05 July, 2013
Workshop on Molecular Thermal Engineering
@ Mech. Eng., UT

Understanding Formation mechanism of carbon nanotubes and graphene from numerical point of view

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Outline of talk

1. Introduction

2. Brief review of recent computational modelling of formation process of nanotubes and graphene

3. *Ab initio* MD simulation for dissociation process of carbon source molecules during nanotube and graphene growth
(Collaboration with Prof. Shimojo (Kumamoto Univ.)

timeline

1.5years

Y. Shibuta

1998.4 — 2001.3 — 2004.3 — 2005.3 — @ material

M — D — PD

2003.10

2013.7

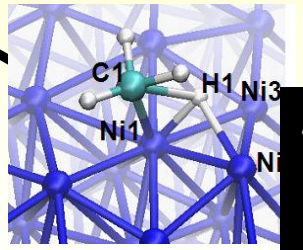
E. Einarsson

2003.10, Dr. Choi farewell party

2004.5, Dennetsu Sympo @ Toyama

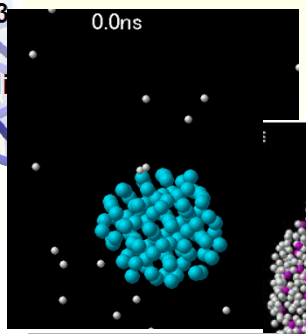
Materials modelling
– from elementary step to phenomelogical model –

Dissociation of CH4 on Ni(111) *1



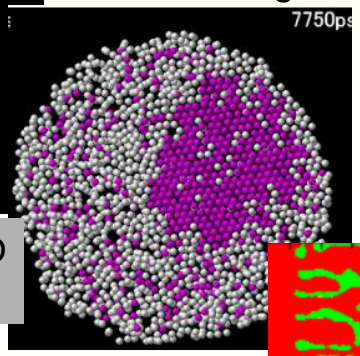
Ab initio MD
（electronic）

CNT growth*2

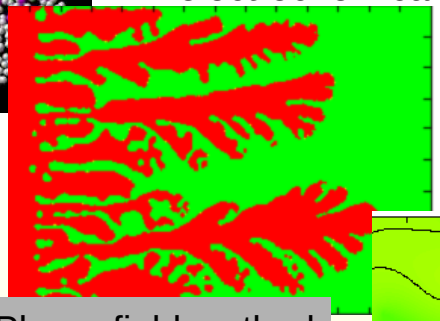


Classical MD
（atomistic）

Phase change in NP*3

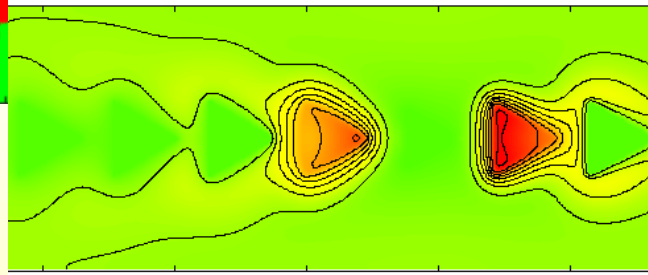


Dendritic growth
In electrochemical step*4



Phase-field method
（Meso-scale）

BZ reaction
in self-oscillation gel*5



Continuum dynamics
（macro）

*1CPL 565 (2013) 92
*2CPL 382 (2003) 381
*3JCP 129 (2008) 144102
*4STAM, 8 (2007) 511
*5JPCB, 112 (2008) 1777

What is desired for materials modelling?

<u>Visualization</u>
Understand process which can not be observed in experimental methods
<u>Parameter optimization</u>
Reduce costs and efforts of experiments

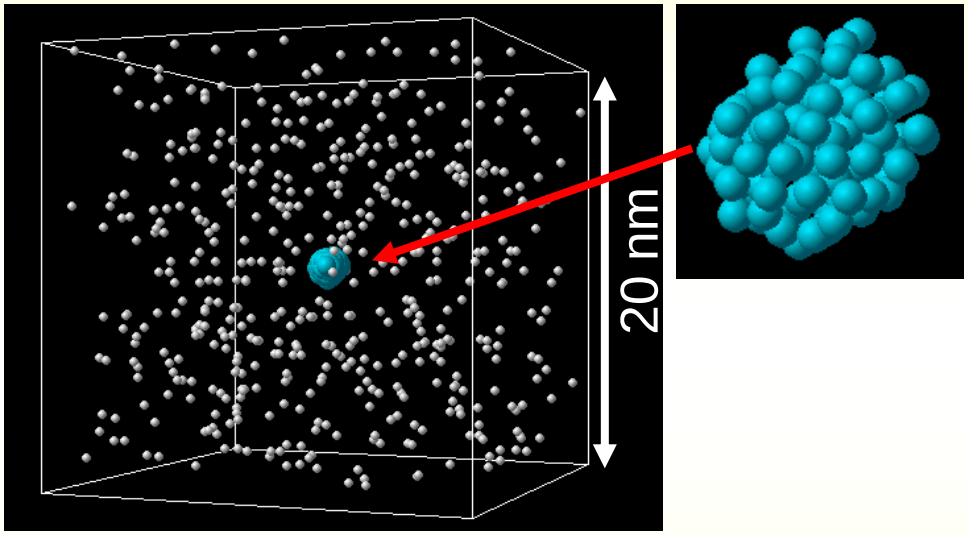
<u>It should not be for theorist itself. It should contribute for experiments.</u>

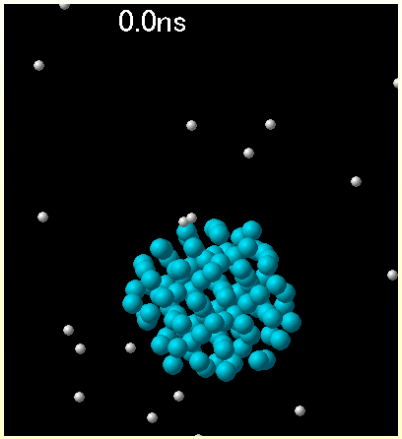
Modeling of metal-catalyzed growth of SWNT

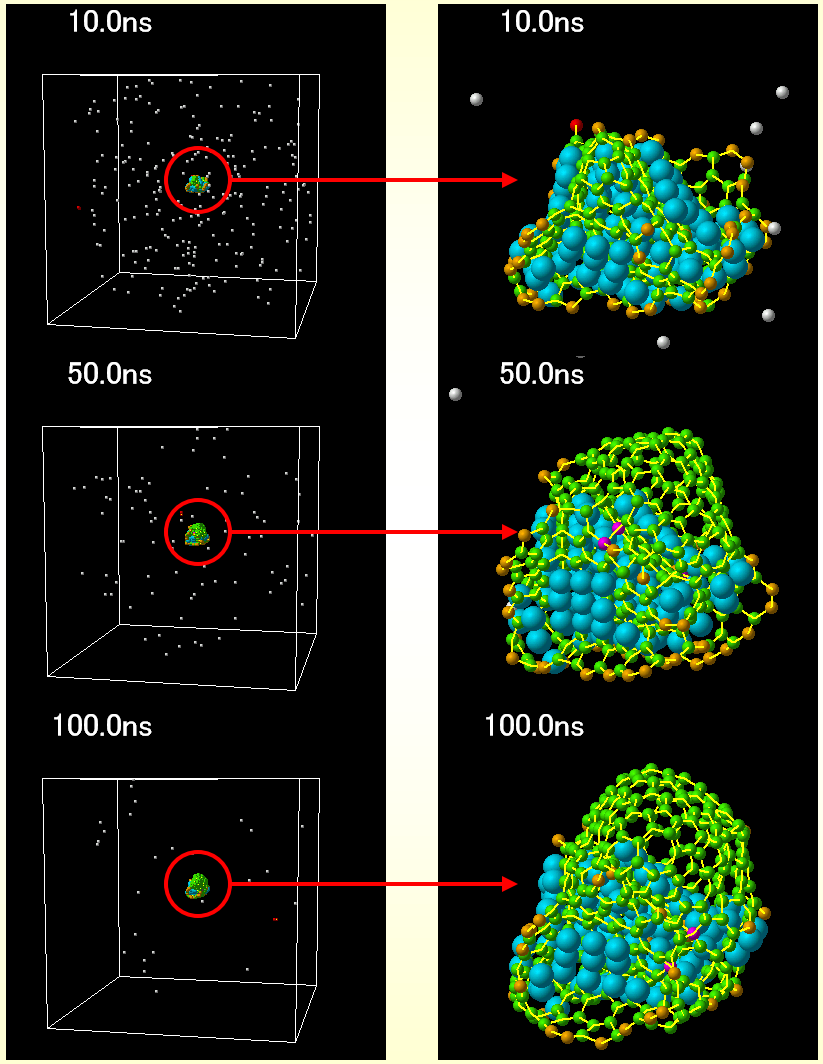
Initial condition: 500 Carbon & Ni_{108} cluster

C-C covalent bonding:
D.W. Brenner,
Phys. Rev. B 42 (1990) 9458.

