Temperature influence on the reactivity of plasma species on a nickel catalyst surface: An atomic scale study

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1. Introduction

Steam methane reforming over a supported nickel catalyst has been a widely used process for hydrogen production for several decades [1]. Because of the potential use of hydrogen as a source of clean energy, there is a continuous interest in this process, but further improvements regarding the efficiency are clearly required to warrant the economic viability. Sehested [1] discussed this issue and summarized the most important challenges of the steam methane reforming process, namely: maintaining the catalyst activity and reducing carbon formation, sintering, and sulfur poisoning. Complementary to the substantial experimental research that has already been carried out, a more fundamental knowledge at the atomic level is needed.

Experimental studies until now mainly focused on the adsorption and decomposition of methane on Ni-catalysts [2–4]. The dissociative adsorption of CH₄ on Ni(1 1 1) was studied with HREELS [2], SIMS and XPS [3,4]. Furthermore, in order to obtain a full description of the reactions and the reaction barriers at the atomic scale, a number of computational studies were performed as well. Density functional theory (DFT) calculations illustrated the higher adsorption and dissociation probability of CH₄ molecules on Ni(1 0 0) and on stepped structures compared to Ni(1 1 1) [5,6].

Additionally, the complete successive dehydrogenation of CH₄ has been recently discussed, also based on DFT calculations [7]. While DFT calculations are very accurate, and suitable for small systems, classical molecular dynamics (MD) simulations are capable of describing the atomic interactions for larger systems, and on a longer timescale. Mueller et al. employed such simulations to study the dissociation of methyl radicals on nickel surfaces as a function of temperature. These authors found a higher reactivity of Ni(1 0 0) and a stepped surface compared to a flat Ni(1 1 1) surface [8]. Although it is found that Ni(1 1 1) is not the most reactive surface, it is still the subject of a lot of research, since it is the most abundant facet in typical nickel catalysts [9–11]. Such research is not only interesting from a pure catalytic point of view, but also for plasma-catalytic applications. This technology is an alternative for improving the conventional steam methane reforming process, since it combines the high reactivity of a plasma with the high selectivity of a catalyst [12,13]. The influence of a plasma on the reactivity was demonstrated by Nozaki, demonstrating that vibrationally excited methane improved the dissociative chemisorption on nickel surfaces [14,15]. Although synergistic effects have been demonstrated before [16], the exact mechanisms of the interactions of the plasma species at the catalyst surface remain unclear [17]. Such interactions are also of importance for the growth of nanostructures, such as carbon nanotubes (CNTs), for which nickel catalysts are also used in combination with plasma technology [18,19]. During the plasma-enhanced chemical vapor deposition of CNTs, precursors such as CH₄, CH₃ and H₂ are used.
MD simulations of the interactions of these precursors on the catalyst surface can provide information regarding the initial mechanisms. Previously, MD simulations were performed in combination with Monte Carlo techniques to study other aspects of the growth of CNTs, such as the influence of the electric field [21].

In our previous work [22], we used molecular dynamics to simulate single and consecutive impacts of CH\(_4\) radicals on four different nickel surfaces, namely Ni(1 1 1), Ni(1 0 0) and two step-edge Ni(1 1 1) surfaces, at a temperature of 400 K, which is typical for cold (i.e., non-thermal equilibrium) atmospheric pressure plasmas. In agreement with previous findings [5,6,8], we observed a higher reactivity on Ni(1 0 0) and the stepped surfaces, and elucidated the different reaction mechanisms occurring on the different surfaces. Furthermore, some CH molecules were formed, although the fraction at this temperature was very small. However, it can be expected that the probability of H\(_2\) formation increases at higher temperatures, which has been suggested before [7].

