Plasma Species Interacting with Nickel Surfaces: Toward an Atomic Scale Understanding of Plasma-Catalysis

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ABSTRACT: The adsorption probability and reaction behavior of CH_x plasma species on various nickel catalyst surfaces is investigated by means of reactive molecular dynamics (MD) simulations using the ReaxFF potential. Such catalysts are used in the reforming of hydrocarbons and in the growth of carbon nanotubes, and further insight in the underlying mechanisms of these processes is needed to increase their applicability. Single and consecutive impacts of CH_x radicals ($x=\{1,2,3\}$) were performed on four different Ni surfaces, at a temperature of 400 K. The adsorption probability is shown to be related to the number of free electrons, i.e. a higher number leads to more adsorptions, and the steric hindrance caused by the hydrogen atoms bonded to the impacting CH_x species. Furthermore, some of the C–H bonds break after adsorption, which generally leads to diffusion of



the hydrogen atom over the surface. Additionally, these adsorbed H-atoms can be used in reactions to form new molecules, such as CH_4 and C_2H_x , although this is dependent on the precise morphology of the surface. New molecules are also formed by subtraction of H-atoms from adsorbed radicals, leading to occasional formation of H_2 and C_2H_x molecules.

1. INTRODUCTION

The interaction of hydrocarbons on nickel catalyst surfaces has an important role in several chemical processes. First, these catalysts are used in the reforming of hydrocarbons to syngas $(H_2 + CO)$, which is an important product in various industrial applications, such as the Fischer–Tropsch process for forming liquid hydrocarbons and the Haber-Bosch process for forming ammonia.¹ Other important chemicals like methanol, dimethyl ether (DME), and formic acid are also formed by reactions involving syngas or one of its components.^{1,2} Although steam reforming and dry reforming of hydrocarbons are both widely used, further optimization is needed, since the energy cost and carbon deposition on the catalyst are too high.^{3–5}

In order to overcome these issues, the combination of nonthermal atmospheric plasma and catalysis, called plasmacatalysis, is gaining more and more interest. This technology not only combines the high reactivity of the plasma with the high selectivity of the catalyst but also leads to additional beneficial synergistic effects.^{6,7} Many experimental studies have been performed, including parameter studies (i.e., frequency, CH_4/CO_2 ratio, applied voltage) and the use of different catalysts, such as nickel.^{6–13} Nevertheless, the exact mechanisms of the interactions of the plasma species at the catalyst surface remain unclear, since it is rather difficult to study these reactions without disturbing the plasma.⁸ As an alternative to experimental work, computer simulations of the interactions between the plasma and the catalyst can allow us to obtain fundamental information about the mechanisms.

Besides plasma-catalysis, the reactivity of hydrocarbons on nickel is also employed in the growth of carbon nanotubes (CNTs), which are characterized by excellent mechanical, optical, and electronic properties.^{14,15} However, the applications of CNTs are currently limited due to the lack of control over the growth and, therefore, the chirality of the tube. As the chirality determines the electronic properties of the CNT, it is of primordial importance to fully understand the growth mechanism to achieve a predefined chirality. As is the case for plasma-catalysis, atomistic simulations of the initial interactions of CNT growth precursors (i.e., hydrocarbon species) with Nicatalysts can increase our insight into the mechanism.¹⁶

The interaction of hydrocarbon species on Ni surfaces was investigated by several authors.^{17–20} Mueller et al. studied the dissociation of adsorbed methyl radicals on nickel surfaces as a function of temperature, by means of molecular dynamics (MD) simulations.¹⁷ It was observed that the Ni(100) surface is more reactive than the Ni(111) surface and that a stepped Ni(111) surface has an intermediate reaction rate. Other studies by the same authors were performed to investigate the dissociation of methane and higher hydrocarbons on nickel surfaces¹⁸ as well as the binding energies of CH_x species on Ni(111).¹⁹ Recently, Liu reported on the dissociative adsorption of methane, ethane, and *n*-butane on Ni(111), for a temperature range of 700 to 1500 K, and proposed a decomposition mechanism for the latter two molecules, again based on MD simulations.²⁰

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Figure 1. (a) Top view of Ni(111), (b) top view of Ni(100), (c) side view of sNi(111)s1, and (d) side view of sNi(111)s2.