Isolated C-C:
Lennard-Jones 12-6



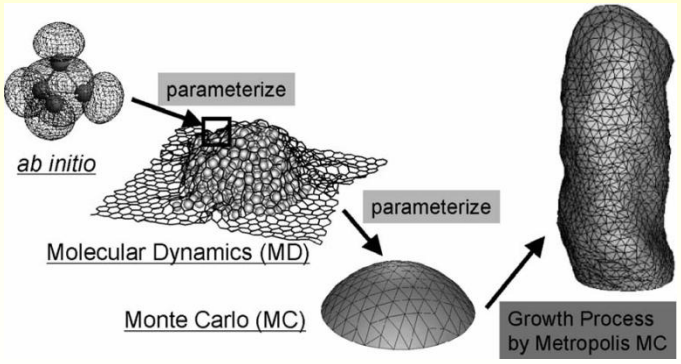




Y. Shibuta, S. Maruyama, Chem. Phys. Lett, 382 (2003) 381.

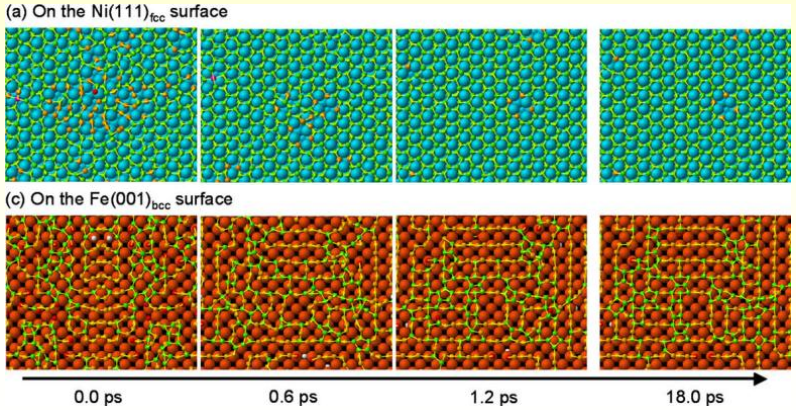
Collaborations on CNT growth

Concept of multi-scale modelling



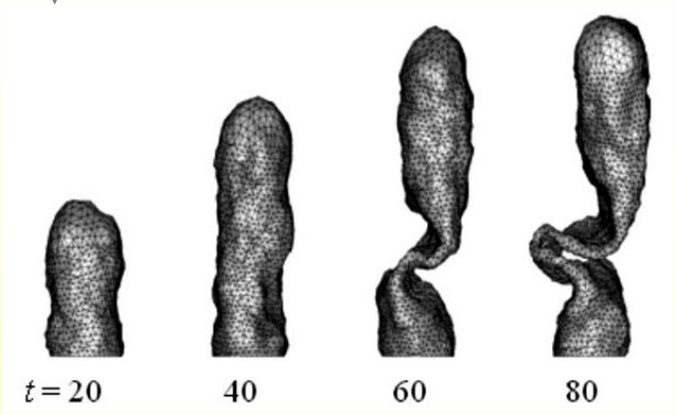
Y. Shibuta, J.A. Elliott,
Chem. Phys. Lett. 427 (2006) 365

Epitaxy between graphite and metal surface



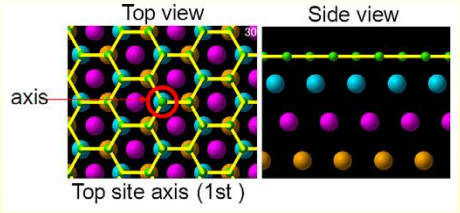
Y. Shibuta, J.A. Elliott,
Chem. Phys. Lett. 472 (2009) 200

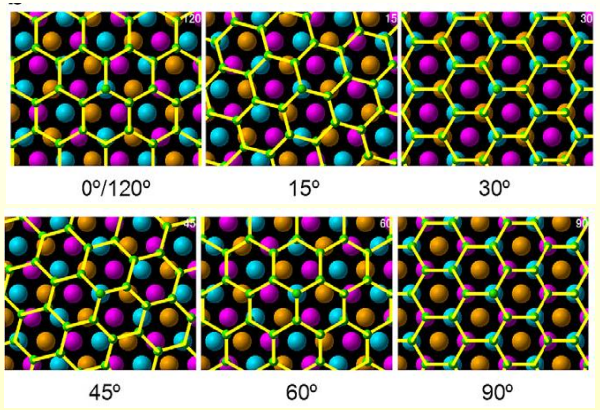
Course grain (MC) simulation for tubular growth process



J.A. Elliott, M. Hamm, Y. Shibuta
J. Chem. Phys, 130 (2009) 034704

Interaction energy for commensurate and incommensurate ORs.

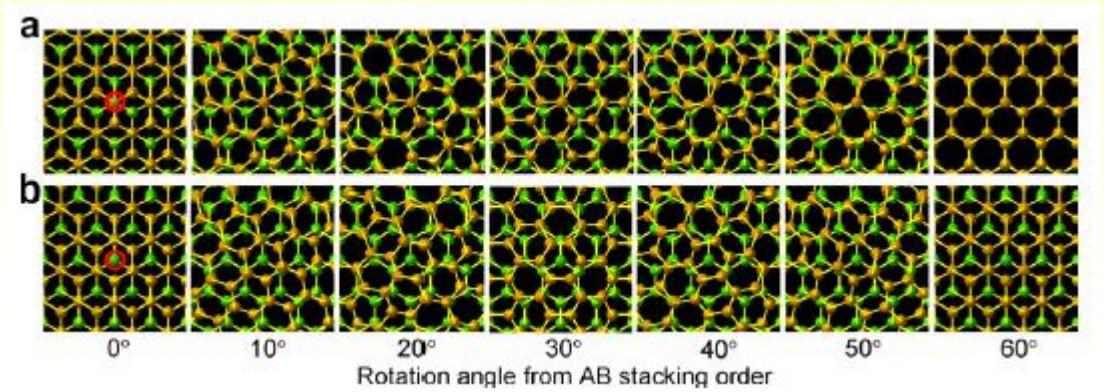


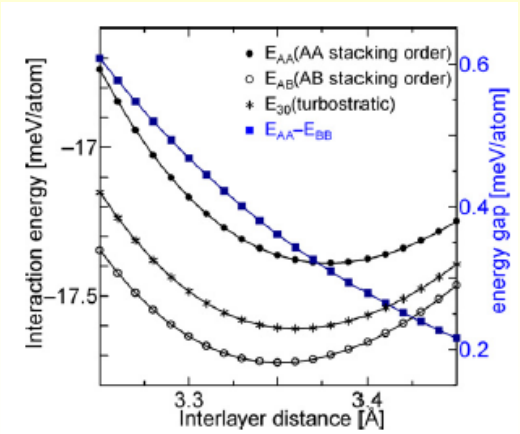


Y. Shibuta, J.A. Elliott, Chem. Phys. Lett. 538 (2012) 112

Collaborations on related topics

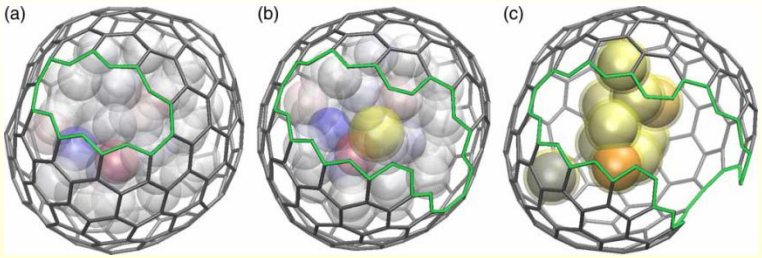
Interaction between two graphene sheets with a turbostratic ORs





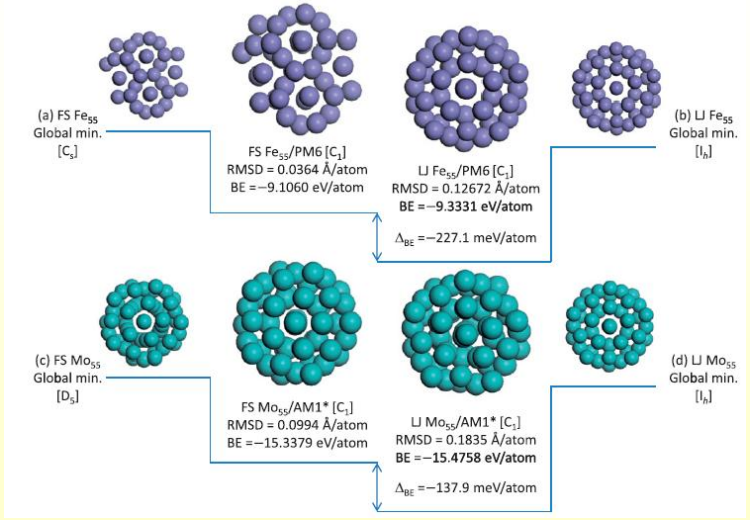
Y. Shibuta, J.A. Elliott, Chem. Phys. Lett. 512 (2011) 146

Semi empirical MO study on freestanding and encapsulated Mo clusters



J.A. Elliott, Y. Shibuta, Mol. Sim. 34 (2008) 891.

