Dissociation mechanism of ethylene molecules with a Ni cluster: *ab initio* molecular-dynamics study

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The dissociation reactions of ethylene molecules on a Ni cluster are examined by means of *ab initio* molecular-dynamics simulations. The dissociation reactions of hydrogen atoms are observed at a rate of about 20 ps^{-1} in our simulations. While more than half of the dissociated hydrogen atoms exist around the Ni cluster, the rest form hydrogen molecules. We also calculate the activation energy for the dissociation reaction of a hydrogen atom to be about 0.52 eV, which corresponds to a rate of only about 0.1 ps^{-1}. To explain the large difference between these reaction rates, we investigate adsorption energies of the ethylene molecule on the Ni cluster. As a result, we clarify that the adsorption energy is more than 1.5 eV, which is three times greater than the activation energy for the hydrogen dissociation. Therefore, the adsorption energy is responsible for the increase of the rate of the dissociation reaction.

§1. Introduction

The synthesis of single-walled carbon nanotubes (SWNTs)[1)] via a catalytic chemical vapor deposition (CCVD) technique[2)–4)] is one of the most popular method on the commercial scale. The SWNTs have been commonly synthesized using a traditionally transition metals (Fe, Co, Ni etc.) as a catalyst, however, the exact role with respect to the SWNTs synthesis is still unclear. Therefore, the effect of catalytic metal on the growth of the SWNTs has been widely discussed.[5),6)] In 2003, molecular-dynamics (MD) simulations, which were associated to the CCVD experiments, were employed first successfully by Shibuta and Maruyama.[7)] In the simulation, a growth of initial cap structure of the SWNT arising from the metal catalysts was observed using classical MD simulations. The metal-catalyzed growth model has been used by a lot of numerical works.[8)–27)] In addition, in situ environmental transmission electron microscopy[28),29)] directly observed the generation process of the initial cap structure of the SWNTs, which proved that the metal-catalyzed growth model was remarkably consistent with the experimental work. Therefore, there has been reached a broad consensus that the cap structure is formed on the surface of the metal catalyst in the earlier stage of the SWNTs nucleation in the CCVD process.

On the other hand, the reactions of carbon source molecules on the metal catalyst surface have not been poorly investigated. This is because these reactions are

intertwined with diffusion and dissociation processes. However, it is extremely difficult to deal with at the same time the dissociation of the carbon source molecules and the subsequent growth of the SWNTs due to that there is a large difference in the time scale between the former and the latter. Therefore, when a nucleation of the nanotube cap structure on the metal catalyst surface is focused on, it has been obliged to exclude the initial dissociation process in the greater part of numerical studies introduced above.

For this reason, we aim to clarify the dissociation of carbon source molecules on the surface of a metal cluster by *ab initio* MD simulation. In particular, the dissociation of ethylene molecules on a Ni cluster is examined, which are the typical combinations employed for the CCVD synthesis of the SWNTs.

§2. Method of calculation

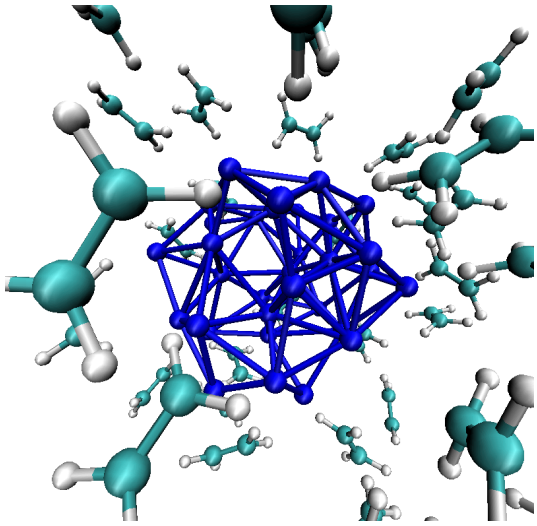

Fig. 1. Snapshot of the initial atomic configuration of a Ni cluster, which is constituted by 32 nickel atoms, and 37 ethylene molecules.