Although these works provide a good description of the interactions of several hydrocarbons on Ni surfaces, the interaction of plasma species on these catalyst surfaces under atmospheric plasma conditions has not been described yet. In this work, we performed classical MD simulations, using the ReaxFF potential as developed and previously used by Mueller et al.,^{17–20} to investigate the interaction between typical CH_x plasma species and various nickel catalyst surfaces at a temperature of 400 K, which is typical for plasma-catalysis. Previously, we successfully employed the same technique to investigate Ni-catalyzed growth of carbon nanotubes for both thermal and plasma conditions.^{21–23}

2. COMPUTATIONAL DETAILS

2.1. Molecular Dynamics Simulations. 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 Reactive Force Field (ReaxFF) potential developed by van Duin and co-workers,²⁴ employing the parameters developed by Mueller and co-workers.¹⁷

ReaxFF is based on the bond order/bond distance relationship introduced by Abell and applied to hydrocarbons by Brenner.²⁵ The total system energy is divided over partial energy terms, related to pair interactions, lone electron pairs, atomic under- and overcoordination, 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 not only covalent bonds but also nonbonded interactions between all atoms. The atomic charges are calculated based on geometry and connectivity using the electron equilibration method.²⁶ A more detailed description of the force field can be found elsewhere.²⁷

As mentioned above, the ReaxFF potential is used to investigate the interaction of hydrocarbon species on Ni surfaces, but it is also very well suited to study phenomena such as silicon fracture,^{28,29} oxidation of silicon surfaces,³⁰ etc., with the obtained results in agreement with experimental observations. Although such results indicate the importance of MD simulations, the applicability is limited by the typical nanosecond time scale that can be reached. Extension of this time scale is an essential step in improving the applicability, and a number of techniques have been developed for this purpose.

One of these techniques is the (uniform acceptance) force biased Monte Carlo (fbMC) method,^{31–33} which has been successfully used in our group.^{21–23} Furthermore, Voter and co-workers developed various techniques, such as Temperature Accelerated Dynamics (TAD),³⁴ hyperdynamics,³⁵ and parallel replica,³⁶ to extend the accessible time scale. All these techniques have improved the applicability of MD simulations; however, in our case, the regular reactive MD simulations are sufficient to obtain valuable information on the interactions of the plasma species on the nickel surface.

2.2. Simulation Method. In this study, we consider four different nickel surfaces: Ni(111), which is the most stable Ni surface and the most abundant surface facet in typical nickel catalysts;^{37,38} Ni(100), which has a higher surface energy and is also present in nickel catalysts;³⁹ and two different step-edged Ni(111) surfaces, since defect (step) sites may be formed at the catalyst surface in a plasma as a result of, for example, ion bombardment.^{17,40}

The Ni(111) and Ni(100) surfaces both consist of 300 atoms equally divided over 6 layers, as illustrated in Figure 1. The two step-edged structures, which we denote as Ni(111)s1 and Ni(111)s2, consist of 255 and 345 atoms, respectively. All surfaces were first equilibrated at 400 K using the Berendsen thermostat⁴¹ 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 total energy (E) of the system is conserved. Furthermore, the number of particles (N) in this isolated system and the volume (V) are kept fixed. In order to simulate an infinite surface, periodic boundary conditions are applied in the {x,y} directions.

The impacting species are CH_x radicals ($x=\{1,2,3\}$), which are typically created in a CH_4 discharge at a gas temperature of 400 K.⁴² These radicals are added to the system at a *z* position of 5 Å above the top layer of the nickel surface and with random {x,y} coordinates. The initial velocity vector of the incident radical is randomized, and its magnitude is set to the root-mean-square velocity corresponding to the substrate temperature of 400 K.

