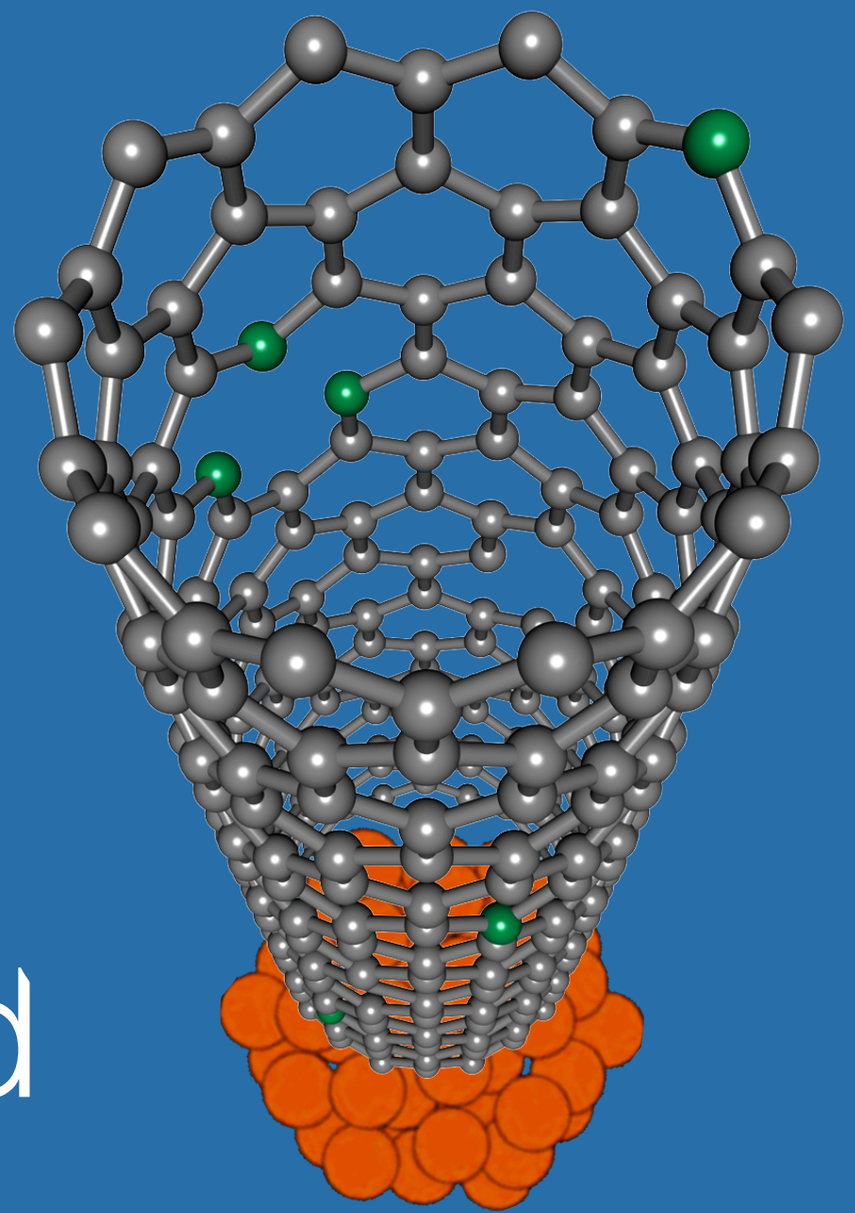
Tuesday 23.10.2012
Tokyo University, Tokyo

Mechanism of nitrogen-doped SWCNT growth



Toma Susi, Stefan Taubert, Giorgio Lanzani,
Kari Laasonen, Albert Nasibulin, Esko Kauppinen

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Outline

- Background
  - Nitrogen doping of SWCNTs
- Experimental
  - Floating catalyst with CO & NH_3
- DFT mechanism study
  - CO & NH_3 reactions
- DFTB MD simulation
  - Role of nitrogen
- Conclusions

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Background

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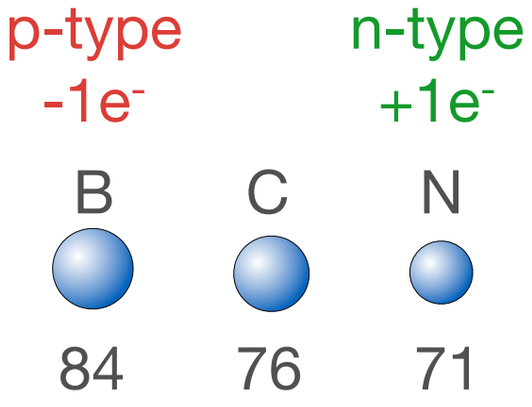
Why dope with nitrogen?