Global minima of transition metal clusters by Finnis-Sinclair potential



J.A. Elliott, Y. Shibuta, D.J. Wales, Philo. Mag., 89 (2009) 3311.

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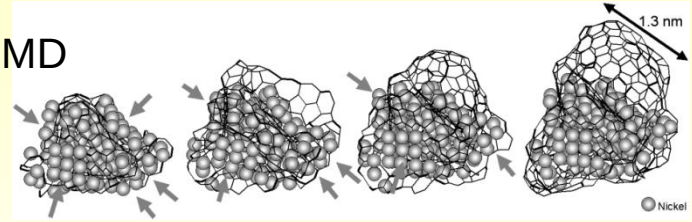
Metal-catalyzed cap growth mechanism

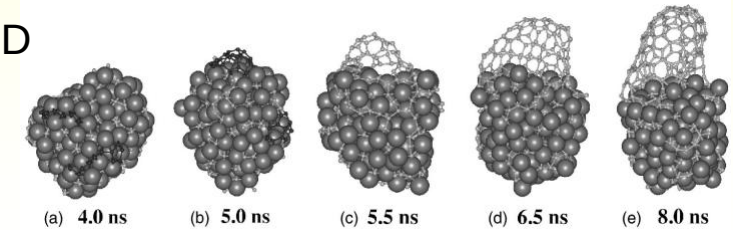
Modelling

MD



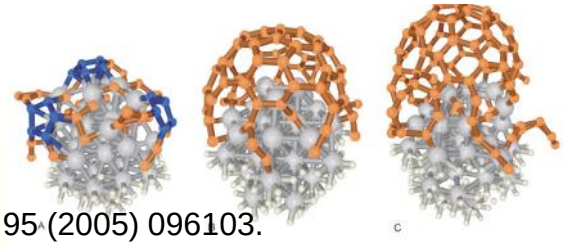
Y. Shibuta, S. Maruyama, Chem. Phys .Lett. 382 (2003) 381.

MD

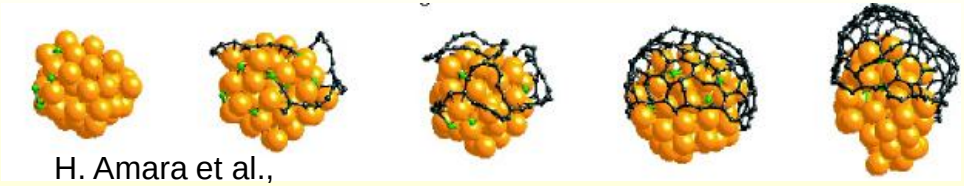


F. Ding, A. Rosen, K. Bolton, J. Chem. Phys. 121 (2004) 2775.

CPMD



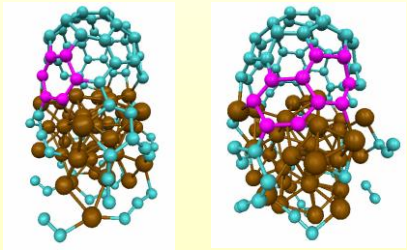
J.Y. Raty et al.,
Phys. Rev. Lett. 95 (2005) 096103.



H. Amara et al.,
Phys. Rev. Lett.100 (2008) 056105.

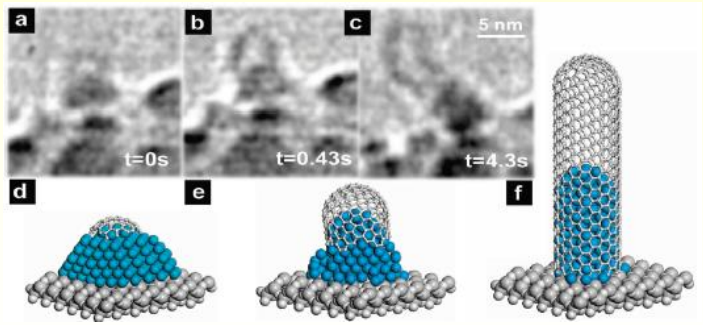
TBMC

DFTB

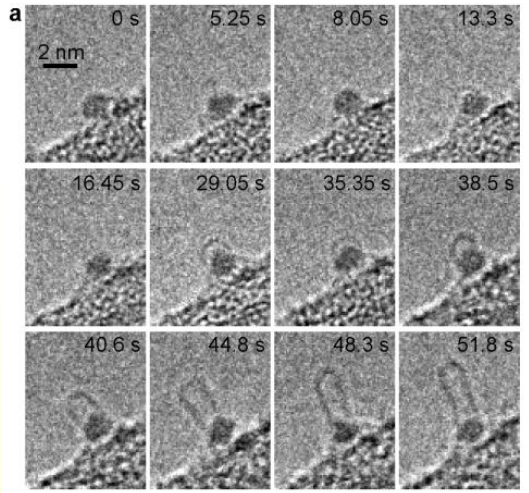


Y. Ohta, Y. Okamoto, S. Irle, K. Morokuma
Carbon 47 (2009) 1270

In-situ TEM Observation of CNT Growth



S. Hofmann et al.,Nano Lett., 7(2007) 602.

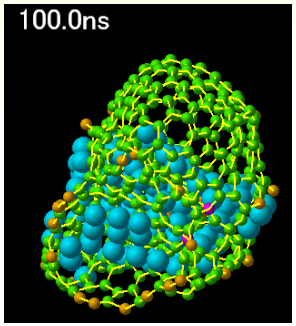


H. Yoshida et al.,Nano Lett., 8(2008) 2082.

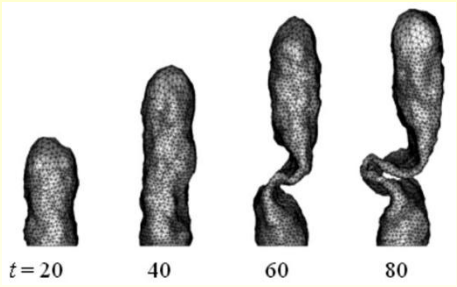
There has been a broad consensus on the cap growth mechanism.

What's happening on the growth modelling?

MD



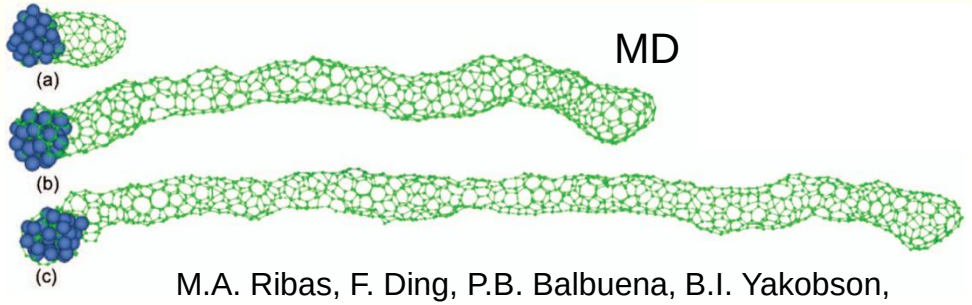
Coarse graining



MC

J.A. Elliott, M. Hamm, Y. Shibuta
J. Chem. Phys. 130 (2009) 034704.

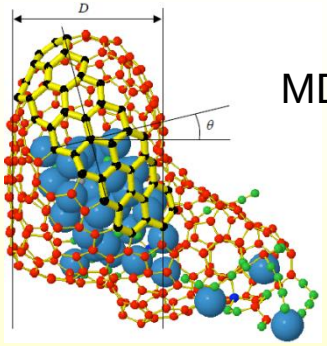
Keep going!



MD

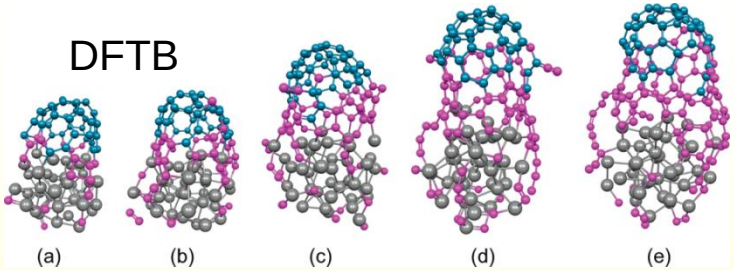
M.A. Ribas, F. Ding, P.B. Balbuena, B.I. Yakobson,
J. Chem. Phys. 131 (2009) 224501.

With more precision



MD+MC

DFTB



A.J. Page, S. Irle, K. Morokuma. J Phys. Chem. C 114 (2010) 8206.