Both nonconsecutive as well as consecutive impacts were performed. The single nonconsecutive impacts provide information concerning the reactivity of the impacting plasma species and their reactions after adsorption. Afterward consecutive impacts were performed to further study the reactions after adsorption and to mimic experimental conditions. The single nonconsecutive impacts, in which each

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Figure 2. (a) adsorption probabilities and associated standard deviations for the single impacts of the CH_x radicals on the four different nickel surfaces. (b), (c), and (d) observed reactions and the associated standard deviations after adsorption of respectively CH_3 , CH_2 , and CH.

impact occurs on a pristine nickel surface, are followed for 4 ps in the NVE ensemble. When the radical impacts on the surface, it is adsorbed, reflected, or decomposed. Each impact of each case is repeated 500 times in order to obtain statistically reasonable reaction coefficients.

The consecutive impacts are performed as follows. Each impact is first followed in the NVE ensemble for 5 ps. Then, the resulting surface is equilibrated to 400 K, to maintain the typical atmospheric plasma conditions. This equilibrated surface is subsequently used as the input configuration for the next radical impact. This sequence is continued until clear trends in the adsorption probability and reactivity are observed. These simulations take much more time than the simulations of the single impacts. Because of this, 5 simulations were performed for each species (instead of 500 simulations for the single, nonconsecutive impacts), and the reported results are the averages over these 5 simulations.

3. RESULTS AND DISCUSSION

3.1. Single, Nonconsecutive, Impacts. *3.1.1. Adsorption Probability.* The adsorption probabilities of the three different CH_x radicals on the four different nickel surfaces are depicted in Figure 2a. The results show that the CH radicals adsorb with the highest probability on all surfaces, followed by the CH_2 radicals, with adsorption probabilities around 99 and 90%, respectively. The CH_3 radicals have the lowest adsorption probability, ranging from 48.5% on Ni(111) to about 56% on the three other surfaces. The differences between the adsorption probabilities of the CH_x radicals can be explained

by the number of free electrons of the radical. This number increases from one in CH_3 to three in CH, leading to a higher reactivity, since these electrons can bond to the surface. However, the increase in adsorption probability from CH_3 to CH_2 is not equal to the increase from CH_2 to CH. Hence, an additional effect influencing the adsorption process must exist. Indeed, the C–H bonds of the radical cause steric hindrance, which shields the free electrons from the surface preventing the radical to bind to it. The higher the number of C–H bonds, the stronger the steric hindrance, which results in a lower adsorption probability. This is very similar to earlier observations of the reactivity of plasma species in both a-C:H thin film growth^{43–45} as well as diamond growth.^{46–48}

The difference between the nickel surfaces is the most significant for the CH₃ impacts. Indeed, the adsorption probability on Ni(100) is about 8% higher than on Ni(111). This difference is related to the connectivity of the nickel atoms in the top layer. In the closer packed Ni(111), each nickel surface atom is connected to six other atoms of the top layer, each at a distance of 2.5 Å. However, in Ni(100), there are only four top layer atoms connected to each nickel surface atom, also at a distance of 2.5 Å. Therefore, the incoming CH₃ radical is less hindered by the surrounding atoms on the (100) surface, which implies a weaker steric hindrance of the C–H bonds compared to impacts on Ni(111). Thus, the reduced connectivity of Ni(100) relative to Ni(111) increases the geometric cross section of the surface nickel atoms and therefore the surface reaction cross section.

