Ab initio molecular dynamics simulation of Ni$_6$

Keiichiro Shiga , Kaoru Ohno* and Yoshiyuki Kawazoe

Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
Fax: 81-22-215-2052 ,e-mail: shiga@imr.edu , kawazoe@imr.edu
*Department of Physics, Faculty of Engineering, Yokohama National University
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
Fax: 81-45-339-4254, e-mail: ohno@ynu.ac.jp

Large scale ab initio molecular dynamics simulations are carried out to investigate the stability of Ni$_6$ and its collision with O$_2$. For the calculation of electronic states under the local spin density approximation (LSDA), we use the all-electron mixed basis approach, in which a one-electron wave function is expressed by superposing truncated numerical atomic orbitals and plane waves. We find that Ni$_6$ having a tetrahedral structure (d=2.33 Å ±0.01 Å) and a magnetic moment of 6 μ_B is stable but, after impact of O$_2$, it is dissociated into various fragments, NiO$_2$, Ni$_2$O$_2$ and Ni$_3$O$_2$, according to the impact angle and energy.
Key words: Ab initio molecular dynamics simulation, Ni$_6$, NiO$_2$, Ni$_2$O$_2$, Ni$_3$O$_2$

1. INTRODUCTION

To study the stability of transition-metal clusters are interesting from many respects. It would help understanding the mechanism of dissociation of larger clusters into smaller ones when a chemical reaction, such as oxidation, takes place. It would be also important in applications in magnetic recording media or future devices using the effect of giant magnetic resistance (GMR). To be specific, in what follows, we will focus on nickel clusters. Experimentally, Wöste et al. [1,2] studied the carbon mono-oxide (CO) adsorption on nickel cluster ions and elucidated the possible structures of nickel clusters. Recently, Ichihashi et al. [3] reported that the reaction cross section of Ni$_n^+$ with a methanol molecule change dramatically with cluster size.

In order to study the stability, reactivity and dissociability of the nickel clusters from theoretical point of view, here we carry out ab initio molecular dynamics simulations of the stability of an isolated Ni$_6$ cluster and the collision of an oxygen molecule (O$_2$) against the Ni$_6$. The method we use in this study is the all-electron mixed basis approach [4-6] based on the local spin-density approximation (LSDA) of density functional theory.

The result of this paper is organized as follows: In section 2, the present all-electron mixed-basis approach and the condition assumed for the present calculations are briefly described. In section 3, we present the results of our simulations. Finally section 4 is devoted to summarizing this paper.

2. METHODOLOGY

The ab initio method we adopt here is the all-electron mixed basis approach [4-6] which uses both atomic orbitals (AOs) and plane waves (PWs). This method is characterized as an efficient expression of a one-electron wave function based on the local spin density approximation (LSDA) [7] in density functional theory. In our approach, AOs are truncated numerical atomic orbitals determined by Herman-Skillman's atomic code. We apply this method to carry out ab initio molecular dynamics simulations of Ni$_6$ and Ni$_6$ + O$_2$ systems. For the calculation, we use 4169 plane waves having cut-off energy of 11Ry, and 1s,2s,2p,3s,3p,3d atomic orbitals for nickel and 1s,2s,2p atomic orbitals for oxygen.

We use a super-cell having a size of 9.6Å× 9.6Å× 9.6Å, which is divided into 64 × 64 × 64 meshes (one mesh = 0.15Å). Molecular dynamics simulations are performed in terms of the Newtonian dynamics, where the force acting on each atom includes the variational force in addition to the Hellmann-Feynman force. The basic time step is $\Delta t = 0.1$ fs. Whenever the atomic position is updated, the calculation of the electronic state is repeated five times using the steepest descent (SD) approach to get to the Borrn-Oppenheimer (BO) surface. At each SD step, the electronic density is mixed by 90 percent to generate a new electronic density distribution.

3. RESULTS

Now we explain the detail of our simulations and show their results. In the present study, we performed two kinds of simulations. First is the structural optimization of an isolated Ni$_6$ cluster and its stability test, and second is the dynamical simulations of the collision of O$_2$ against Ni$_6$.

