Ab initio study of dissociation reaction of ethylene molecules on Ni cluster

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Abstract. The dissociation reaction of ethylene molecules on the Ni cluster surface is investigated by *ab initio* molecular dynamics simulations. We observe that hydrogen atoms are generated from ethylene molecules at a rate of about 20 ps^{-1}. The activation energy for the dissociation of a hydrogen atom is estimated to be about 0.52 eV, which corresponds to a rate of only about 0.1 ps^{-1}. We find that the adsorption energy of an ethylene molecule on the Ni cluster is more than 1.5 eV, which is three times greater than the activation energy for the hydrogen dissociation. It is, therefore, suggested that the adsorption energy is responsible for the increase of the rate of the dissociation reaction. Based on these results, we discuss the microscopic process of the reaction of ethylene molecules on the Ni cluster in detail.

1. Introduction

The formation mechanism of carbon nanotubes (CNTs) [1, 2] via a catalytic chemical vapor deposition (CCVD) technique [3–5] has been widely studied since the CCVD is developed as a promising technique for large quantity synthesis of CNTs. It is well known that catalytic metals are essential to synthesize single-walled carbon nanotubes (SWNTs), whereas multi-walled carbon nanotubes (MWNTs) can be formed without catalytic metals [6]. Therefore, the role of catalytic metal in the growth of SWNTs has been widely discussed [7,8]. In 2003, Shibuta and Maruyama [9] first reported a continuous simulation of metal-catalyzed growth of initial cap structure of the SWNT by classical molecular dynamics (MD) simulation. In the simulation, graphite networks precipitated after isolated carbon atoms dissolved into a Ni cluster, and then a cap structure was formed on the surface of the Ni cluster. The metal-catalyzed growth model was then followed by a lot of numerical works [10–30]. In addition, in situ environmental transmission electron microscopy [31, 32] directly captured the nucleation process of the initial cap structure of SWNTs, which validates the metal-catalyzed growth model predicted by above numerical works. Therefore, there has been a broad consensus up to now that the cap structure is nucleated on the surface of the metal nanoparticle as an initial step of SWNT growth in the CCVD process.

On the other hand, reaction processes of carbon source molecules and additives on the catalytic metal surface are poorly understood since these reactions are complexly intertwined with diffusion and dissociation processes. However, it is not straightforward to treat dissociation process of carbon source molecules and subsequent formation process of graphite network at the
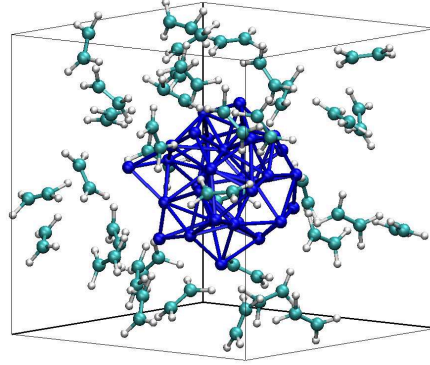
Figure 1. Snapshot of the initial atomic configuration of a Ni cluster, which consists of 32 nickel atoms, and 37 ethylene molecules in a box of dimensions $15\times15\times15$ Å^3.

same time in numerical simulation due to that there is a discrepancy in timescale between dissociation and subsequent graphite formation processes. Therefore, when a formation of the nanotube cap structure on the metal surface is focused on, it has been compelled to ignore the initial dissociation process as in the most of numerical studies introduced above [8–30].

Under such circumstance, we investigate a continuous simulation starting from dissociation of carbon source molecules onto the surface of a metal cluster by *ab initio* MD simulations in this study. Specifically, dissociation of ethylene molecules onto the Ni cluster is examined, which is one of the typical combinations for the CCVD synthesis of SWNTs.

2. Method of calculation

The electronic states are calculated using the projector-augmented-wave (PAW) method [33], which is an all-electron electronic-structure-calculation method within the frozen-core approximation. In the framework of density functional theory, the generalized gradient approximation [34], is used for the exchange-correlation energy. The plane-wave-cutoff energies are 30 and 250 Ry for the electronic pseudo-wave functions and the pseudo-charge density, respectively. The energy functional is minimized iteratively using a preconditioned conjugate-gradient method. The gamma point is used for Brillouin zone sampling. Projector functions are generated for the $3d$, $4s$ and $4p$ states of nickel atom, the $2s$ and $2p$ states of carbon atom, and the $1s$ state of hydrogen atom. MD simulations are carried out at a temperature of 1500 K in the canonical ensemble using the Nosé-Hoover thermostat technique [35]. The equations of motion are integrated numerically using an explicit reversible integrator [36] with a time step of 0.242 fs. All computation time is 2.42 ps. The system studied in our MD simulations consists of a Ni$_{32}$ cluster and 37 ethylene molecules (in total of 254 atoms) in a box of dimensions $15\times15\times15$ Å^3 under periodic boundary conditions. In the initial configuration, the ethylene molecules are arranged around the Ni cluster, which is annealed at 1500 K without ethylene molecules beforehand, as shown in figure 1. The number density of the ethylene molecules corresponds to that of the liquid state. We use our own computer code in the present work.