The steps on the nickel surface also influence the adsorption probability of CH₃. Indeed, the adsorption probability is 55% and 57% on sNi(111)s1 and sNi(111)s2, respectively, which is 6.5% and 8.5% higher than on Ni(111). The presence of the edges locally increases the reaction cross-section between the incoming radical and the surface, which explains the higher adsorption probability compared to the step-less surface. This can be confirmed by investigating the CH₃ binding sites. There are four possible binding sites: μ_1 on-top, μ_2 bridge, μ_3 fcc, and μ_3 hcp (see Figure 3).¹⁴ On Ni(111), all the nickel surface



Figure 3. Four possible binding sites on Ni(111): (a) μ_3 fcc, (b) μ_3 hcp, (c) μ_1 on-top, and (d) μ_2 bridge.

atoms have the same local environment, and almost 40% of the adsorptions take place on a μ_1 on-top site. The remaining 60% of the adsorptions is equally divided over the two μ_3 sites. The μ_2 bridging site is only occupied a couple of times. On the stepped sNi(111)s1 surface, up to 65% of the adsorptions occur on the μ_1 site, mostly near the edges. Indeed, the local Nicoordination is lower at this location, resulting in a higher reactivity. However, the introduction of steps also lowers the fraction of adsorptions on μ_3 sites, since these sites are shielded by the above lying nickel atoms (see Figure 1c and 1d). This shielding is smaller at the sNi(111)s2 surface, due to the longer flat regions. This results in additional adsorptions on μ_3 sites compared to the sNi(111)s1 surface, while the number of adsorptions on the μ_1 site remains the same. As a result, the adsorption probability on the sNi(111)s2 surface is slightly higher.

For the CH_2 and CH impacts, the difference between the adsorption probability on the different nickel surfaces is much smaller. As discussed above, the steric hindrance of these radicals is rather limited while their intrinsic reactivity is higher with respect to CH_3 , such that their adsorption probability is less influenced by steps or surrounding atoms in the top layer of the surface. However, reflection still occurs when the radical impacts with the hydrogen directed straight toward the surface. Since the direction of the incoming radicals is random, their orientation relative to the surface just before the impact varies over all the simulations. This explains the smaller standard deviations in the results of CH and CH_2 impacts, as observed in Figure 2a. The CH radicals are even less likely to impact with the hydrogen directed toward the surface than CH_2 , hence the

smaller variation of their adsorption probabilities on the different nickel surfaces.

3.1.2. Reactions after Adsorption. After adsorption of the CH₃ radicals, we observe that some of the C-H bonds break. This results in the formation of adsorbed atomic hydrogen and CH₂ on the nickel surface. After the bond breaking, both CH₂ and H stay connected to the surface, without reacting further during the simulated time. This process of C-H bond breaking occurs in only 1% of the adsorption events in the case of CH₃ adsorbed on Ni(111) (see Figure 2b). On the other surfaces, there is a slight increase in the bond breaking probability for CH₃, up to 9% on Ni(100). The overall bond breaking reactivity of CH3 is determined by multiplying these values with the corresponding adsorption probabilities, plotted in Figure 2a. Since Ni(111) has the lowest adsorption probability and displays the least reactions after adsorption, it is predicted to be the least reactive surface, although the overall reactivity of CH₃ on the other surfaces also remains low.

The reactivity of CH₂ is much higher than that of CH₃, as appears from Figure 2c. First, the breaking of one C-H bond occurs for more radicals, ranging from 69% to 85%. Second, there is also a small fraction of radicals in which both C-H bonds are broken. This can lead to the formation of H_{2} , although in most cases the two hydrogen atoms remain adsorbed on the surface as single atoms. As shown in Figure 2c, only 1% of the adsorptions on Ni(111) results in the formation of H₂, while the majority of the adsorptions (i.e., \sim 85%) results in the cleavage of a single C-H bond. It should be emphasized, however, that the limited formation of H₂ from single H-atoms on the surface is directly related to the limited time scale of the simulations; longer simulations will almost certainly lead to enhanced H₂ formation. On the two stepped surfaces, fewer radicals are reacting, although the breaking of the two bonds seems to be more favorable on these surfaces compared to the flat surface. The highest reactivity is found for Ni(100). First of all, most adsorbed radicals undergo further reactions, and this surface has the highest probability for breaking both C-H bonds (with and without H_2 formation). In contrast to CH_3 , the adsorption probabilities of CH₂ on the four surfaces are quite similar, such that the difference in the overall bond breaking reactivity is mainly determined by the reactions after adsorption. This makes Ni(100) the most reactive surface for the CH_2 impacts. Indeed, the surface energy of Ni(100) is higher than that of Ni(111), with reported values between 1.487 and 2.426 J/m² for Ni(100) and 1.171 and 2.011 J/m² for Ni(111).³⁹ Using ReaxFF, we find a surface energy of 2.0 J/m² for Ni(100) and a value of 1.2 I/m^2 for Ni(111), thus corresponding well with the literature. The higher surface energy of Ni(100) increases the reactivity of the surface, as observed in our results. The results also imply a higher surface energy for the stepped surfaces compared to the Ni(111)surface, but unfortunately, no data for the surface energy on stepped Ni(111) surfaces are found to validate this observation. However, previous works on the dissociation of CH₄⁴⁹ and CO⁵⁰ on the terraces and steps of Ni(111) surfaces described the higher reactivity along the steps of the surface. This is in good agreement with our findings.