3.1 Isolated Ni$_6$

First, we perform the structural optimization of Ni$_6$. The optimal structure is a regular octahedron (double-pyramid) which is depicted in Figure 1.
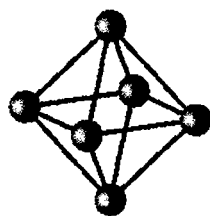
Fig.1. Optimized octahedral structure of Ni_6. The nearest-neighbor distance between Ni atoms is estimated to be $2.33\,\text{Å} \pm 0.01\,\text{Å}$.

The Ni-Ni distance is estimated to be $2.33\,\text{Å} \pm 0.01\,\text{Å}$, the magnetic moment is $6\,\mu_B$, and the binding energy is 3.4 eV/atom. Next, we shift the initial positions of two Ni atoms at the top and bottom of the double-pyramid upward and downward by $0.1\,\text{Å}$, respectively. Starting from this initial geometry, we perform a fully dynamical simulation. We find that, after 40.0 fs, the regular octahedral structure is reproduced. This result clearly indicates that the octahedral structure of Ni_6 is stable. Previously, Reuse [8] et al. reported that the Ni_6 cluster has a slightly distorted structure (one edge of a triangle is $2.32\,\text{Å}$, while one edge of the square of the double-pyramid is $2.35\,\text{Å}$) in LCAO analysis. In contrast, our calculation shows that a regular octahedron is more preferable. Because of LCAO approach , electronic states are rather localized.

3.2 O_2 Collision against Ni_6

In our simulations of an oxygen molecule (O_2) colliding against the six-atom nickel cluster (Ni_6), we have assumed three initial orientations (a, b and c) of the oxygen molecule as described below. In every case, the initial velocity of the oxygen molecule is set toward the center of Ni_6 without any rotational motion. We set the initial kinetic energy of the oxygen molecule at 4 eV, 10 eV and 10 eV, respectively, in the three cases, (a), (b) and (c).

(a)   The O_2 axis is set parallel to the line connecting the uppermost and lowermost vertexes of the double-pyramid. The line connecting the O_2 and Ni_6 centers goes through a corner nickel atom in the square of the double-pyramid (Figure 2a). In this case, the oxygen molecule is finally combined with a single nickel atom and the reaction $Ni_6 + O_2 \rightarrow NiO_2 + Ni_5$ takes place.

(b)   The O_2 axis is set parallel to the line connecting the uppermost and lowermost vertexes of the double-pyramid. The O_2 and Ni_6 centers are on the bisector of the square edge (Ni_2) of the double-pyramid (Figure 2b). In this case, the oxygen molecule is finally combined with a nickel dimer (Ni_2) and the reaction $Ni_6 + O_2 \rightarrow Ni_2O_2 + Ni_4$ takes place.

(c)   The O_2 axis is along the line connecting the Ni_6 and triangle (Ni_3) centers. In this case, the O_2 molecule approaches vertically toward Ni_6 (Figure 2c). In this case, the oxygen molecule is finally combined with a nickel trimer (Ni_3) and the reaction $Ni_6 + O_2 \rightarrow Ni_3O_2 + Ni_3$ takes place.