To quantify the change in the bonding properties of atoms associated with the dissociation reaction of hydrogen atoms, we use a population analysis [37] by expanding the electronic wave functions in an atomic-orbital basis set. Based on the formulation generalized to the PAW method [38], we obtain the gross population for each atom and the bond-overlap population for each atomic pair. From the gross population, we estimate the charge of atoms, and the bond-overlap population gives a semi-quantitative estimate of the strength of covalent bonding between atoms.
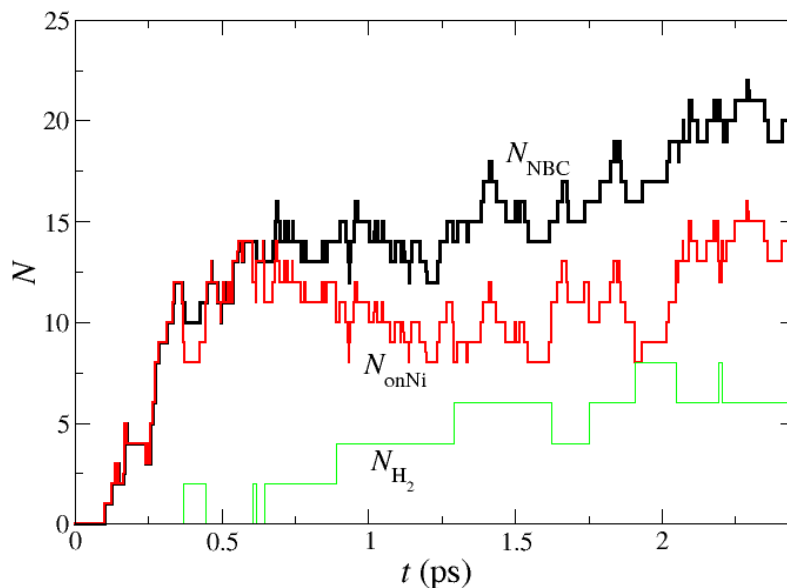
Figure 2. Time evolution of the number of hydrogen atoms. N_{NBC} shows the number of hydrogen atoms which are not bonded to carbon atoms. N_{onNi} shows the number of hydrogen atoms which exist as a hydrogen atom around the Ni cluster. N_{H2} is the number of hydrogen atoms constituting hydrogen molecules.

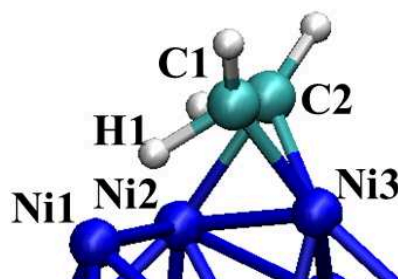## 3. Results and Discussion

3.1. The number of dissociated hydrogen atoms

We observe a lot of dissociation reactions of hydrogen atoms from ethylene molecules on the Ni cluster. The reaction occurs more than 10 times during 400 fs in the beginning of our simulation, which corresponds to a reaction rate of about 20 ps^{-1}. The number of hydrogen atoms, which are not bonded to carbon atoms, N_{NBC} increases with time as shown in figure 2. More than half of them exist as a hydrogen atom around the Ni cluster within 2.42 ps, the number of which is N_{onNi} in figure 2. The rest form hydrogen molecules. N_{H2} in figure 2 is the number of the hydrogen atoms constituting hydrogen molecules. The averaged value of N_{onNi} is nearly constant ~ 11 after 0.5 ps. The number of hydrogen atoms that can exist around the Ni cluster is limited because the Ni cluster has a finite volume. Therefore, hydrogen molecules are generated when the number of the hydrogen atoms exceeds the limitation. Since it is considered that the hydrogen atoms that exist around the catalysts are responsible for inhibiting the synthesis of the CNTs, an efficient process of removing the dissociated hydrogen atoms may be important for a smooth synthesis.
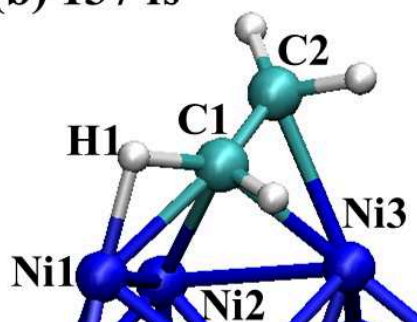
3.2. Dissociation process of a hydrogen atom from an ethylene molecule

