Effect of Cu on Ni Catalyst for the Thermal Decomposition of Methane: A Molecular Dynamics Investigation

Gian Paolo O. Bernardo*, Leonila C. Abella, Joseph Auresenia, Hirofumi Hinode

Abstract–**The dissociation of a single CH_4 molecule on amorphous *Ni* surface and on *Cu*-doped *Ni* surface was investigated via *ab initio* DMol^3 molecular dynamics simulation. Initial simulation used the Local Density Approximation (LDA) with the Perdew-Wang 1992 (PWC) specific local exchange correlation functional, Gaussian double zeta plus polarization function basis set (DNP) at gamma (1x1x1) k-point calculation and orbital cut-off of 3.4 Å, with additional parameters: T = 1300K, time step = 2.5 fs, simulation time of 0.25 ps, with canonical NVT (constant amount (N), volume (V) and temperature) thermodynamic ensemble and Generalized Gradient Moment (GGM) thermostat. Results demonstrate the capacity of *Ni* for carbon deposition, whereas the addition of *Cu* resulted in the following: promoted the disjoining of the *H* atoms from the *C* atom allowing the *C* atom to form more bonds with the metal surface; accelerated the initial catenation of the CH_4 atom (*Ni* = 12.5 fs; *Ni-Cu* = 10.0 fs); and delayed the initial deposition of *C* atom on the metal surface (*Ni* = 30.0 fs; *Ni-Cu* = 37.5 fs). Examination of the decomposition mechanism revealed the initial formation of a metal-*H* bond between one of the *H* atoms of the CH_4 molecule and one of the metal atoms, followed by the re-formation of a transition bond between the *C* atom and the *H* atom bonded to the metal. This brings the *C* atom towards the metal surface for deposition after which the transition *C-H* bond is broken. This implied role of hydrogen in the deposition of carbon agrees with experimental results in literature.**

Keywords— methane thermal decomposition, nickel, copper, Dmol3, molecular dynamics

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I.   Introduction

The synthesis of carbon materials, such as carbon nanotubes, has widely been conducted through Catalytic Chemical Vapor Deposition (CCVD) [1, 2], in which catalysts utilize *Ni* as an active component [3] (mainly due to its susceptibility to carbon deposition). However, such susceptibility is also a deterrent to efficiency as catalytic activity tends to decrease with increasing carbon deposition. As such, various modifications have been done on *Ni*-based catalysts, from varying the support material to introducing dopants or promoters.

One of the most commonly used feedstock for such CCVD processes is CH_4; consequently, one of the most common CCVD technologies is the Catalytic Thermal Decomposition of Methane (CTDM) [4, 5]. In turn, *Ni-Cu* catalysts have been reported to be viable for CTDM mainly due to the promoting property of *Cu* to complement the susceptibility of *Ni* to carbon deposition [6-10].

Though a number of investigations have already been done on *Ni-Cu* catalysts with promising experimental results, only a few [11-14] have considered the mechanisms involved in the actual formation of *C* from CH_4 from a purely theoretical approach, i.e. *ab initio* calculations. Also, even though the role of *Cu* as a promoter has already been mentioned, the theory why *Cu* acts as a promoter to *Ni* in CH_4 decomposition has not yet been fully investigated.

Furthermore, in contrast to majority of literature which consider fixed crystalline structures for metal catalysts, e.g. *Ni*(111) [11, 12, 14], more realistic simulation conditions by instead using amorphous *Ni* should give a more accurate representation of the chemical reactions involved in CCVD.

Hence, in this study, the effect of *Cu* on the decomposition of CH_4 on amorphous *Ni* surface was investigated using *ab initio* considerations.

II.   Design and Methodology

A.   *Model Parameters*

The dissociation of a single CH_4 molecule on amorphous *Ni* surface and on *Cu*-doped *Ni* surface was investigated. *Ni* surface was prepared from a single crystal unit of face-centered cubic (FCC) *Ni*, cleaved to (0 0 -1) and structurally relaxed into an amorphous structure.

Surface doping of *Cu* on *Ni* surface was done by replacing symmetrically located *Ni* atoms into *Cu* atoms, followed by

the relaxation of the structure into the same amorphous state as previously described. The conversion from FCC to amorphous state has relinquished all symmetrical properties.

A single CH_4 molecule was added into the calculation cell by simple layering with a minimum reactant-to-surface distance of 3.3 Å. The bottommost layer was restrained from movement.

