction = " + str(AdsorbNoRxn) + "\n")
outfile.write("  Reaction   = " + str(AdsorbRxn) + "\n\n")

outfile.write("Reaction = " + RxnProbOut + " %\n")

if Adsorb != 0:
    outfile.write("Adsorption = " + StickProbOut + " %\n")
    outfile.write("Reaction After Adsorption = " + StickRxnProbOut + " %\n\n")
    outfile.write("CH Bonds Broken After Adsorption:\n")
    outfile.write("  Average per Adsorbed CH3 = " + BrokenCOperOut + "\n")

```

```

        outfile.write(" 0 Broken = " + FracNoBrokenCOOut + " %\n")
        outfile.write(" 1 Broken = " + FracOneBrokenCOOut + " %\n")
        outfile.write(" 2 Broken = " + FracTwoBrokenCOOut + " %\n")
        outfile.write("Total Frac = " + TotalFracOut + " %\n\n")

    outfile.write("Adsorbed Species:\n")
    outfile.write(" CO2 = " + str(AdsorbNoRxn) + "\n")
    outfile.write(" CO = " + str(AdsorbCO) + "\n")
    outfile.write(" C = " + str(AdsorbC) + "\n")
    outfile.write(" O = " + str(AdsorbO) + "\n")
    outfile.write(" O2 = " + str(AdsorbO2) + "\n")

    outfile.write("Free Species:\n")
    outfile.write(" CO = " + str(FreeCO) + "\n")
    outfile.write(" C = " + str(FreeC) + "\n")
    outfile.write(" O = " + str(FreeO) + "\n")
    outfile.write(" O2 = " + str(FreeO2) + "\n")

    outfile.close()

# PRINT TO SCREEN

print("\nTotal Radical Impacts = " + str(Total))
print("Reflected Radicals = " + str(Reflect))
print("Adsorbed Radicals = " + str(Adsorb))
print(" No Reaction = " + str(AdsorbNoRxn))
print(" Reaction = " + str(AdsorbRxn))
print()
print("Reaction = " + RxnProbOut + " %")

if Adsorb != 0:
    print("Adsorption = " + StickProbOut + " %")
    print("Reaction After Adsorption = " + StickRxnProbOut + " %")
    print()
    print("CO Bonds Broken After Adsorption:")
    print(" Average per Adsorbed CO = " + BrokenCOperOut)
    print(" 0 Broken = " + FracNoBrokenCOOut + " %")
    print(" 1 Broken = " + FracOneBrokenCOOut + " %")
    print(" 2 Broken = " + FracTwoBrokenCOOut + " %")
    print("Total Frac = " + TotalFracOut + " %")
    print()
    print("Adsorbed Species:")
    print(" CO2 = " + str(AdsorbNoRxn))
    print(" CO = " + str(AdsorbCO))
    print(" C = " + str(AdsorbC))
    print(" O = " + str(AdsorbO))
    print(" O2 = " + str(AdsorbO2))
    print()
    print("Free Species:")
    print(" CO = " + str(FreeCO))
    print(" C = " + str(FreeC))
    print(" O = " + str(FreeO))
    print(" O2 = " + str(FreeO2))

```