- Controlling SWCNTs chirality very difficult
- Heteroatom substitution introduces donor/ acceptor states near Fermi level = doping[1]
- N – donor (+1 e^-), B – acceptor (-1 e^-)
  - Intrinsic p-doping in air, n more difficult
- N-MWCNTs since 1994,[2] SW only recently
- A couple of good reviews[3,4]
- N-graphene has gained wide recent interest (e.g. large n-doping and band gap opening)[5]

[1] J.Y. Yi and J. Bernholc, Phys. Rev. B 47 (1993) 1708
[2] O. Stephan *et al.*, Science 266 (1994) 1683
[3] C.P. Ewels and M. Glerup, JNN 5 (2005) 1345
[4] P. Ayala *et al.*, Rev. Mod. Phys. 82 (2010) 43
[5] D. Usachov *et al.*, Nano Lett. 11 (2011) 5401

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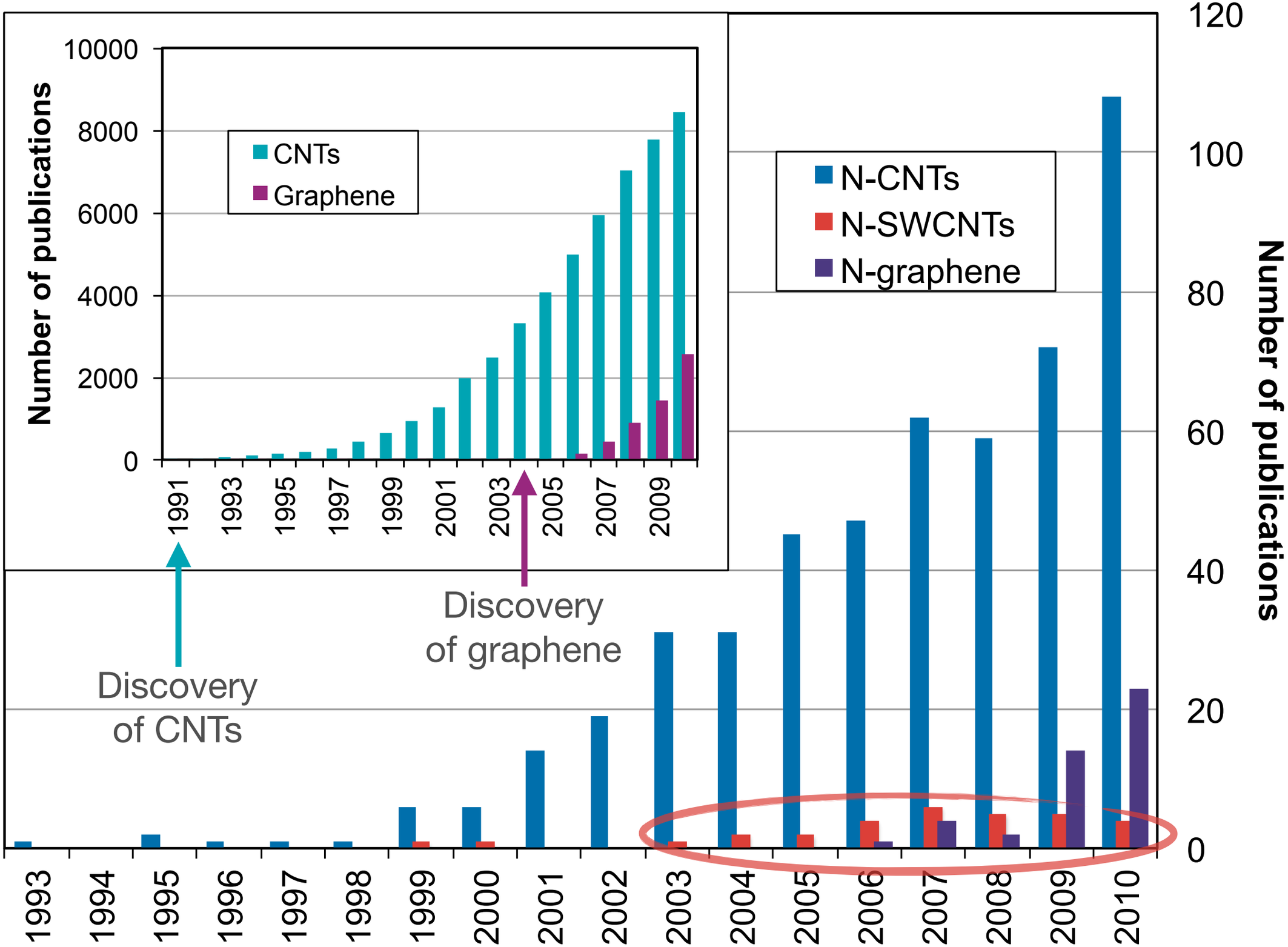

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Synthesis – MWCNx

- First synthesis of N-doped MWCNTs in 1997[1]
- Pyrolysis of liquid or solid C-N compounds: metal pthalocyanines, pyridine, acetonitrile, melamine[2]... N concentration < 10%
- PE-CVD or HF-CVD under N_2 or NH_3 gases[3]
- Spray pyrolysis of metallic salts with organic precursors[4]; N concentration up to 30%
- And many, many more...
- Characteristic “bamboo” structure
- N concentration higher in internal layers and compartments

[1] Yudasaka et al, Carbon (1997)
[2] Terrones et al, APL (1999)
[3] Kurt et al, Carbon (2001)
[4] Glerup et al, Chem Comm. (2003)