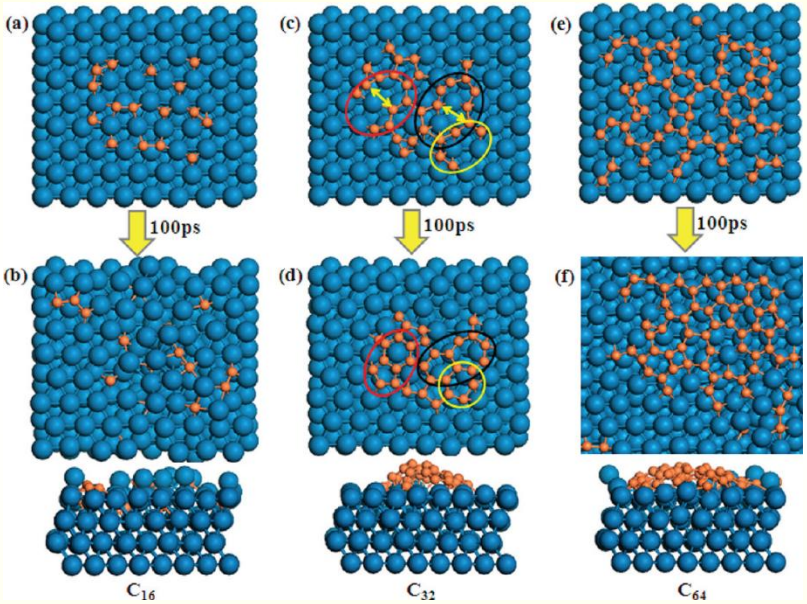
E.C. Neyts, Y. Shibuta, A.C.T van Duin, A. Bogaerts, ACS Nano 4 (2010) 6665.

It is not always enough to keep going with similar kind of simulation to understand formation process of CNT thoroughly.

Recent computational studies on graphene growth on metal surface

Molecular Dynamics Simulation of Chemical Vapor Deposition Graphene Growth on Ni (111) Surface

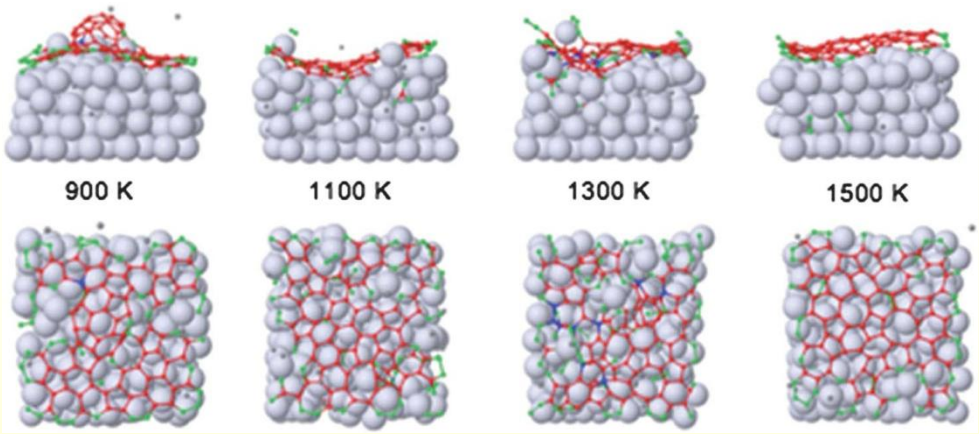
Classical MD simulation with the ReaxFF potential



L. Meng, Q. Sun, J. Wang, F. Ding,
J Phys. Chem. C, 116 (2012) 6097.

Formation of single layer graphene on nickel under far-from-equilibrium high flux conditions

Hybrid MD/MC simulation with ReaxFF potential



E.C. Neyts, A.C.T. van Duin, A. Bogaerts
Nanoscale, in press. (10.1039/c3nr00153a)

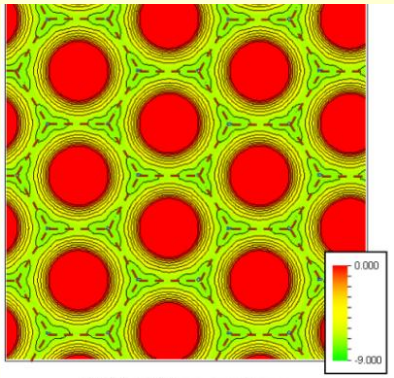
As in the case with CNT growth, dissociation of carbon source molecules is not taken into account in most of computational works.

What are remaining problems?

(1) What determines the chirality of CNTs?

Many researches have pointed out a good epitaxy between graphite network and closed-pack facet (i.e. (111)fcc, (0001)hcp) of transition metals.

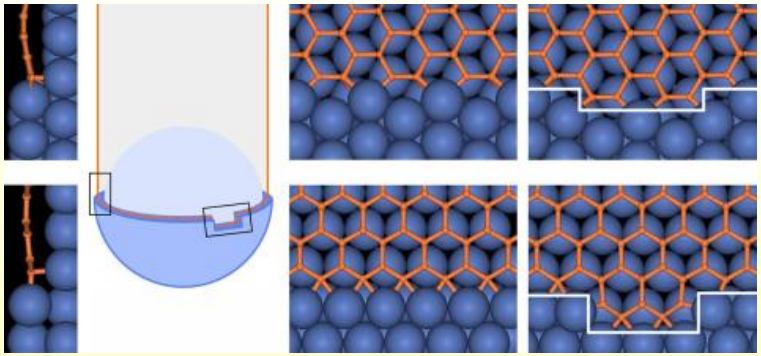
Therefore, The interaction between graphite network and metal (or metal carbide) surface has been widely investigated.



Ni(111)fcc surface

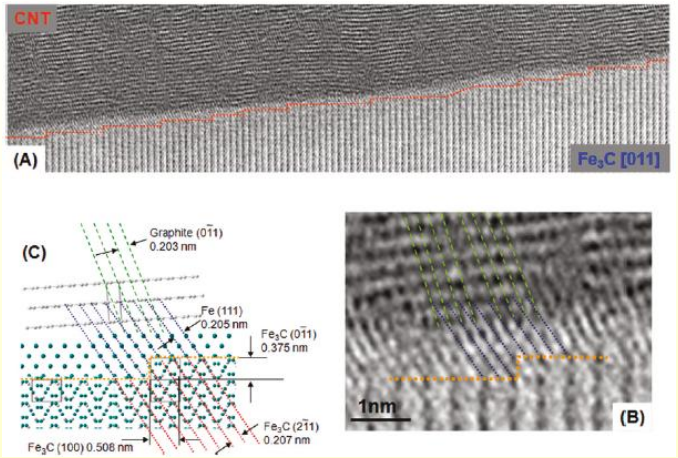
Y. Shibuta, J.A. Elliott,
Chem. Phys. Lett. 472 (2009) 200.

Dislocation theory of chirality-controlled Nanotube growth



F. Ding, A.R. Harutyunyan, B.I. Yakobson,
PNAS 106 (2009) 2506.

MNWT growth from iron-carbide



K.K.K. Koziol, C. Ducati, A.H. Windle,
Chem. Mater. 22 (2010) 4904.

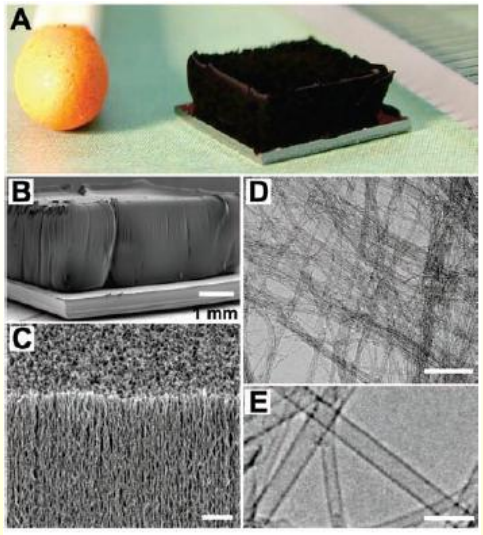
What are remaining problems ?

(2) What happens at dissociation stage of carbon sources molecules ?

It is empirically known that the yield and quality of the CNT products strongly depend on a choice of carbon source molecules and additives. For example,

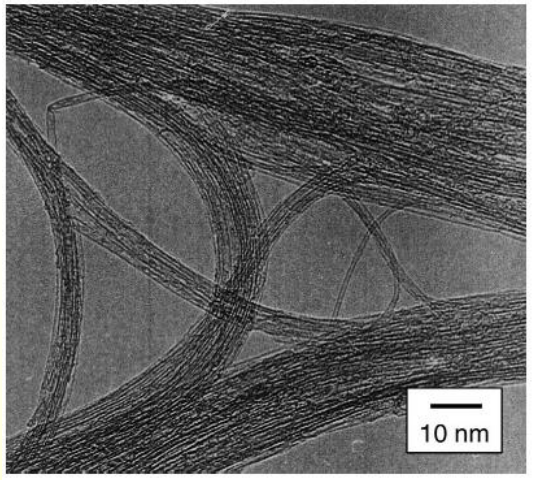
1. The addition of small amount of water enhances activity and lifetime of catalytic metal drastically (super growth technique).
2. The ethanol as carbon source molecules yields large amount of SWNTs without amorphous carbons (Alcohol CCVD technique).

Super growth technique



Hata et al., Science, 306 (2004) 1362.

Alcohol CCVD technique



S. Maruyama et al., Chem Phys Lett 360 (2002) 229.

However, most of computational works on CNT growth does not take the dissociation process into account but starts from isolated carbon atoms.