Finally, for the CH radicals, the highest reactivity is also found on the Ni(100) surface. Most of the carbon atoms remain on top of the surface after the C–H bond cleavage (see Figure 2d). In only 6% of the adsorption events, the carbon atom diffuses into the nickel surface once the C–H bond is broken. The three other surfaces show an equal probability of



Figure 4. (a) Adsorption probabilities and associated standard deviations for the consecutive impacts of the CH_x radicals on the four different nickel surfaces. (b), (c), and (d) average number of adsorptions of respectively the CH_3 , CH_2 , and CH radicals on the different nickel surfaces as a function of the number of impacts per binding site.

bond cleavage without diffusion of the carbon atom into the surface. However, the stepped structures show a higher percentage of carbon atoms diffusing inward, to interstitial sites between the top layer and the first subsurface layer. Corresponding to their relative stabilities, we observe a preferential occupation of the octahedral sites relative to the tetrahedral sites. This shows that the presence of step-edges in the structure lowers the penetration barrier of the top layer, making it easier for the carbon atoms to diffuse to the first subsurface. Similar to the CH₂ radicals, the adsorption probabilities of the OH radicals only have a small influence on the difference in the overall reactivities because of their similar values. Ni(100) is thus the most reactive surface, with a C–H bond cleavage for 93% of the impacting CH radicals.

3.2. Consecutive Impacts. *3.2.1. Adsorption Probability.* The average adsorption probabilities of the radicals after the consecutive impacts (Figure 4a) follow the previously discussed observation of the single impacts, i.e. the CH radical adsorbs the most on each surface and the CH_3 radicals the least. The adsorption probability after the consecutive impacts is, as expected, lower than after the single impacts, since previously adsorbed molecules sterically hinder the adsorption of new incoming molecules.

However, in contrast to the single impacts, the highest difference between the surfaces is obtained for the CH radicals, instead of the CH_3 radicals, as shown in Figures 4b – 4d. In these figures, the average number of adsorptions are shown as a function of the number of impacts per surface binding site, in order to make a proper comparison between the surfaces. Both Ni(111) and Ni(100) have 50 binding sites, while sNi(111)s1

and sNi(111)s2 have, respectively, 55 and 70 binding sites. Ni(111) still has the lowest adsorption probability of CH_3 , but Ni(100) and sNi(111)s1 only have around 4 additional adsorptions after the same number of impacts per binding site. The difference between these three surfaces for the adsorbed CH₂ radicals increases a bit, to maximum 7 additional adsorptions on sNi(111)s1. For the CH impacts, there are maximum 19 adsorptions more on Ni(100) and sNi(111)s1 than on Ni(111). A part of these additional adsorptions are due to the diffusion of C-atoms into the structure, which makes some binding sites available again. This occurs the most on the stepped surfaces, just as after the single impacts (Figure 2d). In contrast to the single impacts, the fraction of C-atoms that diffuse into the structure is higher for Ni(100) than for Ni(111), hence the higher number of adsorptions on Ni(100). There are always more radicals adsorbed on sNi(111)s2 than on the other surfaces after the same number of impacts per binding site. The amount of binding sites on sNi(111)s2 is 1.4 times higher than on Ni(111) and Ni(100) and 1.27 times higher than on sNi(111)s1, while the average number of adsorptions after the same amount of impacts is 1.2 to 1.6 times higher on sNi(111)s2 compared to the other surfaces. This shows that by increasing the surface, thus the number of binding sites, with a certain factor, the average number of adsorptions after the same amount of impacts per binding sites increases with a similar factor.