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Synthesis – SWCNx

- N-SWCNT synthesis much more difficult – still not that many papers
- Arc discharge of melamine-doped graphite rods under nitrogen[1]
- CVD using acetonitrile[2], benzylamine[3], pyridine[4], and water-plasma CVD[5] using NH_3 have also been successful
- Laser ablation of C-Ni:Y target under nitrogen atmosphere[6]
- Catalyst selection, support and reactor atmosphere important for good product[7]

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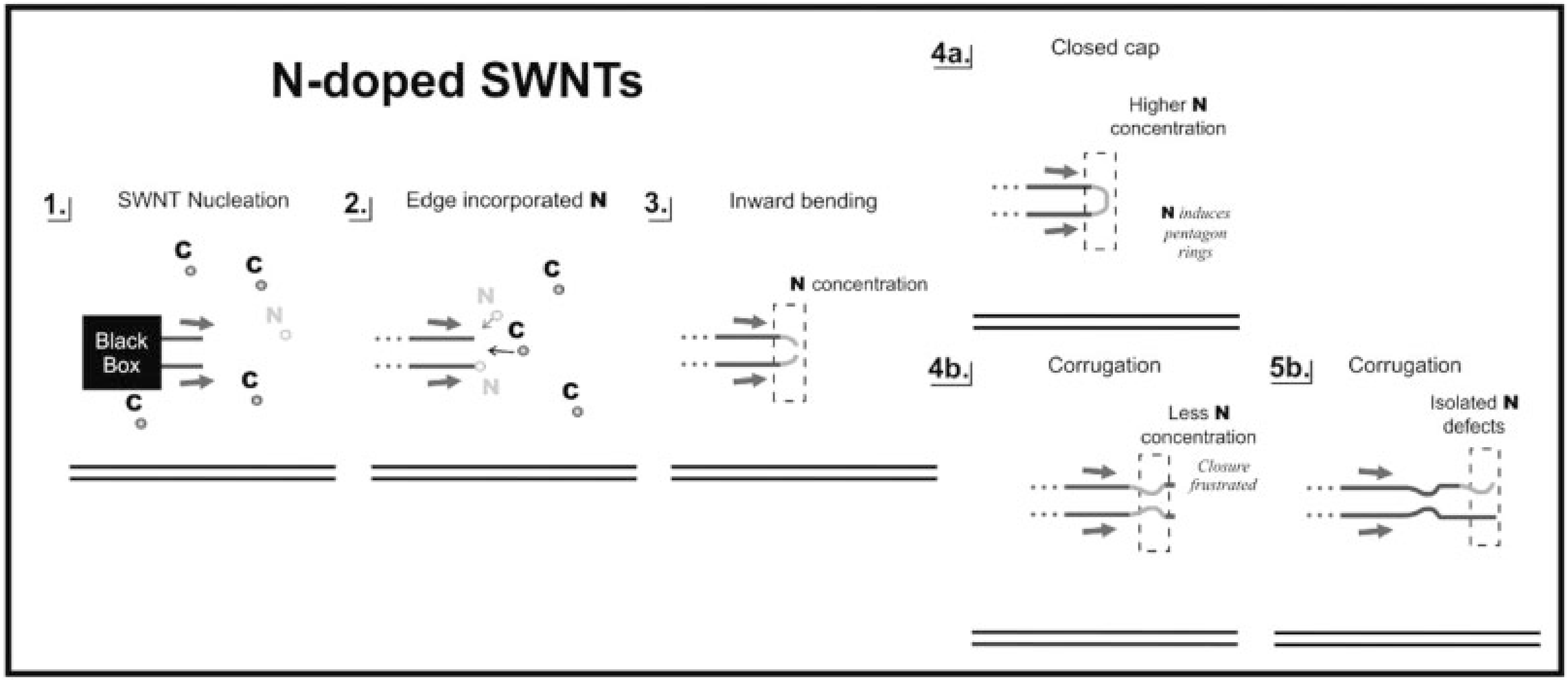
Proposed growth model



N atoms induce local curvature which closes tube?

Sumpter, Int. J. Quantum. Chem. 109 (2009) 97

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Proposed growth model

- C.P. Ewels et al., "*Nitrogen and boron doping in carbon nanotubes*" (in Chemistry of Carbon Nanotubes, 2007):

  "To further complicate the discussion [...] most groups when synthesising doped nanotubes use **complex molecules as their carbon and nitrogen feedstock**, and even mixtures of molecules. This significantly complicates the issue, particularly since to date **no studies** that we are aware of have been **aimed at elucidating the mechanism** whereby feedstock molecules are broken down."

N atoms induce local curvature which closes tube?