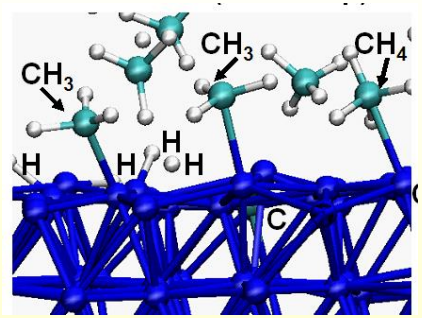
Our present situation and objectives

At the moment, there is few computational works on the dissociation of carbon source molecules on CNT/graphene growth with taking into account both chemical reactions at *ab initio* level and dynamics simultaneously.

***Ab initio* molecular dynamics simulation** satisfies above requests at the same time, while it takes very high-computational cost.

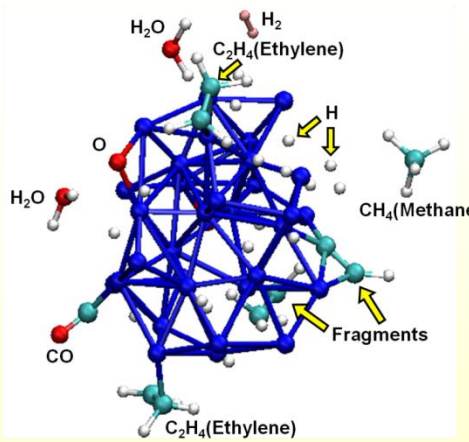
The dissociation of carbon source molecules during initial stage of CNT and graphene growth is investigated by *ab initio* molecular dynamics simulation on high-performance computer.

In particular..



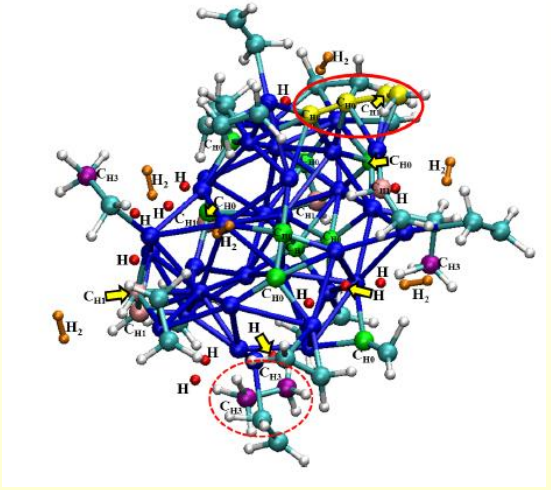
CH_4 dissociation on Ni(111) surface

(Shibuta et al. CPL 565 (2013) 92.)



C_2H_5OH dissociation on Ni_{32} cluster

(Oguri et al. JPCC 117(2013)9983.)



C_2H_4 dissociation on Ni_{32} cluster

(Shimamura et al. submitted.)

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Simulation methodology

DFT with plane wave function.

GGA (generalized gradient approximation) for the exchange-correlation energy.

PAW (projector-augmented-wave) method for electronic state.

Valence electron:

Ni : $3d^8\ 4s^2$ C : $2s^2\ 2p^2$ H : $1s^1$

The plane-wave-cutoff energies :

30 Ry (electronic pseudo-wave functions), 300 Ry (pseudo-charge density)

The gamma point used for Brillouin zone sampling.

Hellmann-Feynman force is derived from DFT.

MD part

Δt = 0.242 fs, 21000 steps (5082 fs)

T = 1500 K with NVT const.

Nose-Hoover thermostat for T control.

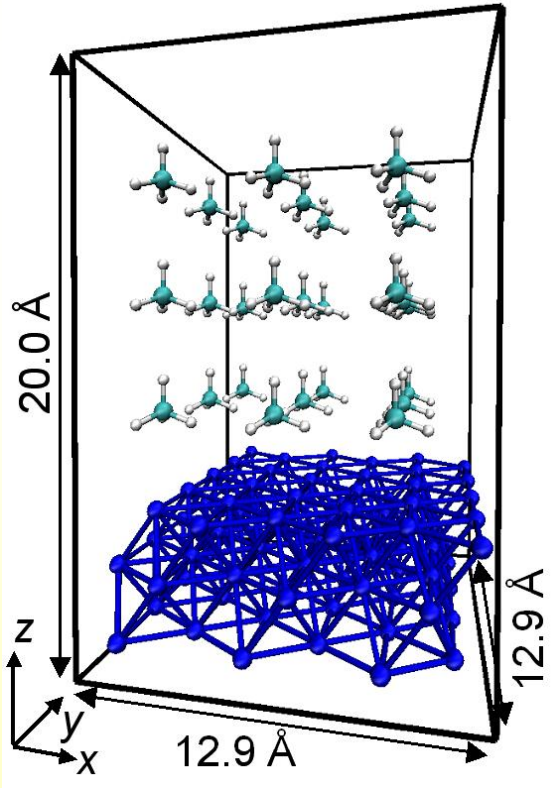
Initial configuration

Three layers of nickel (111) planes (30 atoms per each layer) and 27 Methane atoms.

Nickel atoms in the bottom layer are fixed.

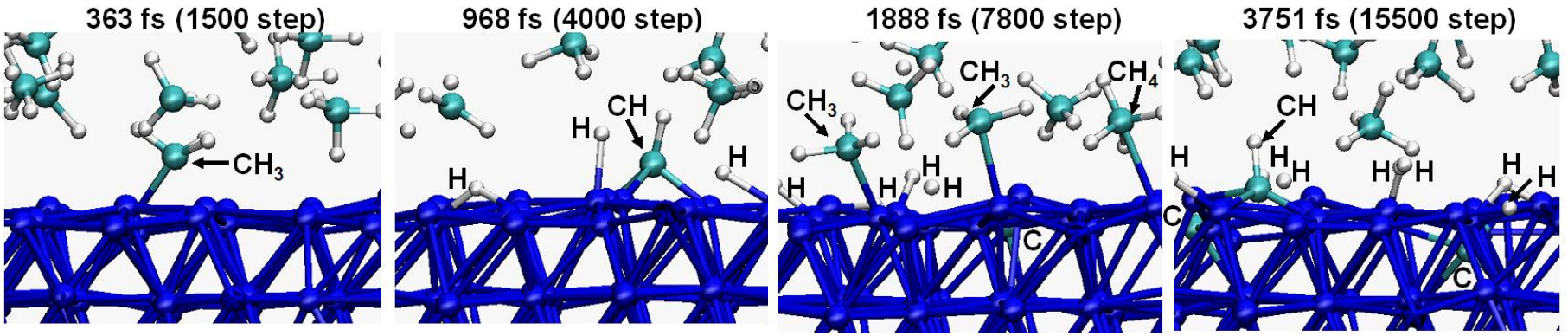
Apparatus:

64 Core parallel calculation with 8CPUs, Intel E5-2690 (8core, 2.9GHz)



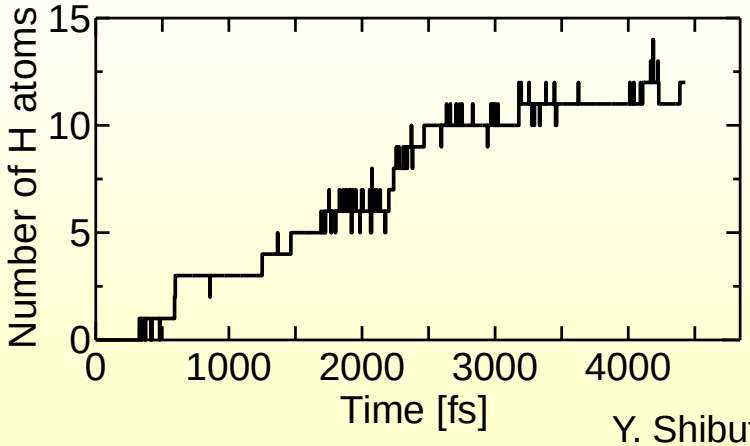
Methane dissociation on the Ni(111) surface

Snapshots of Ni(111)surface and molecules near the surface during calculation



As the dissociation progresses, dissociated hydrogen atoms cover the nickel surface with hopping on the nickel atoms, which inhibit further adsorption and dissociation of methane molecules.