In this work, we have increased the temperature to the region of the so-called warm plasmas [23–25], i.e. 1000–2000 K, in order to determine the temperature onset for H\(_2\) formation. For instance, in the transitional regime of a gliding arc discharge, the non-equilibrium properties of low-temperature plasmas are maintained, while the gas temperature is slightly increased. This leads to an increase in the number of excited species, which, as mentioned above, leads to an enhanced dissociation. Furthermore, the increased gas temperature might also improve the reactivity of the catalyst, and thus create a synergistic effect. In the first part of this contribution, we compare the results of consecutive CH\(_4\) impacts at 400 K on Ni(1 1 1) employing the Bussi thermostat [26] and the Berendsen thermostat [27], in order to verify the equivalence of both methods to study this system. We specifically verify the equivalence of both thermostats in simulating this system, in order to demonstrate the validity of the comparison between the results obtained in this work and in our previous work. In the second part, consecutive CH\(_4\) impacts are performed in a temperature range from 800 to 1600 K, again on the Ni(1 1 1) surface, with the focus on H\(_2\) formation.

2. Computational details

2.1. Interatomic potential and thermostat

Reactive molecular dynamics (MD) simulations are performed, based on the Reactive Force Field (ReaxFF) potential [28] to derive the forces between the atoms, using parameters developed by Mueller and coworkers [8]. Furthermore, these authors validated the accuracy of the parameter set by comparison of a large number of hydrocarbon reactions on nickel surfaces with quantum mechanics calculations. Moreover, the same force field has also been used to simulate the growth of CNTs in close agreement with experiments [29–31]. ReaxFF is based on the bond order/bond distance relationship introduced by Abell [32]. The total system energy is the sum of multiple partial energy terms, related to pair interactions, lone electron pairs, atomic under- and overcoordination, valence and torsion angles, conjugation and hydrogen bonding. Furthermore, van der Waals and Coulomb interactions are also included, so that not only covalent bonds are described, but also non-bonded interactions between all atoms. Charge distributions are calculated with the electron equilibration method [33], which is based on the geometry and connectivity of the system. A more detailed description of the force field can be found elsewhere [34].

Upon impact on the substrate, the impinging particles exchange a part of their kinetic energy with the nickel surface atoms. In the microcanonical (NVE) ensemble, the total energy of the system remains constant throughout the simulated impact. This ensemble was used in our previous simulations [22]. After each impact, however, the surface needed to be re-equilibrated at 400 K prior to each new impact. For this re-equilibration, we used the Berendsen thermostat [27], in which the velocities are rescaled at each time step in order to enforce the desired temperature (i.e., the total kinetic energy) of the system. However, although the Berendsen thermostat allows control of the simulated system’s temperature, it does not generate the true canonical (NVT) ensemble.

Bussi et al. proposed another thermostat which, similar to the Berendsen thermostat, also rescales the atomic velocities using a certain scaling factor depending on the current and desired temperature of the system [26]. It differs from the Berendsen thermostat in the way the scaling factor is calculated. Whereas the Berendsen formalism relies on a simple deterministic function to obtain the rescaling factor during each time step, Bussi’s approach is a stochastic procedure where the rescaling factor is randomly sampled from a specified distribution. In contrast to the Berendsen thermostat, this thermostat is able to correctly generate the canonical ensemble, and is therefore used in this work.

The simulations in this work are intended to capture the dynamics of the system, and do not necessarily capture the correct thermodynamics. In this respect, however, it should be noted that we specifically focus on the short timescale dynamic phenomena, such as adsorption and desorption. In order to capture the thermodynamics of the system, a different simulation method would be required. For this purpose, we plan to use the Grand Canonical Monte Carlo method in our further research.

2.2. Simulation method

The studied Ni(1 1 1) surface consists of 300 atoms equally divided over 6 atomic layers. Prior to the consecutive impacts, the surface is first equilibrated at the desired temperature using the Bussi thermostat with a coupling constant of 100 fs, in the range 400–1600 K, with a 200 K interval. In order to simulate an semi-infinite surface, periodic boundary conditions are applied in the \((x,y)\) directions.