Sumpter, Int. J. Quantum. Chem. 109 (2009) 97

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Phys. Status Solidi B **247**, Nos. 11–12, 2726–2729 (2010) / **DOI** 10.1002/pssb.201000312

physica status solidi b
www.pss-b.com
basic solid state physics

Nitrogen-doped SWCNT synthesis using ammonia and carbon monoxide

doi:10.1002/pssb.20100312

Toma Susi[**,1], **Zhen Zhu**[1], **Georgina Ruiz-Soria**[2], **Raul Arenal**[3], **Paola Ayala**[2], **Albert G. Nasibulin**[*,1], **Hong Lin**[3,4], **Hua Jiang**[1], **Odile Stephan**[5], **Thomas Pichler**[2], **Annick Loiseau**[3], and **Esko I. Kauppinen**[***,1]

CHEMISTRY OF MATERIALS

ARTICLE

pubs.acs.org/cm

doi:10.1021/cm200111b

Nitrogen-Doped Single-Walled Carbon Nanotube Thin Films Exhibiting Anomalous Sheet Resistances

Toma Susi,[*,†] Antti Kaskela,[†] Zhen Zhu,[†] Paola Ayala,[‡] Raul Arenal,[§,∥] Ying Tian,[†] Patrik Laiho,[†] Juha Mali,[†] Albert G. Nasibulin,[†] Hua Jiang,[†] Giorgio Lanzani,[⊥,#] Odile Stephan,[▽] Kari Laasonen,[#,○] Thomas Pichler,[‡] Annick Loiseau,[§] and Esko I. Kauppinen[*,†]

Experimental

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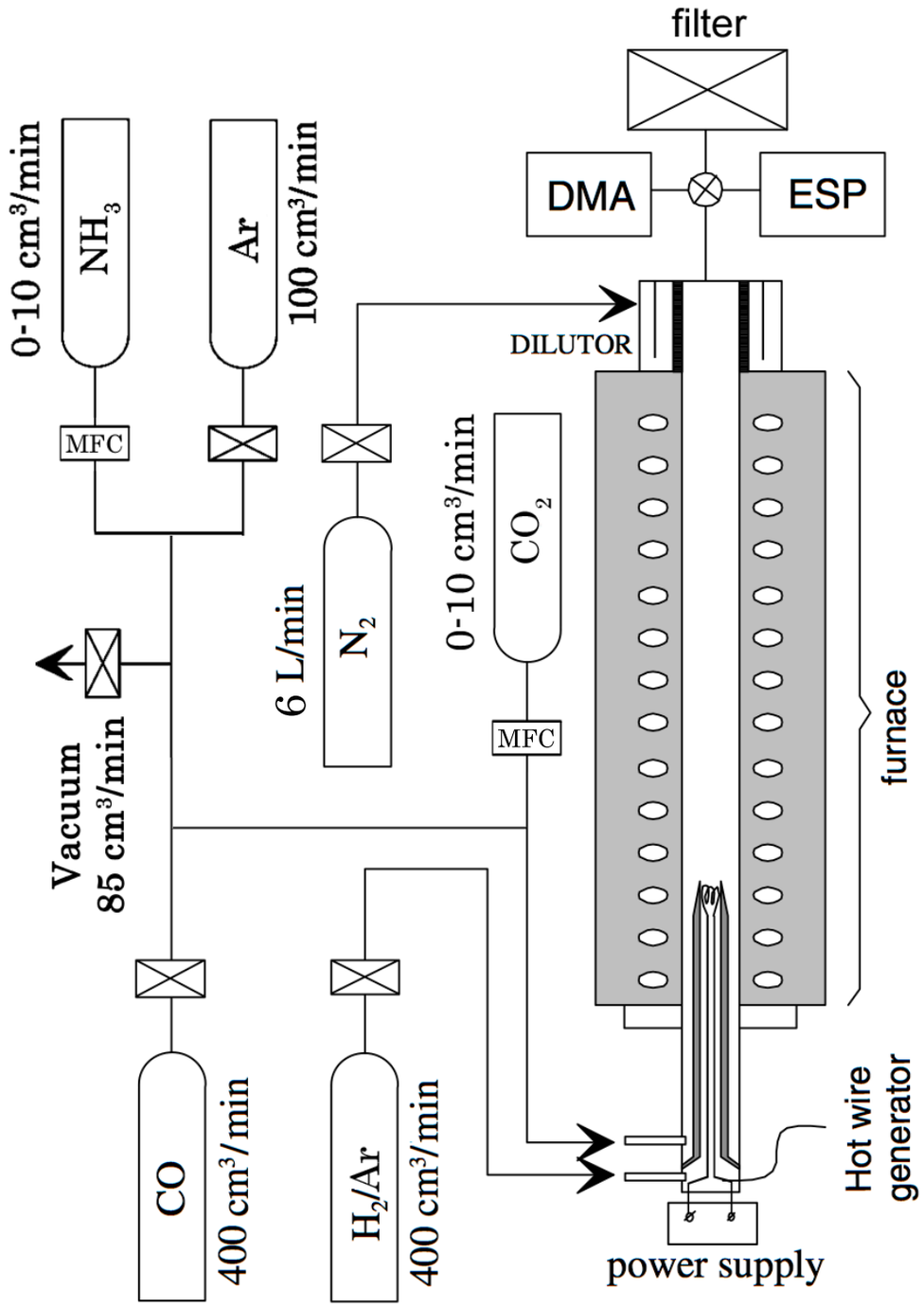
HWG reactor