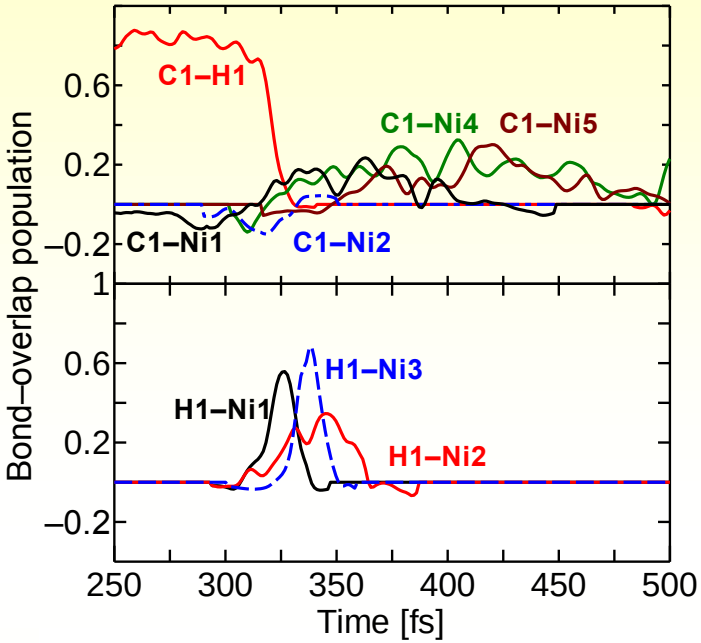
Time series of number of dissociated hydrogen atoms

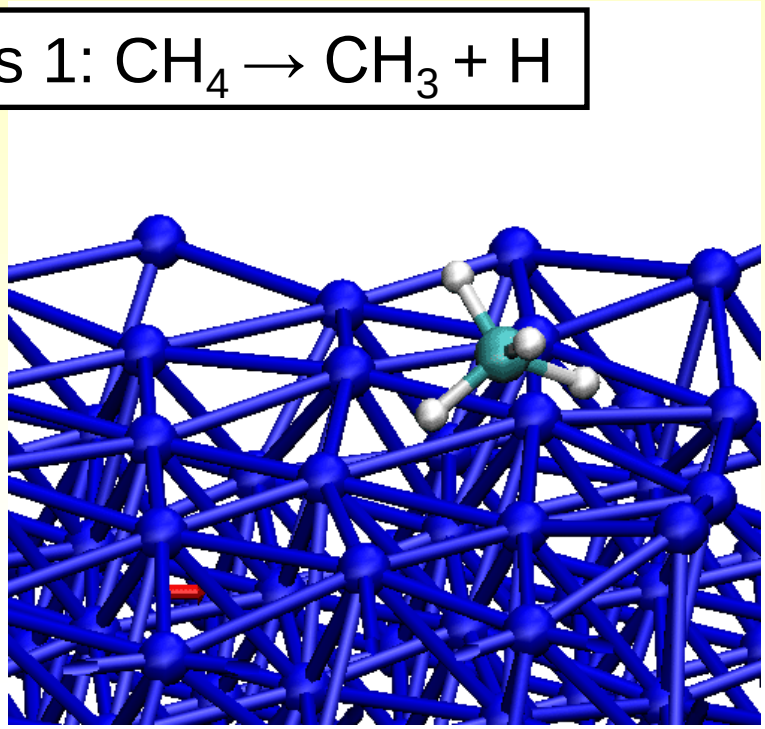


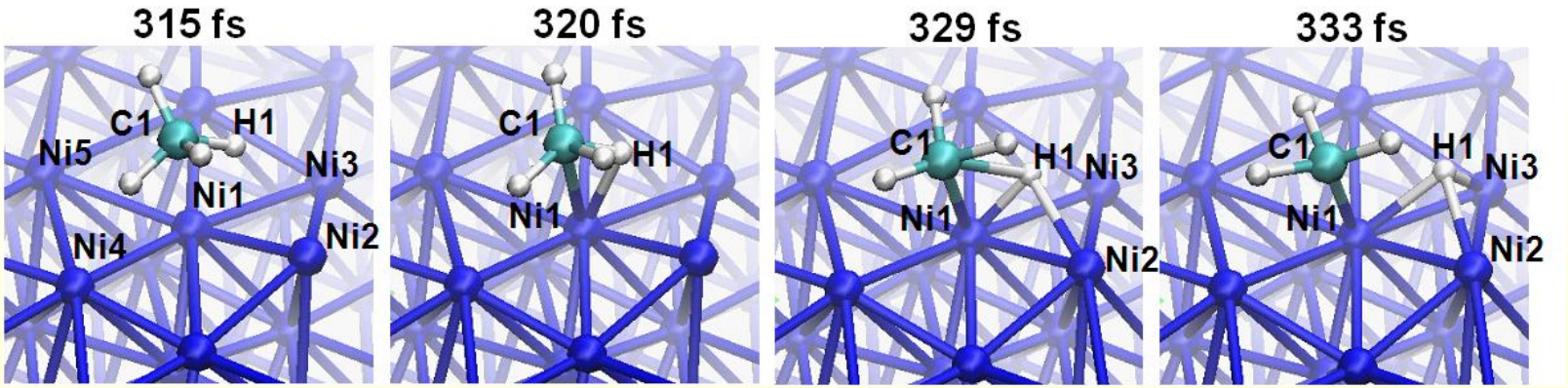
H_2 molecules from hydrogen atoms are not generated on the nickel surface, although H_2 are generated on the Ni32 cluster in our previous simulation.

Y. Shibuta, R. Arifin, K. Shimamura, T. Oguri, F. Shimojo, S. Yamaguchi
Chem. Phys. Lett., 565 (2013) 92-97.

Multi-step dissociation processes 1: $CH_4 \rightarrow CH_3 + H$



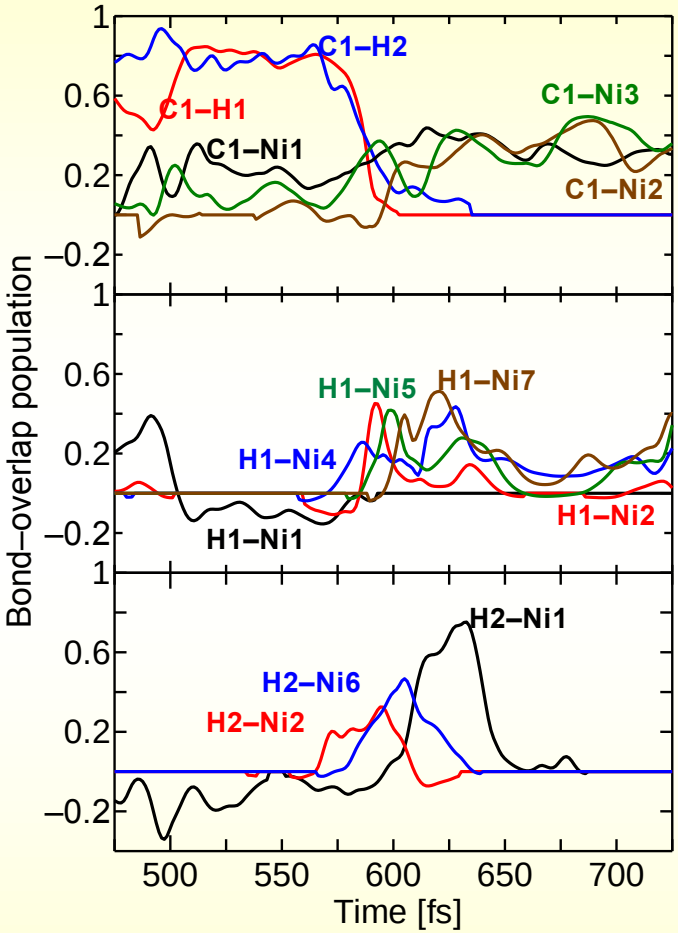


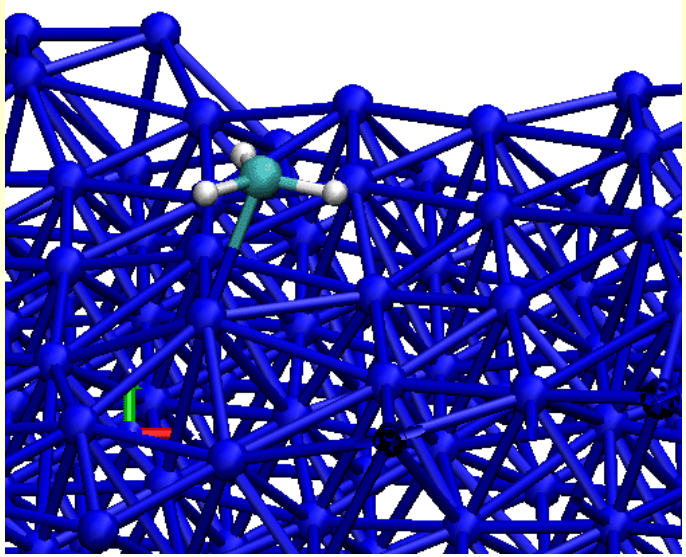


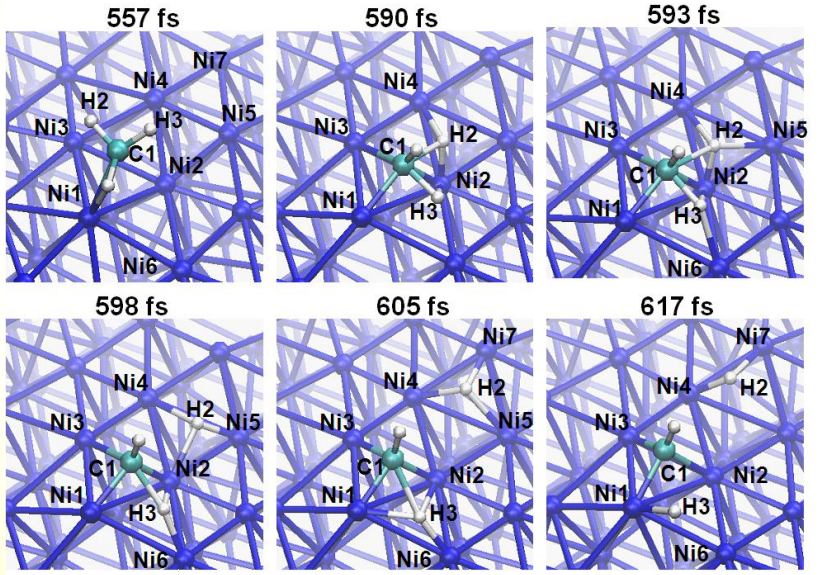
The methane molecule are dissociated into the CH_3 fragment and H atom.
(The other methane molecules and fragments are not shown in the snapshots for clarity. The same applies hereinafter.)