The impacting species are CH\(_4\) radicals \((x = (1,2,3))\), which are added to the system at a \(z\) position of 10 Å above the top layer of the nickel surface. The initial \((x,y)\) coordinates and the initial velocity vector are randomized. Each impact is followed for 6.25 ps, in which the radicals can be adsorbed, decomposed or reflected. In the case of reflection, the radicals are removed from the system. The resulting surface is subsequently used as the input configuration for the next impact. This sequence is repeated 150 times for the CH\(_3\) impacts, and 250 times for the CH\(_2\) and CH impacts. The lower number of simulated CH\(_3\) impacts is due to fact that after 150 impacts there are no more adsorptions or reactions on the surface, while in the case of CH\(_2\) and CH, more impacts are needed for saturation to occur. After this number of impacts, clear trends in the reactivity after impact are observed. For each case, i.e., the sequence of impacts of each species at the six different temperatures, three different simulations were performed and the results reported here are the averages over these three simulations with the associated standard deviations. Thus, in total, 54 simulations were carried out, accounting for a total of 11,700 impacts.

It is essential to keep in mind that these simulations approach the effect of plasma on a catalyst through the reactivity of the radicals. Experimentally, this increases the concentration of active species near the catalyst surface and can enhance the energy efficiency. It is also important to realize, however, that not all possible effects of plasma on the catalyst can be described in these simulations. For instance, the influence of electrons, and therefore the electron density, on carbon deposition through direct electron impact dissociation of methane cannot be taken into account in our simulations. This process would effectively and drastically reduce
the catalytic activity. However, note that the electron density of the transitional regime of a gliding arc discharge is \(10^{12} \text{ cm}^{-3}\), while the typical value in a DBD is around \(10^{14} - 10^{15} \text{ cm}^{-3}\) [25,35]. Furthermore, in the transitional regime of a gliding arc discharge \(T_e \approx 1 \text{ eV}\), which is a characteristic value for non-thermal plasmas. Since the electron energy is comparable for DBD and gliding arc discharges (in the transitional regime), and the electron density is lower for the latter discharge, we expect that the temperature will have the most substantial influence on a process such as carbon deposition.

Additionally, the plasma might alter the reactivity of the catalyst by changing the crystallinity. As discussed in our previous work [22], the type of nickel surface indeed influences the reactivity after impacts of plasma species. For this purpose, our next study will further focus on the reactivity on several nickel surfaces, ranging from polycrystalline to amorphous structures.

3. Results and discussion

3.1. Comparison of the Berendsen and Busssi thermostats

Both the adsorption probability and the reactions after adsorption as obtained from the simulations with the Busssi thermostat are compared with our previous results, which were obtained from simulations under the NVE ensemble in combination with the Berendsen thermostat [22]. As shown in Fig. 1, the average adsorption probability after 150 consecutive \(\text{CH}_3\) impacts is almost equal for both methods, with only a small difference of less than 0.5\% between the two values. The difference between the average adsorption probabilities obtained with both methods slightly increases for the \(\text{CH}_2\) impacts, i.e. up to 1\. However, when considering the standard deviations on these averages, both methods still give very similar results. Only in the case of the consecutive CH impacts, there is a noticeable difference between the average adsorption probabilities obtained with both methods, even though it remains low (3\%). The progressing adsorption probability after each consecutive impact is determined by the reactivity of the incoming radical, i.e. the number of free radical electrons, as well as by the steric hindrance induced by the radicals which are already adsorbed on the surface. Since the reactivity of the incoming radicals does not change during the simulations, the difference between the adsorption probabilities obtained using both methods can be allocated to the different steric hindrance of the nickel surface and its adsorbed species toward the incoming radicals. The types of adsorbed species are determined by the reactions after adsorption, in which new non-adsorbed species are formed. These reactions involve the breaking of C\(=\)H bonds of the adsorbed radicals, and thus, result in adsorbed species with less H-atoms, such as CH radicals and C-atoms. The latter species present a lower steric hindrance compared to \(\text{CH}_3\) or \(\text{CH}_2\) radicals adsorbing on the surface. A comparison between the average numbers of formed non-adsorbed species in both simulation methods can therefore assist in further studying the small difference in the adsorption probabilities.