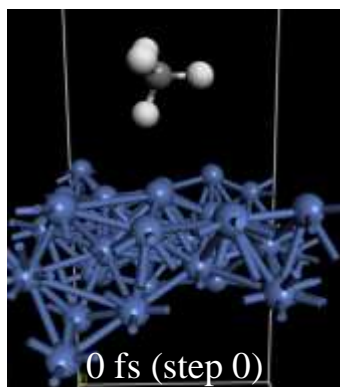The resulting initial state structures are shown in Fig. 1 and 2.

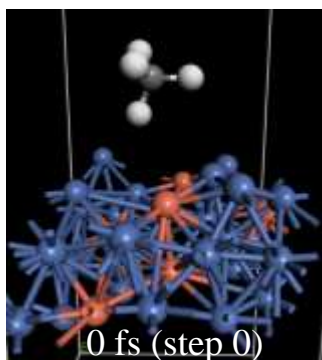Figure 1.   Initial State Structure for CH_4-Ni, 38 Ni atoms

Figure 2.   Initial State Structure for CH_4-Cu-doped-Ni, 34 Ni atoms and 9 Cu atoms

The following Figure Labels apply to every other figure pertaining to the molecular model throughout this paper: bluish spheres for Ni atoms; orange spheres for Cu atoms; grey sphere for C atoms; white spheres for H atoms; and bonds are represented as lines in between the bonded atoms.

B.   *Computational Parameters*

The investigation of the *ab initio* molecular dynamics (MD) was through DMol^3 [15] with the Local Density Approximation (LDA) [16-18] with the Perdew-Wang 1992 (PWC) [19] specific local exchange correlation functional and Gaussian double zeta plus polarization function (DNP) basis set [20]. The gamma k-point (1x1x1) was used for Brillouin zone sampling with an orbital cut-off of 3.4 Å.

Dynamics calculations were done with a time step of 2.5 fs (~100 a.u.) for a total simulation time of 0.25 ps (or 100 steps). The canonical NVT (constant amount (N), volume (V) and temperature (T)) thermodynamic ensemble [21] and

Generalized Gradient Moment (GGM) [22] was used for temperature control at T=1300K. The software environment and interface were contained in BIOVIA Accelrys Material Studio.

III.   Results and Discussion

From this point onwards, the H atom nearest to the metal surface shall be referred to as H^1. Snapshots of the MD simulation were taken at critical points in the dissociation process characterized either by a formation or a catenation of an atomic bond relative to the CH_4 molecule, as follows: initial state; catenation of H^1-C bond; formation of H^1-*metal* bond; formation of C-*metal* bond/s; and the formation of intermediate bonds between those points. Electrostatic potential maps have been generated to elucidate the electric nature of the system at key intervals.

A.   *CH₄ on Amorphous Ni*

The snapshots for MD simulation for CH_4 *on Ni* are shown in Fig. 3. The initial catenation of the H^1-C bond occurred in 12.5 fs brought by the molecular vibration of CH_4 at T=1300K in combination with the electronic acitivty of the *metal* surface, as represented (1)

$$CH_4 \xleftrightarrow{\quad Ni \quad} H^{1+*} + CH_3^{-*} \qquad (1)$$
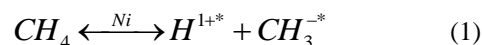
where the superscript * denotes that the reacting species is a radical.

This was immediately followed by the formation of weak intermediate H^1-*metal* bonds associated with Van der Walls interaction forces (2).

$$H^{1+*} + 2Ni(metal) \xleftrightarrow{\quad Ni \quad} Ni^{\pm} - H^{1+*} - Ni^{\mp} \quad (2)$$
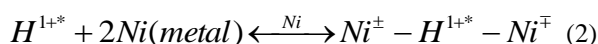
where – denotes the Van der Waals interaction forces between the two reacting species and the superscripts ± and ∓ represent a partial charge on the Ni atoms.

It must be noted that the H^1 atom formed two intermediate and highly unstable bonds to two separate Ni atoms. As shown in Fig. 4, this intermediate bond generated an electrically negative region (blue field) in between the Ni surface and the C atom as a result of the migration of electrons from the surface of the metal. This surplus in electrons resulted in the gravitation of the remainder of the positive-charged H atoms bonded to the C atom towards the negative region, causing the "flatening" of the CH_3 molecule and the resultant "pulling" of the C atom towards the Ni surface.

