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

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ABSTRACT

In recent years, the potential use of hydrogen as a clean energy source has gained considerable attention. Especially H_2 formation by Ni-catalyzed reforming of methane at elevated temperatures is an attractive process. However, a more fundamental knowledge at the atomic level is needed for a full comprehension of the reactions at the catalyst surface. In this contribution, we therefore investigate the H_2 formation after CH_x impacts on a Ni(1 1 1) surface in the temperature range 400–1600 K, by means of reactive molecular dynamics (MD) simulations using the ReaxFF potential. While some H_2 formation is already observed at the lower temperatures, substantial H_2 formation is only obtained at elevated temperatures of 1400 K and above. At 1600 K, the H_2 molecules are even the most frequently formed species. In direct correlation with the increasing dehydrogenation at elevated temperatures, an increased surface-to-subsurface C-diffusivity is observed as well. This study highlights the major importance of the temperature on the H_2 formation.

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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 CH_4 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 CH_4 molecules on Ni(1 0 0) and on stepped structures compared to Ni(1 1 1) [5,6]. Additionally, the complete successive dehydrogenation of CH_4 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 CH_4, CH_3 and H_2 are used

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[20]. 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_x radicals on four different nickel surfaces, namely Ni(1 1 1), Ni(1 0 0) and two step-edged 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 H_2 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 temperature, 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_x 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_x 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_x 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

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