The reactions after the adsorption of \(\text{CH}_3\) radicals are very rare, resulting in only 2 broken C\(=\)H bonds on a total of 150 impacts for both methods. Both bond breaking events subsequently lead to the formation of 2 \(\text{CH}_2\) molecules. Since the reactivity is found to be equal for both methods, the resulting nickel surfaces will strongly resemble each other; hence, the adsorption probability of \(\text{CH}_3\) is similar for both methods, as discussed above. The type of non-adsorbed species formed after \(\text{CH}_2\) and \(\text{CH}\) impacts is the same for the simulations with the Berendsen and Busssi thermostat, as shown in Fig. 2. Especially for the formation of \(\text{CH}_4\) and \(\text{CH}_3\) species, the differences are very small. Even for the formation of \(\text{CH}_2\) species there is only a limited influence of the thermostat, such that the resulting nickel surfaces will not differ significantly, and therefore, adsorption probabilities within the same range are expected.

The results above show that although the simulated ensemble is different, the use of the Busssi thermostat and the Berendsen thermostat in combination with NVE simulations result in the same reactivity of small hydrocarbons on a \(\text{Ni}(1 1 1)\) surface.

3.2. Temperature effect

3.2.1. \(\text{H}_2\) formation

It is important to point out that in our previous simulations, at a temperature of 400K, no \(\text{H}_2\) formation was observed after \(\text{CH}_x\)
CH₂ impacts

3.2.1.1. On other nickel surfaces, only a small amount of H₂ was formed at the same temperature. So it is essential to know if H₂ formation can occur after CH₃ impacts on Ni(1 1 1), and, if so, what the threshold temperature of this reaction is.

3.2.1.1. CH₃ impacts. After 150 consecutive CH₃ impacts on Ni(1 1 1), no H₂ formation is observed up to a temperature of 1200 K (see Fig. 3a). It has been demonstrated by Mueller [7] that adsorbed CH₃ is kinetically stable on Ni(1 1 1) at low temperatures, and that higher temperatures are required to overcome the barrier for C–H bond breaking (0.80 eV). This is also observed in our simulations, where the number of broken C–H bonds, and thus the number of CH₄ molecules formed is increasing as a function of temperature. This implies that the impacting radicals have enough energy to abstract a H-atom from the adsorbed species or from the nickel surface. However, the recombination of two hydrogen atoms to form H₂ still requires too much energy. Our simulation results indicate that a temperature of 1400 K is required for this barrier to be overcome, with an average of 2 H₂ molecules formed on a total of 150 impacts. The H₂ formation further increases to nearly 6 molecules on a total of 150 impacts, when increasing the temperature to 1600 K. This means that 4% of the CH₃ impacts are followed by H₂ formation. Additionally, there is a decrease in the number of CH₄ molecules formed, since the H-atoms adsorbed on the nickel surface now recombine into H₂.

3.2.1.2. CH₂ impacts. Even at 400 K, the reactivity of CH₂ and CH was found to be much higher than the CH₃ reactivity, giving rise to the formation of CH₄, reflected CH₂ and CH₃, and a small fraction of C₂ species. The species formed after 250 consecutive CH₂ and CH impacts can be divided into 3 groups: H₂, CH₄ and C₂H₆ species. As illustrated in Fig. 3b, a low number of H₂ molecules is formed at 800 K, 1000 K and 1200 K upon the CH₂ impacts. However, this number increases significantly at temperatures of 1400 K and 1600 K, up to 41 H₂ molecules for the latter temperature, thus 16% of the CH₂ impacts is followed by H₂ formation. This is even higher than the number of CH₃ species formed, in contrast to the results at lower temperatures, where the number of CH₄ species is larger than that of H₂. Furthermore, this result is in agreement with previous research on thermal methane cracking [36], where a temperature of more than 1600 K was needed to generate H₂ as the main component of the evolving gas. At temperatures up to 1200 K, most of the surface-bound H-atoms react with the impacting radicals to form CH₄ species. In some rare occasions, the H-atoms have enough energy to recombine into H₂. As is also the case for the CH₃ impacts, this process is activated at a temperature of 1400 K, and at even higher temperatures most H-atoms are found to recombine, thus causing a reduction in the number of CH₄ species formed. The energy barrier for the recombination of 2 H-atoms to H₂ is calculated with the nudged elastic band (NEB) method [37], and is found to be 1.66 eV. This is higher than the calculated barrier for H-diffusion over the nickel surface, which we calculated as 0.35 eV. The increase in temperature is thus essential for crossing the energy barrier for H₂ formation. Additionally, some C₂H₄ species are formed, although their formation is hardly influenced by the temperature.