Figure 3 shows a typical example of the dissociation process of a hydrogen atom from an ethylene molecule on the Ni cluster. The snapshot at 100 fs (figure 3(a)) represents an atomic configuration just after the adsorption on the Ni cluster. In this configuration, the C-C bond is a single bond because the carbon atoms are bonded to the nickel atoms. After the formation of a bonding state spreading over nickel, carbon and hydrogen atoms labeled "Ni1", "C1" and "H1", respectively, at around 137 fs (figure 3(b)), the dissociation reaction of H1 occurs at about 155 fs (figure 3(c)). On the other hand, the C-C bond is a little bit strengthened during the reaction of the dissociation. Actually, the dissociation of C-C bonds does not occur even once in our simulations.
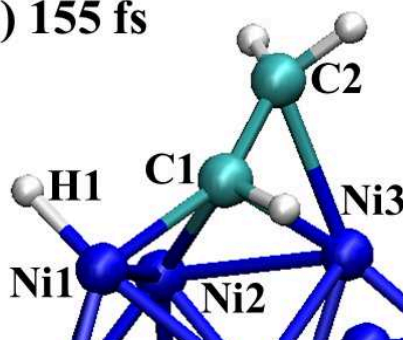
Figure 3. A typical example of the dissociation process of a hydrogen atom from an ethylene molecule on the Ni cluster. Atomic configurations at 100, 137 and 155 fs are shown.

3.3. Snapshot of atomic configuration

Figure 4 shows a snapshot of atomic configuration at 2.42 ps in our simulations. 17 ethylene molecules are adsorbed on Ni cluster, some of which dissociate hydrogen atoms. The number of the carbon atoms which dissociate one hydrogen atom (labeled "C_{H1}" in figure 4) are 7, and the number of the carbon atoms which dissociate two hydrogen atoms (labeled "C_{H0}" in figure 4) are 5. The dissociated hydrogen atoms exist around the Ni cluster (labeled "H" in figure 4), or as hydrogen molecules (labeled "H_2" in figure 4) as described in the section 3.1. Since the C-C bonds are never broken, it is considered that pairs of carbon atoms are the smallest components for the synthesis of CNTs rather than single carbon atoms in the case of the ethylene molecule as a carbon source molecule. We observe actually a carbon chain formed from two pairs of carbon atoms as shown in the circle of figure 4.
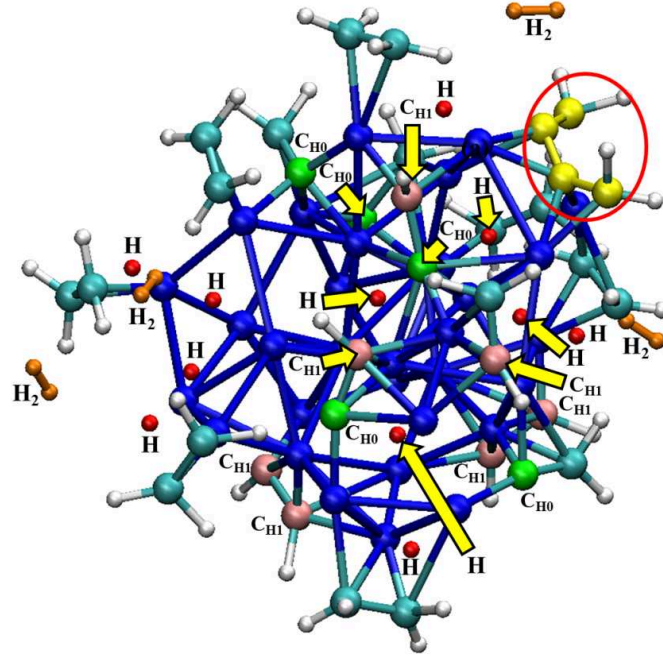
Figure 4. Snapshot of atomic configuration at 2.42 ps in MD simulations. Spheres labeled "C_{H1}" are carbon atoms that are bonded to one hydrogen atom. Spheres labeled "C_{H0}" are carbon atoms that are not bonded to hydrogen atoms. Spheres labeled "H" are dissociated hydrogen atoms. Pairs of spheres labeled "H_2" are hydrogen molecules. The numbers of C_{H1}, C_{H0}, H and H_2 are 7, 5, 11 and 4, respectively. The circle shows a carbon chain which consists of four carbon atoms.