Calculations for electronic states are carried out within density-functional theory (DFT) by using the projector-augmented-wave (PAW) method[30] within the frozen-core approximation. For the exchange and correlation energies, we use the generalized gradient approximation.[31] 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 an iterative scheme. 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. The Γ point is used for Brillouin zone sampling. MD simulations are carried out at 1500 K, as controlled by a Nosé-Hoover thermostat.[32] The equations of motion for atoms are solved numerically using an explicit reversible integrator[33] with a time step of 0.242 fs. All computation time is 4.84 ps. The system, which consists of a Ni_{32} cluster and 37 ethylene molecules (in

total of 254 atoms), is used in MD simulations with a unit cell of the size 15×15×15 Å^3 under periodic boundary conditions. In the initial atomic configuration, after we put a Ni cluster in the center of the supercell, which is annealed at 1500 K in the absence of ethylene molecules beforehand, ethylene molecules are placed around it, as shown in Fig. 1. The number density of the ethylene molecules is taken from that of the liquid state.

We use a population analysis[34] to clarify the change in the bonding properties of atoms associated with the dissociation reaction of hydrogen atoms. By expanding the electronic wave functions in an atomic-orbital basis set, we obtain the bond-overlap population for each atomic pair and the gross population for each atom, which are based on the formulation generalized to the PAW method.[35] The bond-overlap population gives a semi-quantitative estimate of the strength of covalent bonding between atoms, and we estimate the charge of atoms from the gross population.

§3. Result and Discussion

3.1. *The number of dissociated hydrogen atoms*

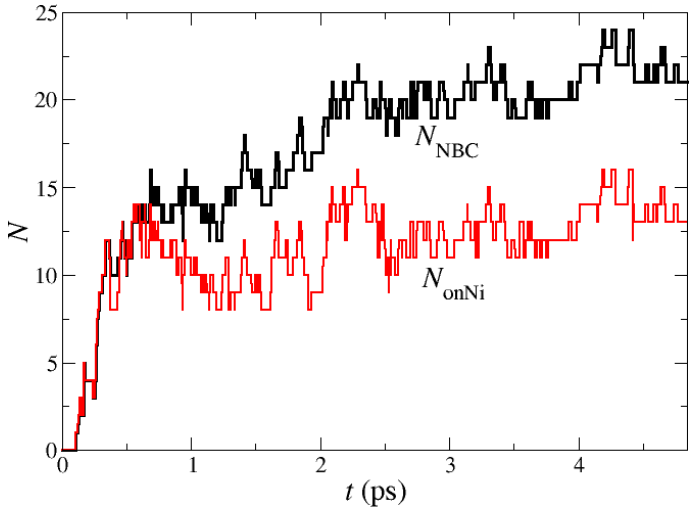

Fig. 2. Time evolution of the number of hydrogen atoms within the simulation time of 4.84 ps. N_{NBC} shows the number of hydrogen atoms which are not bonded to carbon atoms. N_{onNi} shows the number of hydrogen atoms around the Ni cluster.

A lot of dissociation reactions of hydrogen atoms from ethylene molecules on the Ni cluster are observed in our simulations, the reaction rate of which amounts to about 20 ps^{-1}. The number of hydrogen atoms, which are not bonded to carbon atoms, N_{NBC} increases with time as shown in Fig. 2. The majority of them exist around the Ni cluster with a single atom, the number of which is N_{onNi} in Fig. 2. The rest form hydrogen molecules. N_{H2}, which is the number of hydrogen atoms constituting the hydrogen molecules, can be obtained by subtracting N_{onNi} from N_{NBC}. Note that average value of N_{onNi} is nearly constant ∼12 after 0.5 ps, while

N_{H2} increases consistently during the simulation. This indicates that the number of hydrogen atoms that can exist around the Ni cluster is limited due to the finite volume of the Ni cluster. Therefore, we consider that the generation of hydrogen molecules may occur when the number of the hydrogen atoms exceeds the limitation.