3.2.1.3. CH impacts. The H₂ formation due to CH impacts (Fig. 3c) is initiated at 800 K. As is the case for the CH₂ impacts, a significant increase in the H₂ formation is observed at temperatures of 1400 K and 1600 K. Furthermore, the trend concerning the number of CH₄ species formed as a function of the temperature is maintained. Indeed, at the lower temperatures, the CH₄ species are the most occurring species, while at 1600 K, the H₂ molecules are the dominant species formed. At this temperature, 12% of the CH impacts are followed by H₂ formation, corresponding to an average of 30 H₂ molecules formed after 250 consecutive impacts. This is lower than the number of H₂ molecules formed due to CH₃ impacts, as can be expected since there are less H-atoms in the CH-system. The stability of H-atoms on Ni(1 1 1) has been investigated by Mueller [7]. It was found that at low temperatures, most hydrogen atoms are adsorbed on the surface, since the energy for chemisorption is −0.59 eV per H. However, at higher temperatures the adsorbed H-atoms tend to recombine to H₂, as is the case in our simulations. In contrast to the results of the CH₂ impacts, the C₂H₆ formation is slightly dependent on the temperature, although the C₂H₆ fraction remains small. Furthermore, the ionization energy of these species is lower than that of CH₄ species, i.e. 11.56 eV for C₂H₆ versus
3.2.2. Carbon diffusion into the nickel surface

The results discussed above indicate the positive effect of increasing the temperature on the H\textsubscript{2} formation. However, the temperature also influences the diffusion of the carbon atoms into the nickel surface, which is not a desired effect. Indeed, in the steam methane reforming process, carbon deposition can reduce the performance of the catalyst, for example by blocking the active sites of the catalyst. As mentioned above, the reactivity in the case of the CH\textsubscript{3} impacts is rather low, especially when comparing these results with the reactivity of the other impacting radicals. Only a few CH\textsubscript{3} radicals become fully dehydrogenated after adsorption, and consequently, the resulting C-atoms can diffuse into the nickel surface. Up to 1400 K, the C-atoms only diffuse into the first subsurface layer, but at a temperature of 1600 K, the diffusion goes deeper into the nickel structure, i.e., until the third subsurface layer.

The same effect is also observed for the dehydrogenated C-atoms originating from CH\textsubscript{2} and CH impacts. Little diffusion, i.e., in the range of 16 diffused C-atoms on a total of 250 CH\textsubscript{2} impacts, is observed up to temperatures of 1000 K, while more extensive diffusion, i.e., in the range of 91 diffused C-atoms, occurs at a temperature of 1600 K. Since many C–H bonds are broken to form H\textsubscript{2}, the number of dehydrogenated C-atoms is much higher than in the case of CH\textsubscript{3} impacts, where 24 C-atoms diffused into the nickel surface after 150 CH\textsubscript{3} impacts. Fig. 4 illustrates the carbon diffusion into the nickel surface for CH\textsubscript{3} impacts at various temperatures. It is observed that the C-atoms only diffuse to the first subsurface layer up to a temperature of 1000 K. At higher temperatures, the C-atoms can reach lower-lying Ni-layers. The same is observed for the diffusion after the CH impacts, indicating that the C-atoms gain enough energy to diffuse to lower layers. The energy barrier for the diffusion of a C-atom from the first layer to the octahedral site in the first subsurface layer is calculated with the NEB method, and is found to be 1.29 eV. This is significantly lower than the energy required for further diffusion into the surface. For instance, the diffusion from an octahedral site in the first subsurface layer to a tetrahedral site in the second subsurface layer requires 2.47 eV. The same type of diffusion from the third to the fourth subsurface layer also needs a similar amount of energy, namely 2.26 eV. Thus, as observed in Fig. 4, high temperatures are required to overcome the energy barrier of diffusion to lower subsurface layers. The diffusion pathways of C-atoms on a Ni(1 1 1) surface have been extensively investigated by Abild-Pedersen [40]. It was found that for the diffusion of a C-atom from the first layer of a clean surface to the first subsurface, an energy of about 1.00 eV was needed, which is in agreement with our findings.