Consequently, after 30 fs, the C atom formed a single bond with a Ni atom (3) – the initial phase of carbon deposition. Note that Ni, now singular, assumed a positive charge.

$$CH_3^{-*} + Ni^+(metal) \xleftrightarrow{\quad Ni \quad} NiCH_3 \qquad (3)$$
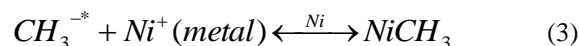
No further changes in the system were observed after this stage, aside from the continuous migration of the H^1 atom around and on the *Ni* surface.

These findings are in agreement with literature [11] whereas a similar $NiCH_3$ structure was observed by MD simulation, but with different simulation parameters.

In summary, the attraction of the *C* atom towards the *Ni* surface was brought by the attraction of the *H* atoms still bonded to the *C* atom towards the *Ni* surface, whereas the formation of the *CNi* bond was a matter of satisfying the octet rule. This demonstration suggests the role of hydrogen in CVD in the production graphene products, where it serves both as the attracting species for the migration of the *C* atom towards the *Ni* surface (H^1 atom) and as the attracted species which migrates the *C* atom toward the *Ni* surface (*H* atoms bonded to the *C* atom). This is in agreement with experimental results suggesting the influence and role of H_2 in CVD processes [23-25].
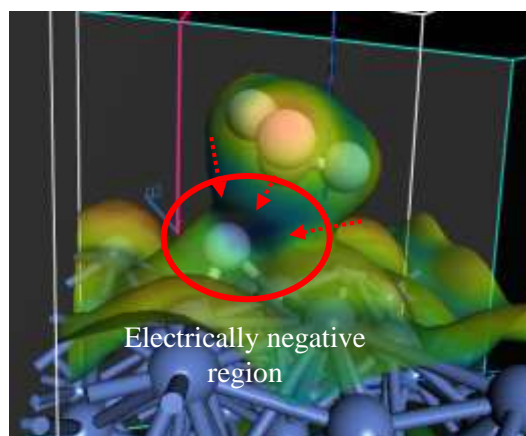
Figure 4.   Electrostatic Potential Map for CH_4 on *Ni* at t=22.5 fs

B. *CH₄ on Cu-doped Amorphous Ni*

The snapshots for MD simulation for CH_4 on *Ni* are shown in Fig. 5. Catenation of the H^1 atom took place after 10 fs (4), where the decrease in catenation time is associated with the change in the electric nature of the surface of the metal brought by the presence of *Cu*. This was followed by the formation of the H^1-*Ni* Van der Waals interaction type of bond after 15 fs (5). Examination of the electrostatic potential map in Fig. 6 reveals the formation of an also similar electrically negative region in between the *C* atom and the *H* atom bonded to the *Ni* surface, but with the addition of an electrically positive region (red field) brought by the *Cu* atom.

$$CH_4 \xleftrightarrow{Ni-Cu} H^{1+*} + CH_3^{-*} \qquad (4)$$

$$H^{1+*} + Ni(metal) \xleftrightarrow{Ni-Cu} Ni - H^{+1*} \qquad (5)$$
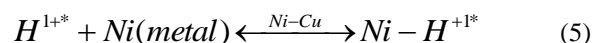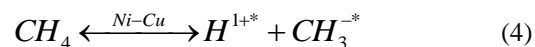
At 27.5 fs, the H^1 atom bonded to a *Ni* atom formed a second intermediate and, hence, inherently unstable bond with the *C* atom (6).

$$Ni - H^{1+*} + CH_3^{-*} \xleftrightarrow{Ni-Cu} Ni - H^{1+*} - CH_3^{-*} \quad (6)$$
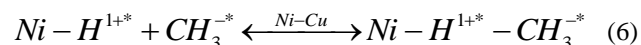
At this point, the increase in intensity in the electrically positive regions both on the *Cu* atom and one of the *H* atoms (from 15 fs to 27.5 fs, visible in Fig. 6) implies an increase in the repulsive interaction between these two atomic constituents, while the increase in intensity in the electrically negative region implies the migration of the electrons in the CH_4 molecule towards the *C* atom and the intermediate double bond formed by the H^1 atom. It must be noted that (6) suggests that the overall charge of the CH_3 radical is negative.