Y. Shibuta, et al., Chem. Phys. Lett., 565 (2013) 92-97.

Multi-step dissociation processes 2: $CH_3 \rightarrow CH + 2H$





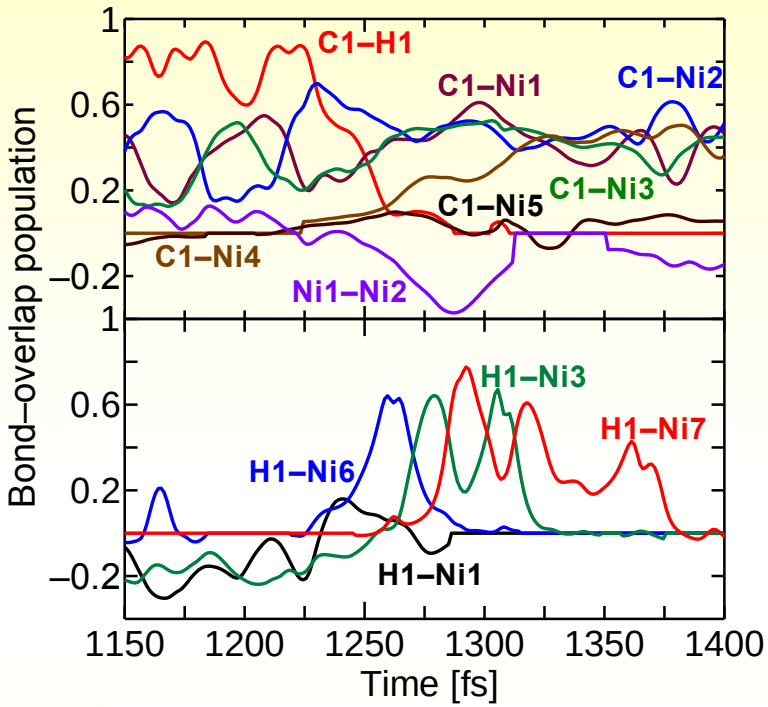


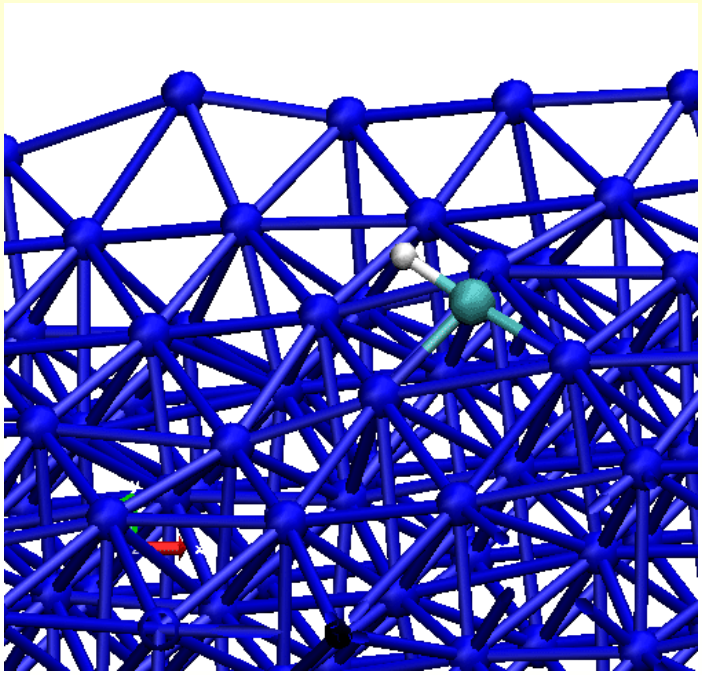
<u>Two hydrogen atoms are dissociated almost simultaneously.</u>

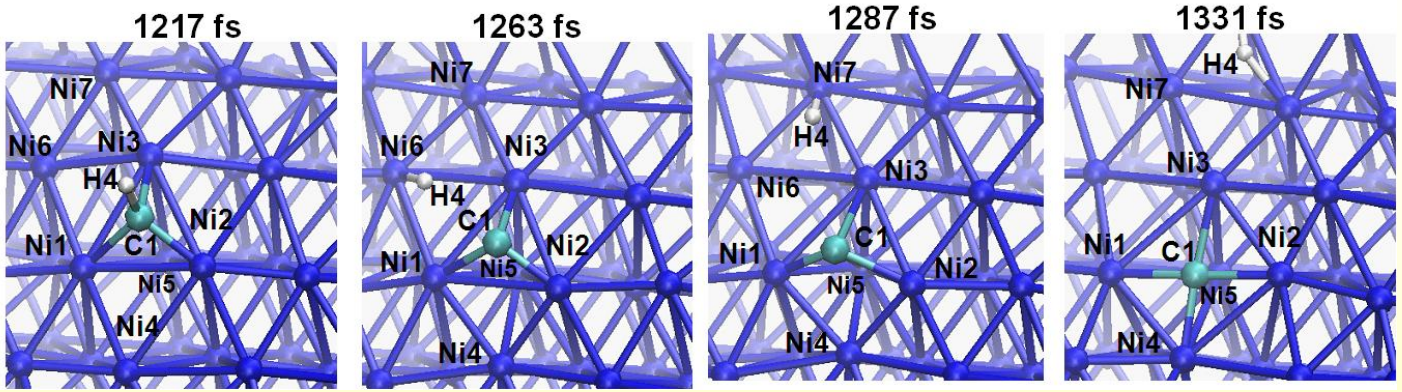
The simultaneous dissociation of two hydrogen atoms is also observed in the dissociation of two other methane molecules afterward.