The results discussed above show that an optimal operating condition is at a temperature around 1400 K, since at higher temperatures, the diffusion of C-atoms into the nickel surface becomes too dominant, and at lower temperatures the H\textsubscript{2} formation is too limited. A similar general conclusion was reached by Nikoo and Amin [41]. These authors concluded that a high temperature (>1173 K) was required for the optimal production of syngas (H\textsubscript{2} + CO) during the dry reforming of methane. Furthermore, Nozaki [14] discussed the dominance of thermal reactions on the catalyst surface at temperatures exceeding 973 K. Such thermal activation is also observed in our results. Note that in these studies also oxidative species were present, such as H\textsubscript{2}O or CO\textsubscript{2}, in contrast to our simulations. These species will oxidize the adsorbed C-atoms, and release them from the surface as CO. In combination with the H\textsubscript{2} formation, this is the general mechanism for syngas production during steam methane reforming. In future work, we plan to perform MD simulations for a full description at the atomic level of the steam methane reforming process.

4. Summary and conclusions

The influence of the temperature on the reactivity of CH\textsubscript{4} species on a Ni(1 1 1) surface was investigated using reactive molecular dynamics simulations, with a specific emphasis on H\textsubscript{2} formation.

First, we compared the use of two different ensembles for the simulation of this system, viz. the microcanonical ensemble in combination with the Berendsen thermostat, and the canonical Bussi thermostat, to validate the comparison with our previous results. It is demonstrated that there are no significant differences in the results as obtained from both methods, indicating that the obtained
processes and mechanisms are not sensitive to the exact temperature control method.

Second, it is shown that H2 formation can occur after CH₂ impacts on Ni(111) at sufficiently high temperatures. The reactivity toward H₂ formation is the lowest in the case of the CH₂ impacts. Only at a temperature of 1400 and 1600 K, the system has sufficient energy to cross the barrier of 1.66 eV for the recombination of 2 H-atoms into a H₂ molecule. At lower temperatures, the H-atoms react with the impacting CH₂ radicals to form CH₃. The same high temperatures of 1400 K and 1600 K are also required to obtain a significant amount of H₂ formation after CH₂ and CH impacts. Again, at lower temperatures, most surface-adsorbed H-atoms will react with the impacting species, instead of forming H₂. At 1600 K, about 4%, 16% and 12% of the CH₂, CH₂ and CH impacts, respectively, are followed by H₂ formation.

Finally, it is also illustrated, in agreement with experimental observations, that the high temperatures do not only lead to an increase in the H₂ formation, but also promote the diffusion of C-atoms into the subsurface region of the crystal. At temperatures of 1400 K and 1600 K, the diffusion barrier to lower subsurface layers can be overcome, reducing the possibility to oxidize the adsorbed C-atoms into CO, if oxidative species are present. Overall, the results imply that an optimal temperature for an efficient H₂ formation on Ni(111) lies around 1400 K. At higher temperatures, the diffusion of C-atoms into the nickel surface becomes overly dominant, while at lower temperatures the H₂ formation is too limited. The temperature of 1400 K is reached in warm plasmas, which are also characterized by the high number of reactive excited species. Therefore, a synergistic effect might be obtained, which makes it an interesting technology for the methane reforming process.

This study further elucidates the importance of the temperature on the methane reforming process, which is an important step toward efficient H₂ formation as a source of clean energy.

Acknowledgments

This work was carried out using the Turing HPC infrastructure at the CalCua core facility of the Universiteit Antwerpen (UA), a division of the Flemish Supercomputer Center VSC, funded by the Hercules Foundation, the Flemish Government (department EWI) and the UA.

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