- Reactor temperature 890°C (optimum for long bundles)
- CO used as carbon precursor, CO_2 as etchant
- 0 to 300 ppm NH_3 as the nitrogen source
  - Diluted with Ar to control very low amounts
- Catalyst particles from resistively heated iron wire, current ~2.7 A



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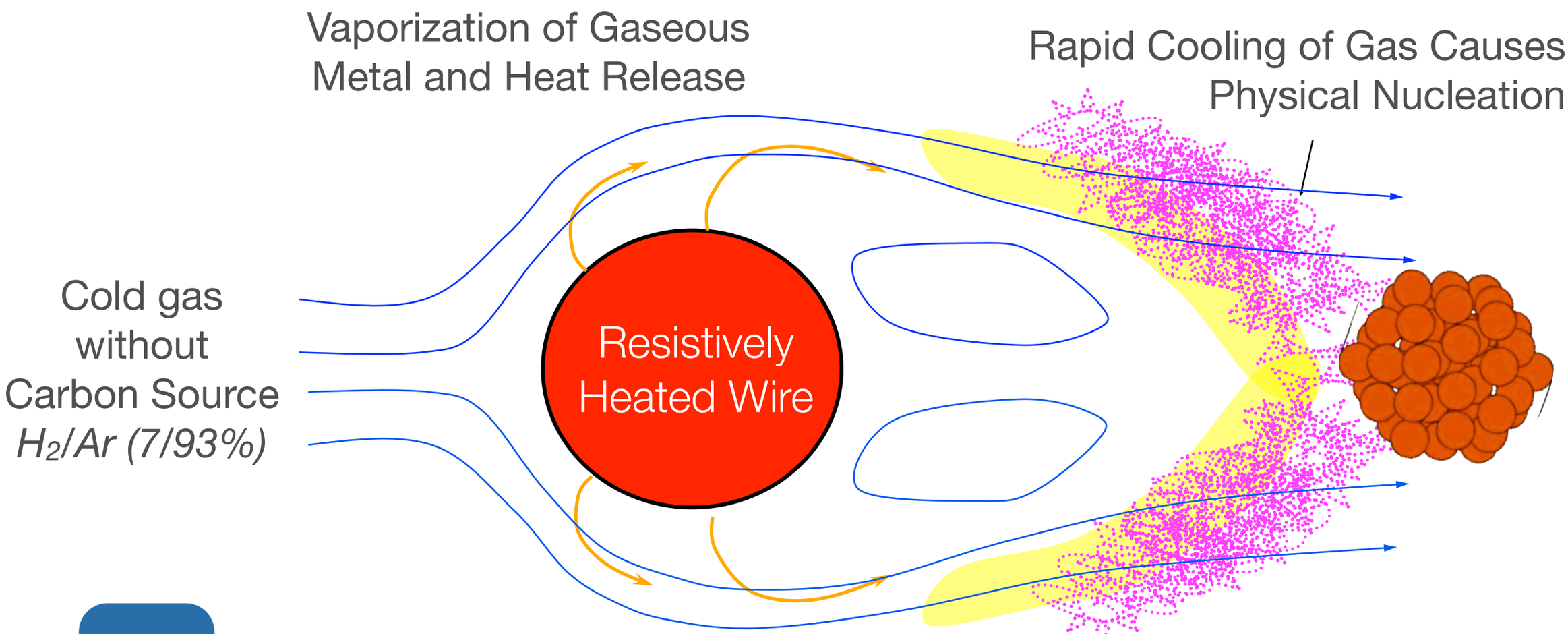
Nanoparticle production in a hot wire generator



