Applied Catalysis B: Environmental 154–155 (2014) 1–8

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Interactions of plasma species on nickel catalysts: A reactive molecular dynamics study on the influence of temperature and surface structure

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ARTICLE INFO

Article history:
Received 8 November 2013
Received in revised form 25 January 2014
Accepted 30 January 2014
Available online 6 February 2014

Keywords:
Molecular dynamics simulation
ReaxFF
Hydrocarbons
Nickel catalyst
Plasma catalysis

ABSTRACT

Methane reforming by plasma catalysis is a complex process that is far from understood. It requires a multidisciplinary approach which ideally takes into account all effects from the plasma on the catalyst, and vice versa. In this contribution, we focus on the interactions of CH_x ($x = \{1,2,3\}$) radicals that are created in the plasma with several nickel catalyst surfaces. To this end, we perform reactive molecular dynamics simulations, based on the ReaxFF potential, in a wide temperature range of 400–1600 K. First, we focus on the H_2 formation as a function of temperature and surface structure. We observe that substantial H_2 formation is obtained at 1400 K and above, while the role of the surface structure seems limited. Indeed, in the initial stage, the type of nickel surface influences the C–H bond breaking efficiency of adsorbed radicals; however, the continuous carbon diffusion into the surface gradually diminishes the surface crystallinity and therefore reduces the effect of surface structure on the H_2 formation probability. Furthermore, we have also investigated to what extent the species adsorbed on the catalyst surface can participate in surface reactions more in general, for the various surface structures and as a function of temperature. These results are part of the ongoing research on the methane reforming by plasma catalysis, a highly interesting yet complex alternative to conventional reforming processes.

1. Introduction

The Ni-catalyzed reforming of methane is a commonly used process for the production of synthesis gas, a potential clean energy source. However, the associated chemical reactions are strongly endothermic and thus energy-intensive [1]. Combination of plasma and catalysis, so-called plasma catalysis, seems promising. The plasma can activate inert molecules such as CH_4 and induce reactions at reduced temperatures, while the catalyst can increase the selectivity towards specific reaction products. However, plasma catalysis is a technology which is far from understood due to its inherent complexity [2,3]. Indeed, in addition to the inherent complexity of catalysis and the plasma processes taking place, the plasma and catalyst also often demonstrate synergistic effects.

For instance, the presence of the catalyst in the discharge volume affects the retention times of the plasma species in the reactor. Indeed, the plasma species adsorb on the catalyst surface and are therefore longer available to the discharge to interact with other species. This leads to additional reactions and reaction products, which changes the reactive species densities [4,5]. The presence of the catalyst in the discharge volume can also create a so-called packed bed effect, which enhances the electric field. Such an effect, which is also created by adding dielectric materials in the plasma reactor, influences the electron energy distribution function [6,7]. Furthermore, microdischarges may be formed in catalyst pores. All these factors lead to a change in the plasma characteristics, and a concurrent change in the chemistry. In turn, the plasma may reduce the catalyst to increase the catalytic activity. This has for instance been demonstrated for nickel catalysts (with or without a support material), where NiO is reduced to Ni [8]. The plasma also enhances the formation of smaller catalyst nanoparticles, which results in a higher dispersion and thus a larger surface area of the catalyst [9]. Such high catalyst dispersion also reduces coke formation on the catalyst surface [10]. Furthermore, the reactive plasma species can induce several reactions at the catalyst surface, and lower the activation barrier of some reactions. The latter can occur for example in reactions with vibrationally excited species, since they have more energy compared to the ground state of the species.

The interactions between plasma and catalyst described above and their resulting effects demonstrate the complexity of plasma catalysis, and the necessity of a full understanding of these interactions for improving the applicability of this technology. This can

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http://dx.doi.org/10.1016/j.apcatb.2014.01.061

only be accomplished through multidisciplinary research, including both experimental and computational studies.

Recently, a number of studies on such combined effects of plasma and catalyst were performed [6,11–16], although most studies focus on the aspect of the plasma. Both experimental and computational studies on the plasma-based reforming intend to find the optimal working conditions, e.g. to determine which type of discharge is the most advantageous and energy-efficient [17–23]. Mainly cold atmospheric plasmas, like dielectric barrier discharges (DBDs), are being studied. However, warm plasmas, such as gliding arc or microwave discharges, are also investigated in this research field [24–26]. From the catalytic point of view, various experimental studies describe the adsorption and decomposition of CH_4 on nickel catalysts [27–29]. Furthermore, Density Functional Theory (DFT) calculations were performed to further describe these processes [30,31]. In addition to the DFT calculations, classical molecular dynamics (MD) simulations were done to describe the dissociation of methyl radicals adsorbed on nickel surfaces [32,33]. Ab initio MD simulations on the initial stages of the growth of carbon nanotubes and graphene also investigate the adsorption and dehydrogenation of CH_4 on nickel surfaces, albeit at higher temperatures (1500 K) [34]. The studies mentioned above include species derived from CH_4, that are also formed in plasmas, and insight in the interactions of these species with catalyst surfaces can contribute to a more fundamental understanding of methane reforming through plasma catalysis.