At 37.5 fs, the intermediate Ni-H-CH_3 bond breaks and the *C* atom bonds with the *Cu* atom (8). An examination of the electrostatic potential map in Fig. 6 reveals an increase in both the electrically positive region on the *Cu* atom and the electrically negative region on the *C* atom. This "coupling
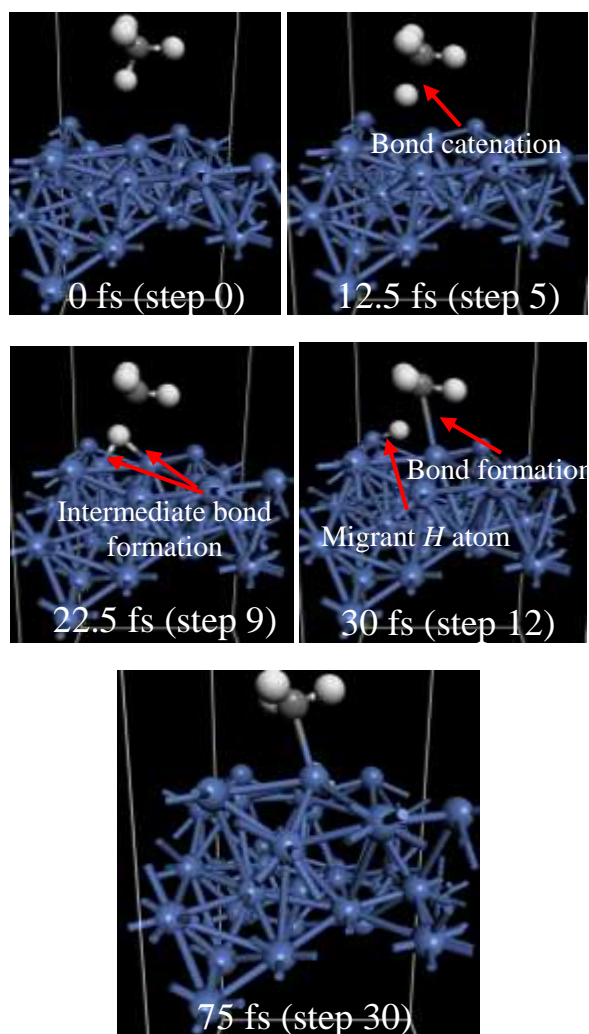

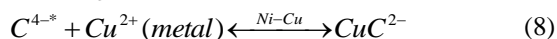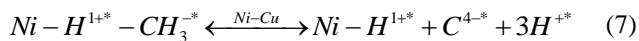Figure 3.   Time-course Molecular Dynamics for CH_4 on amorphous *Ni*

effect" resulted in the formation of the *C-Cu* bond and in the annihilation of the *CH₄* molecule caused by the repulsive forces between the *H*-atoms and the *Cu* atom.

$$Ni - H^{1+*} - CH_3^{-*} \xleftarrow{Ni-Cu} Ni - H^{1+*} + C^{4-*} + 3H^{+*} \quad (7)$$

$$C^{4-*} + Cu^{2+}(metal) \xleftarrow{Ni-Cu} CuC^{2-} \quad (8)$$

The complete destruction of the *CH₄* atom made the dissociation of the *C* atom onto and into the surface of the *metal* possible through the formation of additional bonds (at 52.5 fs and much later at 225 fs). Note that this dissociation process neutralizes the overall negative charge implied in (8).
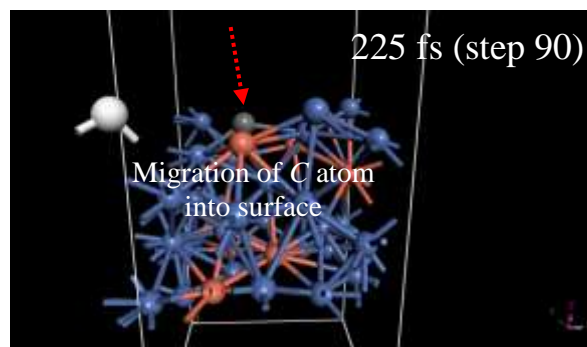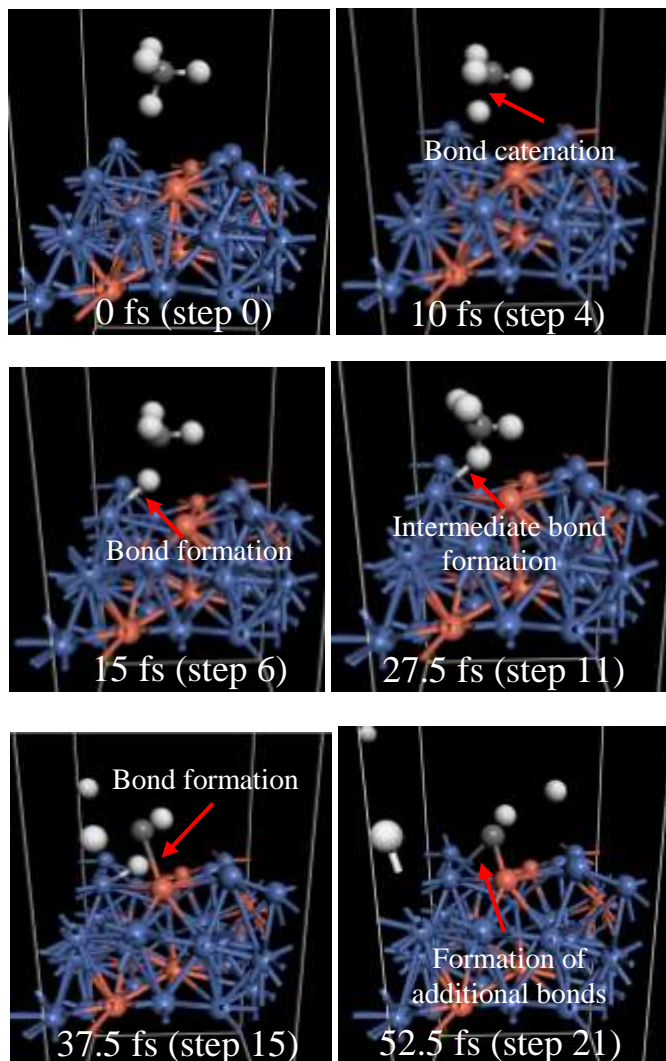