Nasibulin CPL 402 (2005)
Image courtesy of David Brown

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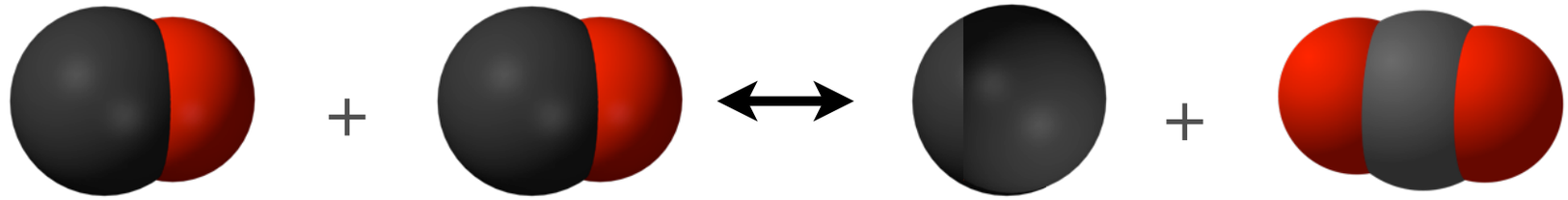
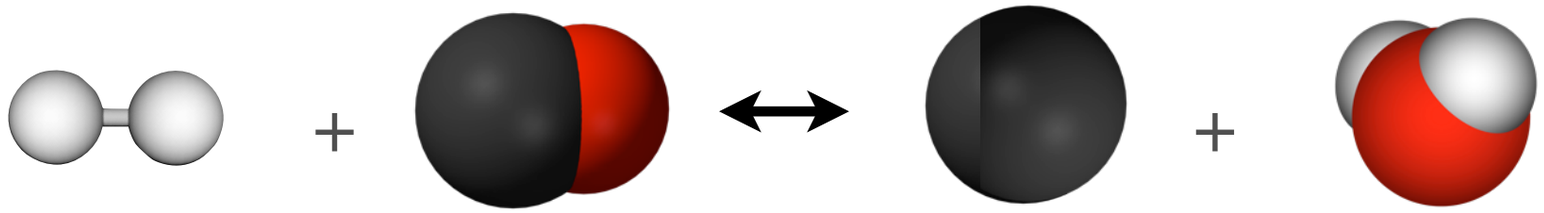
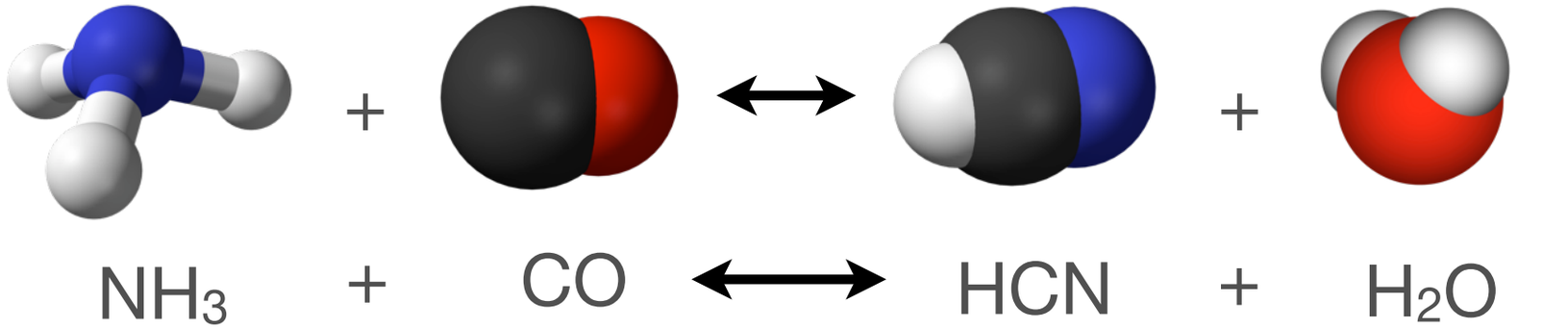


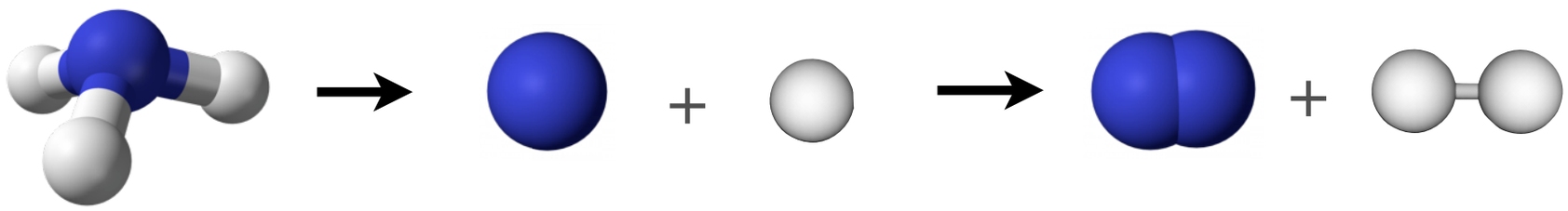
$CO + CO \longleftrightarrow C + CO_2$



$H_2 + CO \longleftrightarrow C + H_2O$



$NH_3 + CO \longleftrightarrow HCN + H_2O$



$2\ NH_3 \longrightarrow 2\ N + 6\ H \longrightarrow N_2 + 3\ H_2$

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Formation mechanism?

NH_3 (ppm)	N content (at. %)		Mean diameter ± variance (nm)
	EELS	XPS	
0	**-**	**-**	**1.4±0.3**
100	**1.2**	**0.2**	**1.2±0.3**
200	**1.7**	**0.7**	**1.1±0.2**
300	**-**	**1.1**	**1.1±0.2**

Susi *et al.*, Chem. Mater. 23 (2011) 2201

- How does the chemistry work in the early stages of the CVD?
  - How does N affect the growth process and the properties of the tubes?
  - Why is N enriched in tubes: from 100 ppm (0.001%) in gas to ~0.2% (and locally >1%)?
- Ultimate goal: tune the process to get certain N-SWCNTs with desired properties?
  - Diameter reduction, chirality control?
  - N-content tuning, control of doping configurations, distribution?