3.2. *Dissociation mechanism of a hydrogen atom from an ethylene molecule*

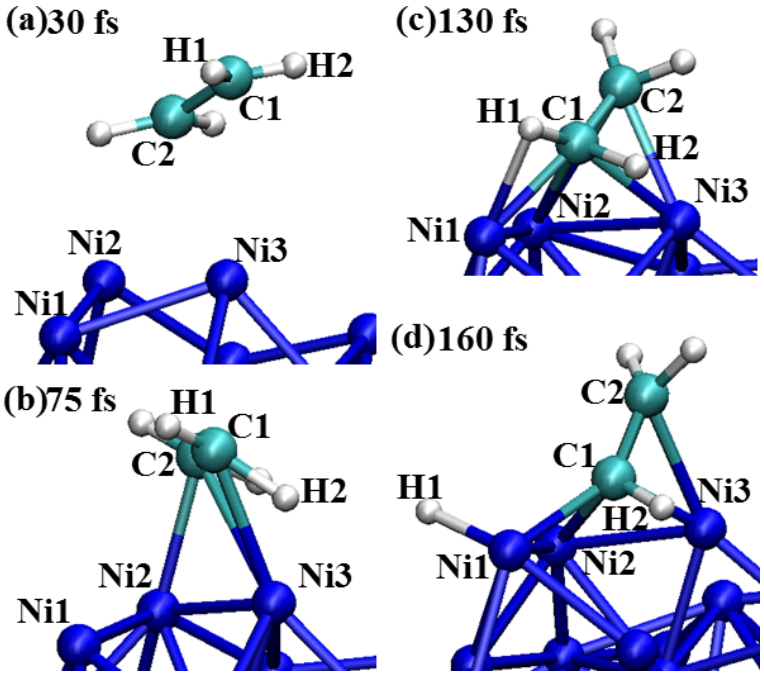

Fig. 3. A typical example of the dissociation process of a hydrogen atom from an ethylene molecule on the Ni cluster. Atomic configurations at 30, 75, 130 and 160 fs in our simulations are shown.

A typical example of the dissociation process of a hydrogen atom from an ethylene molecule on the Ni cluster is shown Fig. 3. The snapshot at 30 fs (Fig. 3(a)) represents the atomic configuration before the ethylene molecule is adsorbed on the Ni cluster, where the chemical bond for C1-C2 is still a double bond. However, the strength of the bond weakens rapidly until 75 fs (Fig. 3(b)). This reaction indicates that the bond becomes a single bond because the carbon atoms are bonded to the nickel atoms. At about 130 fs (Fig. 3(c)), a bonding state spreading over Ni1, C1 and H1 is formed. Subsequently, the dissociation reaction of H1 occurs as shown in the snapshot of 160 fs in Fig. 3 (d). Meanwhile, the strength of C1-C2 bond is enhanced a little during the dissociation reaction. Actually, we do not observe the dissociation of C-C bond even once throughout our simulations.

3.3. *Snapshot of atomic configuration*

Figure 4 shows a snapshot of atomic configuration at 4.84 ps in our simulations. 17 ethylene molecules are adsorbed on the Ni cluster, and some of these dissociate hydrogen atoms. The number of the carbon atoms which dissociate one hydrogen

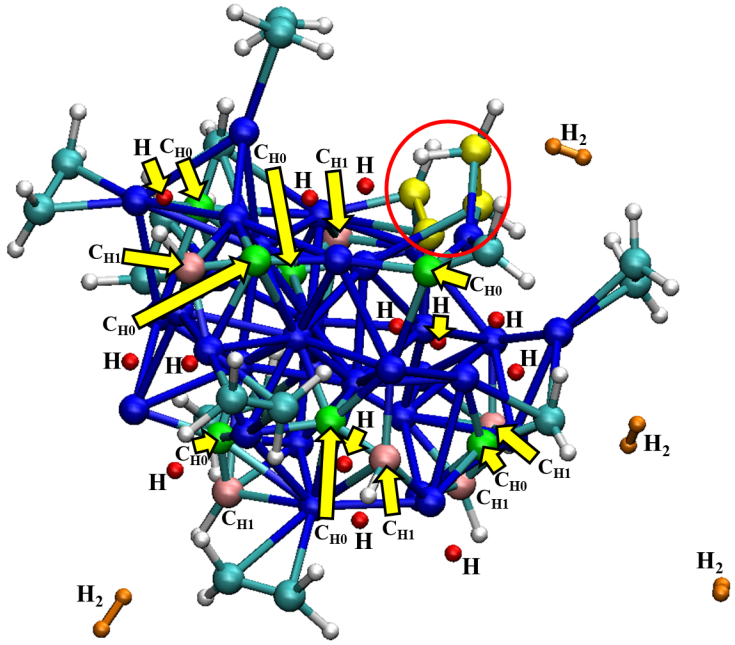

Fig. 4. Snapshot of atomic configuration from MD simulations at 4.84 ps. Spheres labeled "C_{H1}" are carbon atoms that are bonded to one hydrogen atom. Spheres labeled "C_{H0}" are carbon atoms that are not bonded to hydrogen atoms. Spheres labeled "H" are dissociated hydrogen atoms. Pairs of spheres labeled "H_2" are hydrogen molecules. The numbers of C_{H1}, C_{H0}, H and H_2 are 6, 7, 13 and 4, respectively. The circle shows the carbon chain composed of four carbon atoms.