3.4. Rate of the dissociation reaction

To find the minimum energy path of the dissociation reaction of a hydrogen atom from an ethylene molecule on the Ni cluster, we adopt the nudged elastic band (NEB) method [39]. As a discrete representation of a path from the reactant configuration $\mathbf{R_0}$ to the product configuration $\mathbf{R}_M$, $M - 1$ replicas of the system are created and connected together with springs. The images are then relaxed toward the minimum energy path. In this paper, we use $M = 10$. The reactant and product configurations are prepared as follows. Firstly, we pick up the atomic coordinates of the Ni cluster and the dissociated ethylene molecule just before and after the dissociation reaction reported in the section 3.2. Secondly, we perform the structural optimization for the two systems to obtain the initial and final states for the NEB calculation. The activation energy for the reaction is estimated to be about 0.52 eV, which corresponds to a reaction rate of only about 0.1 ps^{-1} according to the transition state theory [40]. However, the dissociation reaction occurs actually at a much faster rate of about 20 ps^{-1} in our simulations as mentioned in the section 3.1. Obviously, it is much faster than the reaction rate estimated from the activation energy.

In order to explain the large difference between these reaction rates, we investigate adsorption energies of the ethylene molecule on the Ni cluster. We calculate the adsorption energy as follows. Firstly, we calculate the sum of potential energies of two isolated systems, an isolated Ni cluster and an isolated ethylene molecule. Secondly, we calculate the potential energy of a system in which an ethylene molecule is put on the Ni cluster. Thirdly, the latter energy is subtracted from the former to obtain the adsorption energy. Figure 5 shows one of the adsorption sites on the Ni cluster, which has the adsorption energy of 1.573 eV. It is clarified that the ethylene
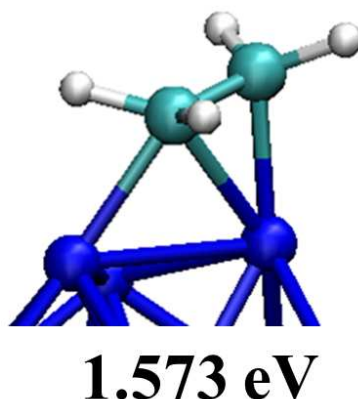
Figure 5. Atomic configuration of an adsorption site of an ethylene molecule on the Ni cluster. The value of the adsorption energy is shown.

molecule can obtain more than 1.5 eV when it is adsorbed on the Ni cluster. This value is about three times larger than the activation energy of 0.52 eV. Therefore, the adsorption energy is responsible for accelerating the reaction rate.

4. Summary

To investigate the microscopic process of the dissociation reaction of the ethylene molecules on the Ni cluster in detail, we perform *ab initio* molecular dynamics simulations. We observe a lot of dissociation reactions of hydrogen atoms from ethylene molecules on the Ni cluster at a fast rate of about 20 ps^{-1}. While more than half of the dissociated hydrogen atoms exist around the Ni cluster, the rest form hydrogen molecules. Since there is a limit for the number of hydrogen atoms around the Ni cluster, hydrogen molecules are generated when the number of hydrogen atoms exceeds the limitation. We also calculate the activation energy and the reaction rate for the dissociation reaction. The reason why the reaction rate of the dissociation reaction is so fast is that the ethylene molecules obtain the adsorption energy of at least 1.5 eV, which is about three times larger than the activation energy of 0.52 eV for the dissociation reaction.