In Figures 4b - 4d, two stages can be distinguished, the most obvious in the last two figures. In the first stage, the average number of adsorptions per binding site increases at the same rate for all surfaces. In the second stage, differences in the



Figure 5. (a) Average number of broken C–H bonds, sometimes followed by CH_4 formation, and the associated standard deviations of the adsorbed CH_3 radicals on the different nickel surfaces after 150 consecutive impacts. (b) Average number of formed molecules after 200 consecutive CH_2 impacts on the different nickel surfaces. (c) Average number of H-atoms adsorbed on the different nickel surfaces as a function of the number of CH_2 impacts. (d) Average number of formed nonadsorbed species after 200 consecutive CH impacts on the different nickel surfaces.

adsorption numbers arise between the surfaces, which is maintained for the remaining impacts. The start of the second stage is not so clear for the CH_3 impacts. After 0.2 impacts per binding site the first small difference between the surfaces is observed, but this difference first increases during the following impacts before remaining stable. The start of the second stage for the CH_2 and CH impacts is more obvious and nearly coincides for both cases, namely after about 0.7 impacts per binding site. At this moment, a large part of the surface area is covered by the adsorbed radicals, which hinders the adsorption of new incoming radicals. The further reactions at the surface, including the diffusion into it, influence the number of available binding sites and hence the number of adsorptions.

3.2.2. Reactions after Adsorption. The results of the single impacts illustrated the low reactivity of the CH₃ radicals, which is also observed for the consecutive impacts (Figure 5a). The number of broken C–H bonds remains low, with comparable values for the different surfaces. Interestingly, however, the mechanism for this bond breaking process is found to be dependent on the surface morphology. On Ni(111), a C–H bond of an adsorbed radical can be broken only if the hydrogen atom involved is subtracted by an incoming radical, forming a volatile CH₄ molecule. This mechanism rarely occurs on Ni(100), on which the C–H bond simply breaks without interacting with another incoming radical. On the two stepped structures, both mechanisms are observed.

During the consecutive impacts of CH₂ and CH radicals, a wider range of molecules is formed in comparison to the CH₃ impacts. After 200 CH₂ impacts, incoming radicals have recombined to form CH3 or even CH4, but also C2H4 and C_2H_6 are formed (see Figure 5b). The H_2 formation as observed in the single impact simulations still occurs on Ni(100) and the stepped surfaces but is not increased. The four surfaces show similar results, although there are two important differences. First, there is a difference in the possible mechanisms for the formation of CH₃ and CH₄ between the Ni(100) and the (111) surfaces. On the (111) surfaces, these species are formed by subtraction of the C-H bonds of the adsorbed molecules by incoming radicals. The C-H bonds of the adsorbed molecules can also be broken without interaction with the incoming radicals, resulting in an adsorbed H-atom on the surface. However, the adsorbed H-atoms on the (111) surfaces do not react further and simply remain adsorbed as single atoms, so there is only one mechanism for CH₃ or CH₄ formation (see Figure 5c). On Ni(100), CH₃ and CH₄ are also formed by subtraction of the C-H bonds of the adsorbed molecules by the incoming radicals. Furthermore, they can also be formed when the H-atoms adsorbed on the surface are subtracted by the incoming radicals. Thus, on Ni(100) there are two mechanisms for forming CH₃ and CH₄. Second, an increased formation of C2H4, C2H6, and H2 is observed on sNi(111)s1 compared to the Ni(111) surface. Indeed, the

surface steps increase the reactivity toward the formation of these molecules.