In our previous work [33], we focused on the interactions of CH_x ($x = \{1,2,3\}$) radicals with several nickel surfaces at a temperature of 400 K, i.e. a typical temperature of a DBD. By performing MD simulations, using the Reactive Force Field (ReaxFF) potential [35], we found that the surface type influences the C–H bond breaking after adsorption as well as the reactivity towards formation of CH_x and C_2H_x species [33]. Little H_2 formation was observed at 400 K. Thus, a temperature study with the emphasis on H_2 formation was performed on Ni(1 1 1), in the temperature range of 400–1600 K [36]. This maximum temperature is for example reached in the transitional regime of a gliding arc discharge. A substantial number of H_2 molecules were indeed formed after CH_x impacts at 1400 and 1600 K. However, these high temperatures also induce the diffusion of C-atoms into the nickel surface, which is more desired for e.g. (plasma-)growth of carbon nanotubes [37] or graphene [38] than for a reforming reaction. It would be more interesting to obtain significant H_2 formation, with less carbon diffusion. Since the type of nickel surface influences the reactivity at 400 K, we should consider the role of the nickel surface on the H_2 formation and carbon diffusion at higher temperatures as well.

In this work, we therefore first investigate the direct H_2 formation on the catalyst surface for five different nickel surfaces, in the temperature range of 400–1600 K. Subsequently, we will also try to obtain a more general insight in the temperature effect on the reactivity of adsorbed plasma species.

2. Computational details

The reaction behavior of the CH_x ($x = \{1,2,3\}$) radicals on the catalyst surface is described with molecular dynamics (MD) simulations, based on the ReaxFF potential [35]. ReaxFF has been applied to a wide variety of systems, including silicon oxides [39], biochemical systems [40] and hydrocarbons [35]. For this work, we used parameters for the Ni/C/H set developed and validated by Mueller and coworkers [32]. Previously, we validated this force field for our purposes, and successfully applied it in our earlier studies on plasma catalysis [33,36], carbon nanotube growth [41–43] and graphene growth [38], demonstrating the wide application range of the Ni/C/H force field. The computational setup is the same as used in our previous studies [33,36]. A detailed description of the force field can be found in [44].

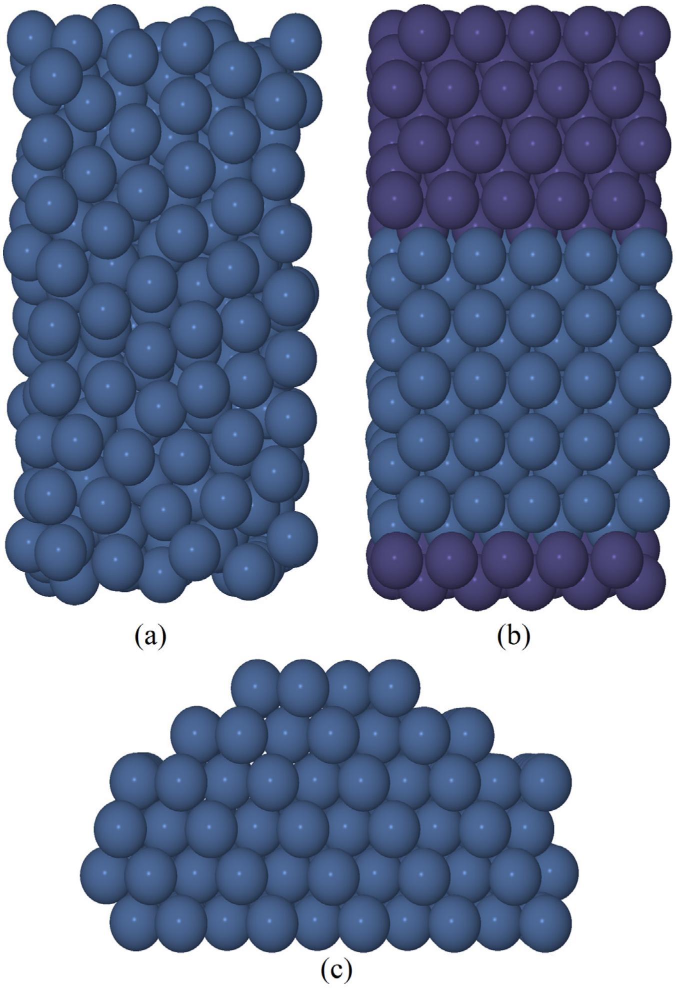

Fig. 1. Top view of (a) aNi, (b) pNi, for which the dark blue spheres represent the (1 1 1) facet and the light blue spheres the (1 0 0) facet, and side view of (c) sNi.

For this study, we constructed five different nickel surfaces, namely: Ni(1 1 1), Ni(1 0 0), a step-edged Ni(1 1 1) surface (denoted as sNi), an amorphous surface (aNi) and a polycrystalline surface (pNi). The first three surfaces were already used in our previous work to study the influence of surface energy and step-edges in the surface on the adsorption probability of the radicals and the reactions after adsorption [33]. However, the crystallinity of the surface might change due to the interactions with the plasma. Consequently, this can alter the reactivity of the catalyst. For this reason, aNi and pNi are included in this study, to elucidate this effect of change in crystallinity. The flat surfaces, i.e. Ni(1 1 1), Ni(1 0 0) and pNi, each consist of 300 Ni-atoms, equally divided over 6 atomic layers. The pNi structure shows a (1 1 1) facet and a (1 0 0) facet. The amorphous surface also has 300 atoms, randomly distributed in the cell volume such that separate layers are difficult to distinguish. Finally, the sNi surface is created with 255 atoms, divided over 6 layers in a manner that step-edges are present in the surface. The structure of this surface is shown in Fig. 1, together with those of aNi and pNi. The full structures of Ni(1 1 1) and Ni(1 0 0) can be found in our previous work [33], while the (1 1 1) and (1 0 0) facet can also be seen in Fig. 1b.

Prior to the impacts, all the surfaces were equilibrated to the desired temperature, in the range of 400–1600 K, employing the Bussi thermostat with a coupling constant of 100 ps [45]. Subsequently, both single and consecutive impacts of CH_x radicals on