References
[1] Iijima S 1991 *Nature* **354** 56
[2] Iijima S and Ichihashi T 1993 *Nature* **363** 603
[3] Dai H, Rinzler A G, Nikolaev P, Thess A, Colbert D T and Smalley R E 1996 *Chem. Phys. Lett.* **260** 471
[4] Nikolaev P, Bronikowski M J, Bradley R K, Rohmund F, Colbert D T, Smith K A and Smalley R E 1999 *Chem. Phys. Lett.* **313** 91
[5] Maruyama S, Kojima R, Miyauchi Y, Chiashi S and Kohno M 2002 *Chem. Phys. Lett.* **360** 229
[6] Dresselhaus M S, Dresselhaus G and Avouris P 2001 *Carbon nanotubes: synthesis, structure, properties, and applications* (Topics in Applied Physics vol 80) (Berlin: Springer-Verlag)
[7] Banhart F 2009 *Nanoscale* **1** 201
[8] Shibuta Y 2011 *Diamond Relat. Mater.* **20** 334
[9] Shibuta Y and Maruyama S 2003 *Chem. Phys. Lett.* **382** 381

[10] Ding F, Rosén A and Bolton K 2004 *J. Chem. Phys.* **121** 2775

[11] Ding F, Bolton K and Rosén A 2004 *J. Phys. Chem. B* **108** 17369

[12] Ding F, Bolton K and Rosén A 2006 *Comput. Mater. Sci.* **35** 243

[13] Zhao J, Martinez-Limia A and Balbuena P B 2005 *Nanotechnology* **16** S575

[14] Gómez-Gualdrón D A, McKenzie G D, Alvarado J F J and Balbuena P B 2012 *ACS Nano* **6** 720

[15] Shibuta Y and Maruyama S 2007 *Chem. Phys. Lett.* **437** 218

[16] Shibuta Y and Maruyama S 2007 *Comput. Mater. Sci.* **39** 842

[17] Shibuta Y and Elliott J A 2006 *Chem. Phys. Lett.* **427** 365

[18] Shibuta Y and Elliott J A 2009 *Chem. Phys. Lett.* **472** 200

[19] Neyts E C, Shibuta Y, Van Duin A C T and Bogaerts A 2010 *ACS Nano* **4** 6665

[20] Neyts E C, Van Duin A C T and Bogaerts A 2011 *J. Am. Chem. Soc.* **133** 17225

[21] Neyts E C, Van Duin A C T and Bogaerts A 2012 *J. Am. Chem. Soc.* **134** 1256

[22] Amara H, Bichara C and Ducastelle F 2006 *Phys. Rev. B* **73** 113404

[23] Amara H, Bichara C and Ducastelle F 2008 *Surf. Sci.* **602** 77

[24] Amara H, Bichara C and Ducastelle F 2008 *Phys. Rev. Lett.* **100** 056105

[25] Amara H, Roussel J M, Bichara C, Gaspard J P and Ducastelle F 2009 *Phys. Rev. B* **79** 014109

[26] Ohta Y, Okamoto Y, Irle S and Morokuma K 2008 *ACS Nano* **2** 1437

[27] Ohta Y, Okamoto Y, Irle S and Morokuma K 2009 *J. Phys. Chem. C* **113** 159

[28] Page A J, Irle S and Morokuma K 2010 *J. Phys. Chem. C* **114** 8206

[29] Page A J, Minami S, Ohta Y, Irle S and Morokuma K 2010 *Carbon* **48** 3014

[30] Page A J, Yamane H, Ohta Y, Irle S and Morokuma K 2010 *J. Am. Chem. Soc.* **132** 15699

[31] Hofmann S, Sharma R, Ducati C, Du G, Mattevi C, Cepek C, Cantoro M, Pisana S, Parvez A, Cervantes-Sodi F, Ferrari A C, Dunin-Borkowski R, Lizzit S, Petaccia L, Goldoni A and Robertson J 2007 *Nano Lett.* **7** 602

[32] Yoshida H, Takeda S, Uchiyama T, Kohno H and Homma Y 2008 *Nano Lett.* **8** 2082

[33] Blöchl P E 1994 *Phys. Rev. B* **50** 17953

[34] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

[35] Hoover W G 1985 *Phys. Rev. B* **31** 1695

[36] Tuckerman M, Berne B J and Martyna G J 1992 *J. Chem. Phys.* **97** 1990

[37] Mulliken R S 1955 *J. Chem. Phys.* **23** 1833

[38] Shimojo F, Nakano A, Kalia R K and Vashishta P 2008 *Phys. Rev. E* **77** 066103

[39] Jónsson H, Mills G and Jacobsen K W 1998 *Nudged elastic band method for finding minimum energy paths of transitions* Classical and Quantum Dynamics in Condensed Phase Simulations (Singapore: World Scientific)

[40] Truhlar D G, Garrett B C and Klippenstein S J 1996 *J. Phys. Chem. C* **100** 12771