After 200 consecutive CH impacts, a wide variety of nonadsorbed species is formed, i.e. CH_4 , CH_3 , CH_2 , H_2 , and C_2H_x ($x=\{1,2,3\}$), furthermore, reflected CH_3 and CH_2 radicals are also observed, as shown in Figure 5d. In comparison to the single impacts, some H_2 formation is observed, though the yield is small. The resulting surface after 200 consecutive CH impacts on Ni(111) is shown in Figure 6, illustrating the reactivity and



Figure 6. Side view of the Ni(111) surface after 200 consecutive CH impacts, illustrating the complexity of the system.

complexity on the surface. Again, the results between the different surfaces are similar, although some differences compared to the CH_2 impacts are observed. To form the above-mentioned species, incoming radicals can subtract either a H-atom from an adsorbed radical as well as a H-atom adsorbed as an atom on the surface. This occurs on all the surfaces, in contrast to the corresponding process due to CH_2 impacts, in which case this process was only observed on the Ni(100) surface (see above). The influence of the steps is smaller compared to the CH_2 impacts. While the steps induce H_2 formation, the C_2H_x formation stays the same.

4. SUMMARY AND CONCLUSIONS

The interaction of CH_x ($x=\{1,2,3\}$) plasma species on four different nickel surfaces was investigated using reactive molecular dynamics simulations. To mimic typical plasmacatalysis conditions, the temperature was set to 400 K. It is shown that the CH radical has the highest adsorption probability on all surfaces, both for single and consecutive impacts, followed by CH_2 and CH_3 . This decrease in reactivity in the series $CH - CH_2 - CH_3$ can be explained by the decreasing number of free radical electrons and the increasing steric hindrance.

For the single impacts, the differences between the nickel surfaces is the most significant for CH_3 , for which the adsorption probability on Ni(100) and the two step-edged structures is higher than on Ni(111). This results from the increased geometric cross section of the surface nickel atoms of Ni(100) and the two step-edged structures compared to Ni(111) and therefore the higher surface reaction cross section. Furthermore, the breaking of some of the C–H bonds is observed after adsorption, especially for the CH₂ and CH radicals. In most cases, only one C–H bond is broken, and the hydrogen atom remains on the nickel surface after the bond cleavage. Only for a small fraction of the adsorbed CH_2 radicals,

both C–H bonds break. This is followed by either H_2 formation or diffusion of the hydrogen atoms over the surface. The diffusion of the carbon atom into the surface occurs only for adsorbed CH radicals and predominantly on step-edged structures.

For the consecutive impacts, the largest differences in adsorption probability on the various surfaces are observed for the CH radicals. On Ni(100) and the stepped structures, there is more diffusion of adsorbed carbon atoms into the surface, which increases the adsorption probability. During the consecutive impacts, two stages are detected. In the first stage, the average number of adsorptions as function of the impacts per binding site increases at the same rate for all the surfaces. Afterward, in the second stage, differences in adsorption rates arise between the surfaces, which is maintained for the remaining impacts.

The reactivity during the consecutive impacts is high for CH and CH₂ on all surfaces. Different mechanisms are observed during the CH₂ impacts, i.e. the adsorbed H-atoms on Ni(100) are included in the reaction mechanisms, whereas the H-atoms adsorbed on the (111) structures not. The presence of steps in a structure leads to additional C–H bond breaking after CH₃ impacts and to additional C₂H₄, C₂H₆, and H₂ formation after CH₂ impacts. After CH impacts, the steps induce H₂ formation, but the effect is smaller compared to the CH₂ impacts. There is no clear effect of the size of the steps. The results for sNi(111)s1 and sNi(111)s2 are very similar.

These results demonstrate that reactive molecular dynamics simulations are a very useful tool to study the interaction of plasma species on nickel surfaces and, eventually, improve the insight in complex reaction systems, such as plasma-catalysis and CNT growth.

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Notes

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