atom (labeled "C_{H1}" in Fig. 4) are 6, and the number of the carbon atoms which dissociate two hydrogen atoms (labeled "C_{H0}" in Fig. 4) are 7. The dissociated hydrogen atoms exist around the Ni cluster (labeled "H" in Fig. 4), or as hydrogen molecules (labeled "H_2" in Fig. 4) as described in the section 3.1. Since the bond between carbon atoms is never dissociated, pairs of carbon atoms can be the smallest constituent parts for the synthesis of CNTs in the case of the ethylene molecule as a carbon source molecule. We capture actually a carbon chain generated from two pairs of carbon atoms as displayed in the circle of Fig. 4.

3.4. *Reaction rate of the dissociation reaction*

The nudged elastic band (NEB) method[36] is used to determine the minimum energy paths and energy barriers of the dissociation reaction of a hydrogen atom from an ethylene molecule on the Ni cluster. In the NEB method, a discretized path of 10 replicas of the system is constructed by linear interpolation between the initial and final configurations, and then optimized iteratively. The activation energy for the reaction is calculated 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.[37] However, the dissociation reactions take place more than 10 times during 400 fs from the start of the calculation (Fig. 2), of which reaction rate is estimated to be about 20 ps^{-1}. There is a considerable difference in the two reactions rate.

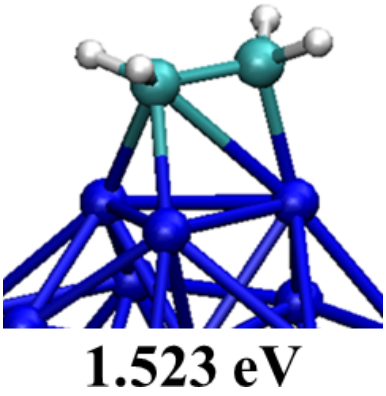

Fig. 5. Atomic configuration of an adsorption site of an ethylene molecule on the Ni cluster. The value of the adsorption energy is displayed.

We investigate adsorption energies of ethylene molecules on the Ni cluster to explain the discrepancy in these reaction rates. The adsorption energies are calculated as follows. Firstly, we calculate the sum of potential energies of an isolated Ni cluster and an isolated ethylene molecule, each of which is individually performed structural optimization beforehand. Secondly, we also perform the structural optimization for the system in which an ethylene molecule is put on the Ni cluster, and then we obtain the potential energy of the system. Thirdly, we subtract the latter energy from the former to get the adsorption energy. Figure 5 shows a typical example of the adsorption site on the Ni cluster, which has the adsorption energy of 1.523 eV. Since the value is about three times greater than the activation energy of 0.52 eV, the adsorption energy is due to the reason that the reaction rate is so fast.

§4. Summary

The atomistic mechanism of the dissociation reaction of the ethylene molecules on the Ni cluster is investigated by *ab initio* molecular-dynamics simulations. We observe a great deal of dissociation reactions of hydrogen atoms from ethylene molecules on the Ni cluster at a fast rate of about 20 ps^{-1}, whereas the bond between carbon atoms never dissociate in our simulations. Most of the dissociated hydrogen atoms exist around the Ni cluster and the rest generate hydrogen molecules. Since there is a limit to the number of hydrogen atoms around the Ni cluster, hydrogen molecules may be formed when extra hydrogen atoms appear. We also calculate the activation energy for the dissociation reaction to be about 0.52 eV using NEB method, and the corresponding reaction rate is estimated to be about 0.1 ps^{-1} according to the transition state theory. We find that there is a large difference from the reaction rate of 20 ps^{-1} above. This is because ethylene molecules obtain much more energy than the activation energy of 0.52 eV when it is adsorbed on the Ni cluster. The energy reaches at least 1.5 eV, which accelerates the dissociation rate.

Acknowledgements

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