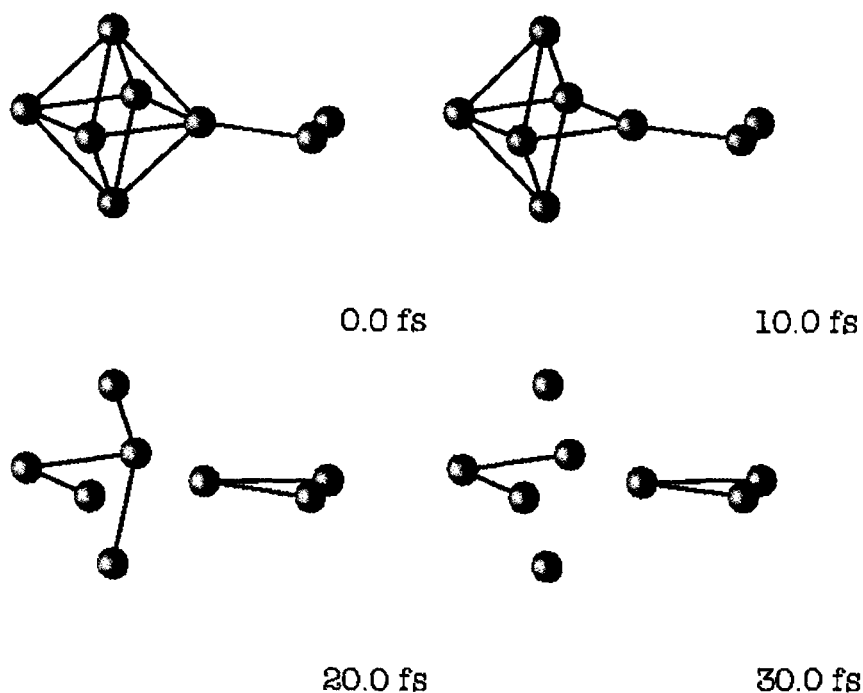
0.0 fs

10.0 fs

20.0 fs

30.0 fs

Fig.2a. Snapshots of the atomic positions in the dynamical simulation (a) of the O_2 collision against Ni_6. In each snapshot, O_2 is located in the right-hand-side and Ni_6 is located in the left-hand-side. Finally, the oxygen molecule is linked with a single nickel atom and NiO_2 is created.
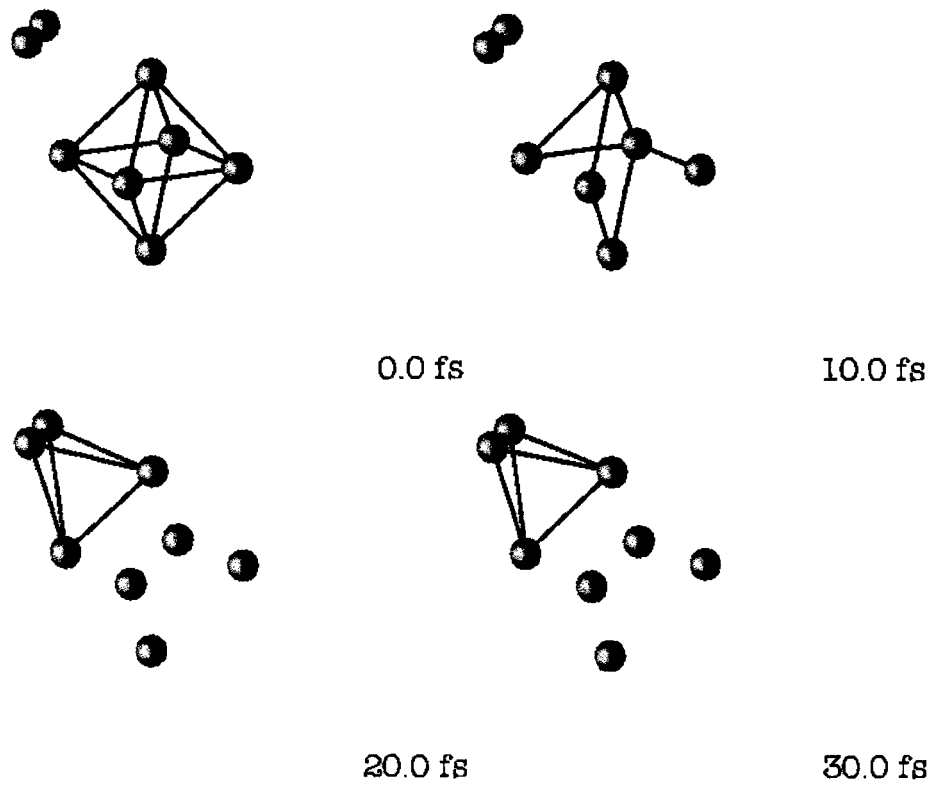
0.0 fs   10.0 fs

20.0 fs   30.0 fs

Fig.2b. Snapshots of the dynamical simulation (b).   Finally, the upper-left O_2 is linked with a nickel dimer.