Figure 5.   Time-course Molecular Dynamics for *CH₄ on Cu*-doped amorphous *Ni*
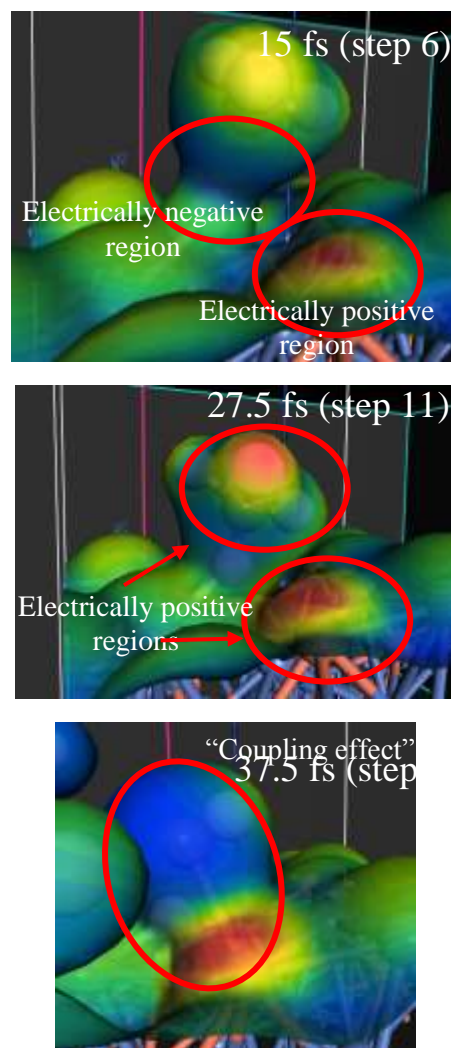

Figure 6.   Electrostatic Potential Map for *CH₄* on *Cu*-doped amorphous *Ni* surface

As a result, the doping of *Cu* on an amorphous *Ni* surface effected the following: the germinate or attracting role of hydrogen (H^1) has not changed; the mechanism through which the *C* atom migrates towards the metal surface is no longer a result of the attraction of the *H* atoms bonded to the *C* atom, but rather of the direct attraction of the *C* atom towards the *Cu*

atom; the complete destruction of the CH_4 molecule, resulting in the release of more free H atoms and thus increasing their capacity to germinate other C deposition mechanisms in the presence of leaner reactant streams; and the dissociation of the C atom onto and into the surface of the *metal* surface.

IV. Conclusions

The effect of *Cu* dopant on amorphous *Ni* surface on the mechanism of carbon deposition was investigated successfully through *ab initio* MD simulations. The addition of *Cu* altered the electric nature of the *metal* surface by localizing an electrically positive region. The presence of such region enhanced the attraction of the C atom towards the *metal* surface, further resulting in the complete destruction of the CH_4 molecule and the migration of the C atom onto and into the *metal* surface in a relatively short time frame of about 225 fs. The germinate role of H_2 and its metallic intermediates was also demonstrated. This, in combination with the release of more H atoms brought by the destruction of the CH_4 molecule, implied an overall increase in chemical activity compared to an un-doped *Ni* surface.

Acknowledgments

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