Y. Shibuta, et al., Chem. Phys. Lett., 565 (2013) 92-97.

Multi-step dissociation processes 3: CH → C + H



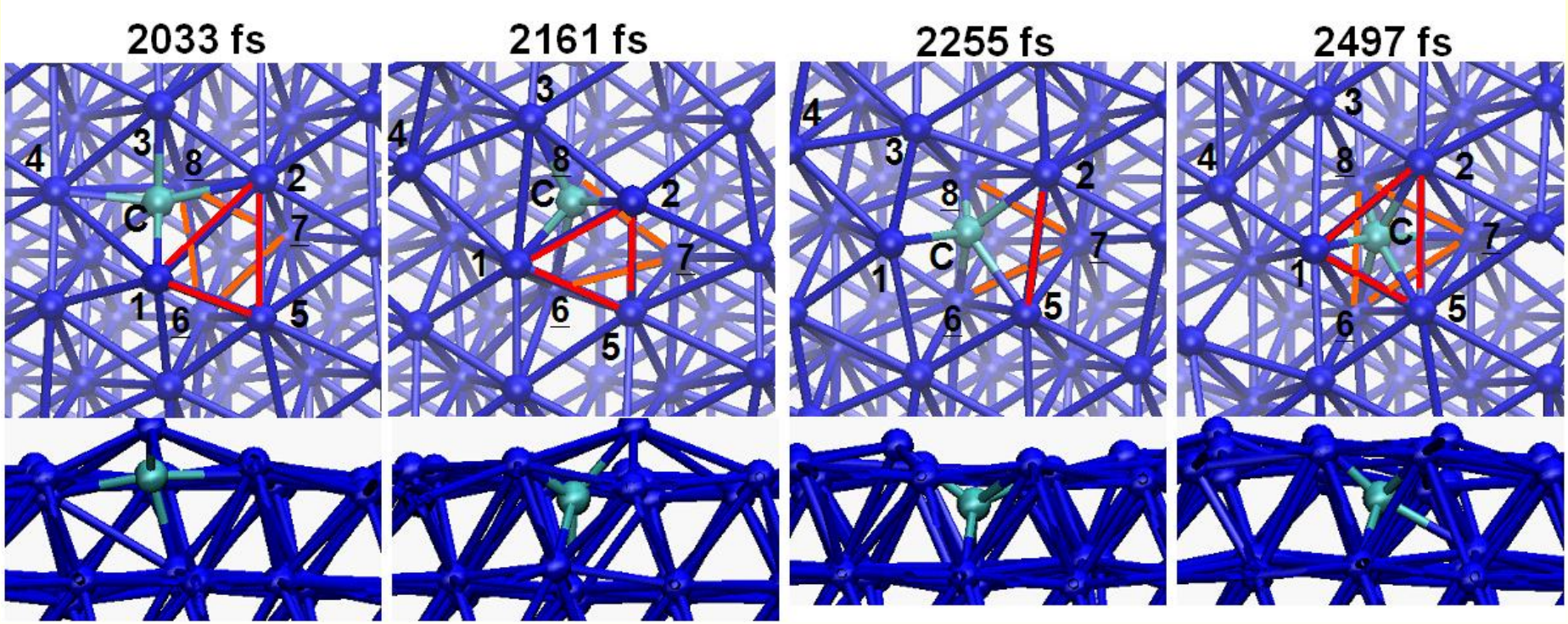


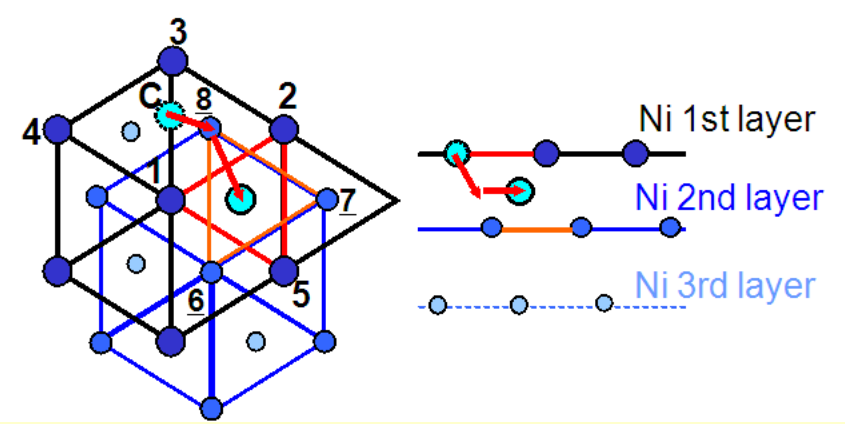


The dissociated carbon atom is buried in the interstitial site of the nickel atoms in the first layer.

Y. Shibuta, et al., Chem. Phys. Lett., 565 (2013) 92-97.

Carbon diffusion into subsurface space between nickel layers



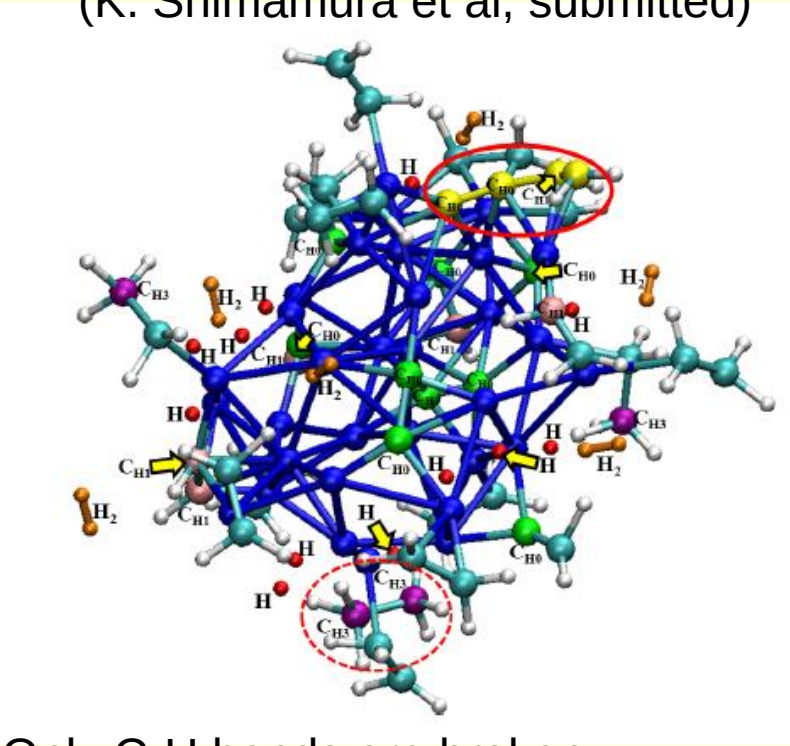


Isolated carbon atoms are buried into the subsurface space between nickel layers via the diffusion through hollow sites.

Y. Shibuta, et al., Chem. Phys. Lett., 565 (2013) 92-97.

Brief introduction of dissociation of carbon source molecules on the nickel cluster

37 Ethylene + Ni32 cluster
(K. Shimamura et al, submitted)

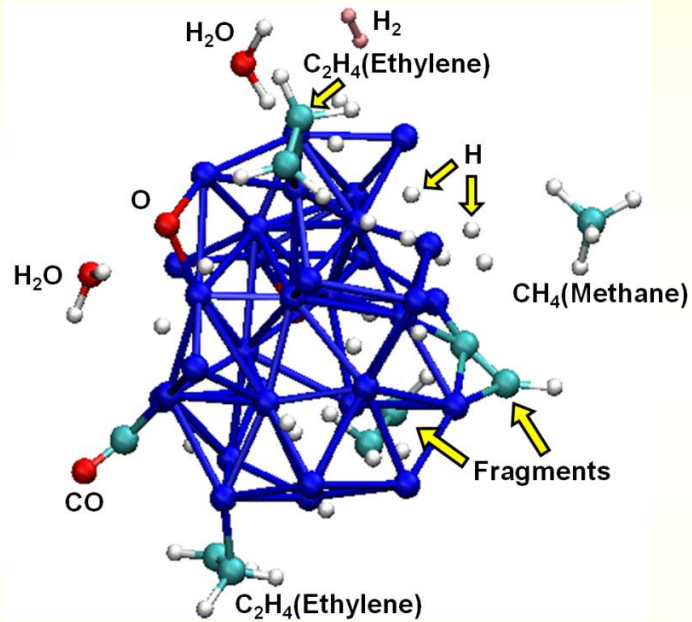


Only C-H bonds are broken.
(C-C bonds are not broken.)

Many ethylene are absorbed on the nickel cluster

H_2 molecules are formed.

30 Ethanol + Ni32 cluster
(T. Oguri et al, JPCC 117(2013)9983.)



C-H, C-C, C-O bonds are broken.

Ethylene are not absorbed on the nickel cluster

H_2 molecules are formed.

Summary of Section 3

Dissociation of methane molecules on the Ni(111) surface is investigated by performing the *ab intio* MD simulation.

Methane molecules are dissociated into isolated carbon and hydrogen atoms via CH_3 and CH fragments with chemisorbing the nickel surface.
(CH_2 fragment is not stable on Ni(111) surface.)

Dissociated carbon atoms are buried into the subsurface space between first and second nickel layers via diffusion through hollow sites in the nickel layers.

Our result supports carbon diffusion into the nickel subsurface, which may indicate precipitation of the graphene or carbon atoms from the nickel subsurface.

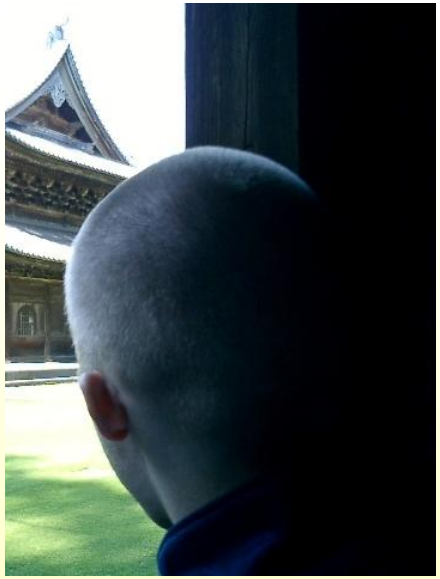
Future works

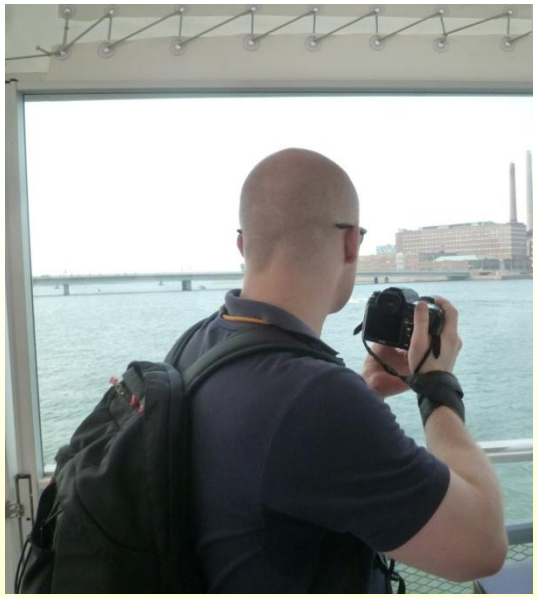
How different the dissociation of methane on Cu(111) or Pt(111) surface is ?

Acknowledgements

Ab initio MD study is a collaboration with Prof. Shimojo at Kumamoto University.
Part of this research is supported by the Grant-in-Aid forYoung Scientists (a) (No. 24686026) from MEXT, Japan.

Was (2004, Dennetsu Sympo@Toyama) Now (2013, NT13@Finland)





E. Einarsson and Y. Shibuta, unpublished.