0.0 fs   10.0 fs
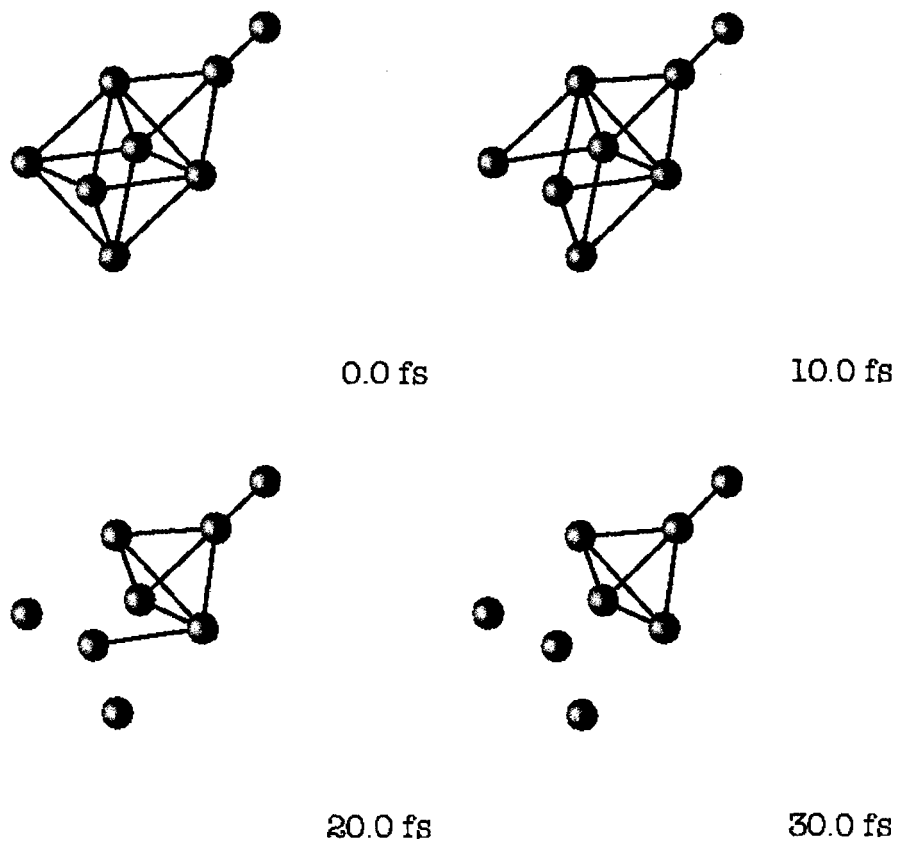
20.0 fs   30.0 fs

Fig.2c. Snapshots of the dynamical simulation (c).   Finally, the upper-right O_2 is linked with a nickel trimer.

4. SUMMARY

In summary, we have investigated the stability of Ni$_6$ and the collision between Ni$_6$ and O$_2$. We found that the regular octahedron is the most stable structure of Ni$_6$ and that after the collision of O$_2$, Ni$_6$ is resolved into NiO$_2$, Ni$_2$O$_2$ and Ni$_3$O$_2$. O$_2$ approaches the nearest Ni atoms and is absorbed to the Ni atoms. Moreover the kinetic energy spreads to the other atoms that are finally detached. We consider that this decomposition plays an important role in the process of oxidization. Here it is interesting to note that a mass-spectrum of nickel cluster ions created by the Ar sputtering of Ni surface under several KeV [3] reveals the generation of small nickel oxide clusters as well as pure nickel clusters. The creation of Ni$_n$O$_2$ in such experiments might correspond indirectly to our dynamical simulations.

REFERENCES

[1] P. Fayet, M. J. McGlinchey and L. H. Wöste, J. Am. Chem. Soc. **109**, 1733(1987).

[2] S. Vajda, S. Wolf, T. Leisner, U. Busolt and L. H. Wöste, J. Chem. Phys. **107**, 3492 (1998).

[3] M. Ichihashi, T.Hanmura,R. T. Yadav and T. Kondow, J.Phys.Chem.A **104**,11885(2000).

[4] K. Ohno, Y. Maruyama, K. Esfarjani and Y. Kawazoe, N. Sato, R. Hatakeyama, T. Hirata and M. Niwano, Phys. Rev. Lett. **76**, 3590 (1996).

[5]T. Ohtsuki, K. Masumoto, K. Ohno, Y. Maruyama, Y. Kawazoe, K. Sueki and K. Kikuchi, Phys. Rev. Lett.**77**, 3522 (1996).

[6] T. Ohtsuki, K. Ohno, K. Shiga, Y. Kawazoe, Y. Maruyama and K. Masumoto,, Phys. Rev. Lett. **81**, 967 (1998).

[7] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[8] F. A. Reuse and S. N. Khanna Chem. Phys. Lett .**234**, 77 (1995).