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JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

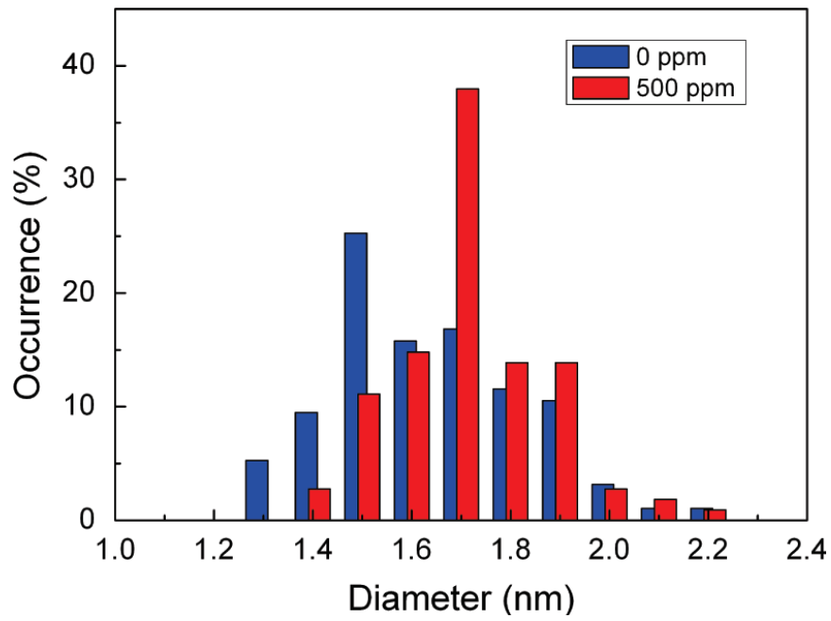
COMMUNICATION

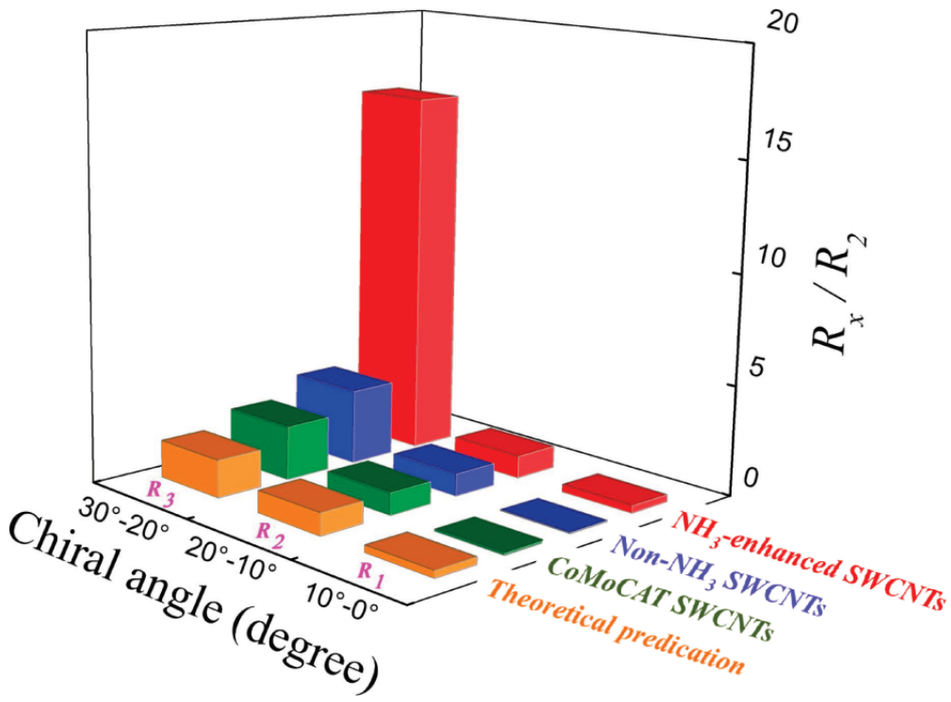
doi:10.1021/ja1087634

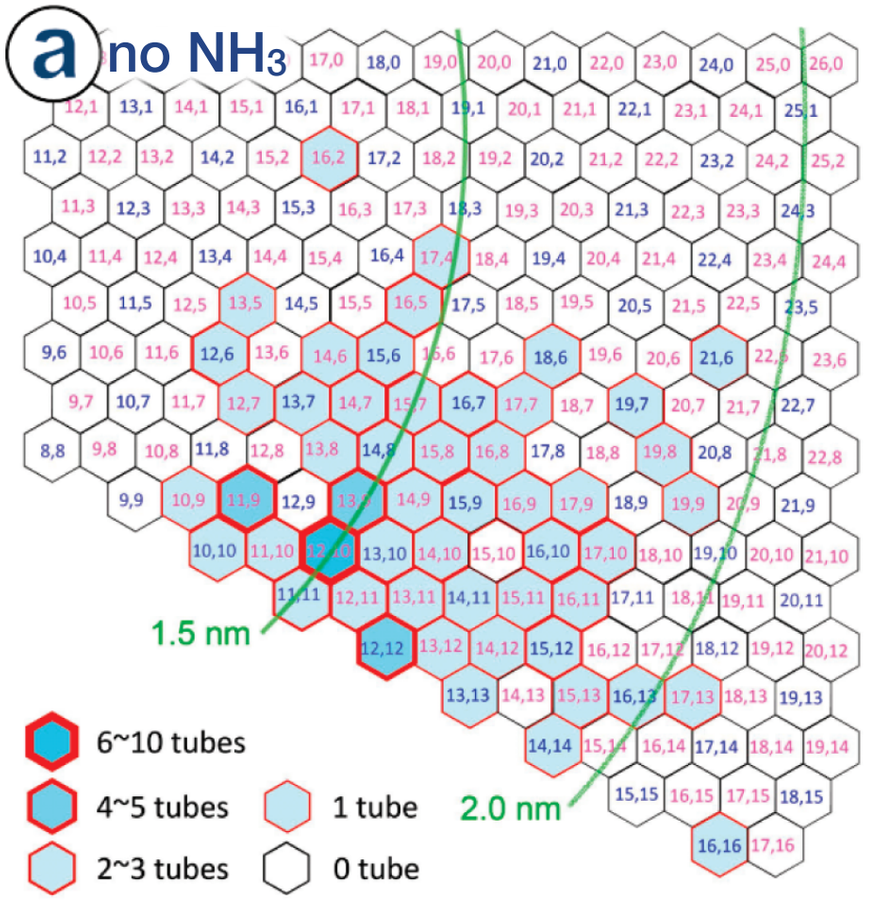
pubs.acs.org/JACS

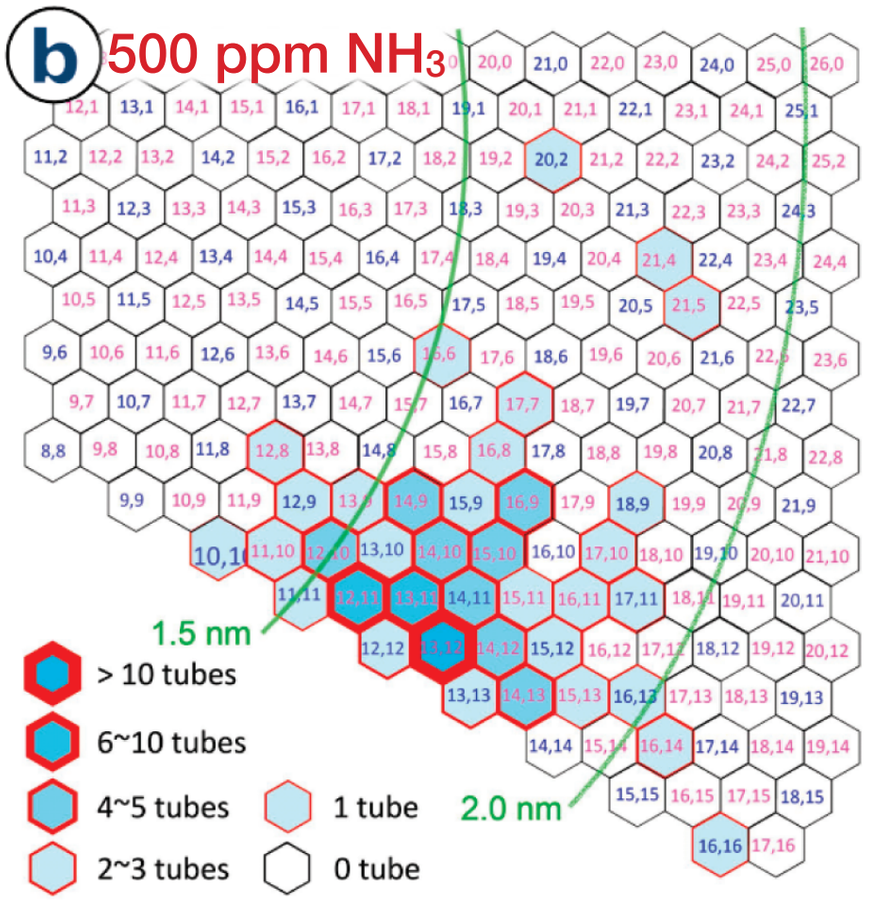
The Use of NH_3 to Promote the Production of Large-Diameter Single-Walled Carbon Nanotubes with a Narrow (*n*,*m*) Distribution

Zhen Zhu, Hua Jiang,* Toma Susi, Albert G. Nasibulin, and Esko I. Kauppinen*









Phys. Status Solidi B **247**, Nos. 11–12, 2708–2712 (2010) / **DOI** 10.1002/pssb.201000226

Mechanism study of floating catalyst CVD synthesis of SWCNTs

Giorgio Lanzani*[,1,2], Toma Susi[3], Paola Ayala[4], Tao Jiang[5], Albert G. Nasibulin[3], Thomas Bligaard[5], Thomas Pichler[4], Kari Laasonen[,2], and Esko I. Kauppinen***[,3]**

doi:10.1002/pssb.201000226

Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 11303–11307

www.rsc.org/pccp

PAPER

Mechanism of the initial stages of nitrogen-doped single-walled carbon nanotube growth†

Toma Susi,*[a] Giorgio Lanzani,[bc] Albert G. Nasibulin,[a] Paola Ayala,[d] Tao Jiang,[e] Thomas Bligaard,[e] Kari Laasonen[cf] and Esko I. Kauppinen*[a]

doi:10.1039/C1CP20454H

Static DFT mechanism study

Background

Experimental

DFT mechanism study

DFTB MD simulation

Conclusions

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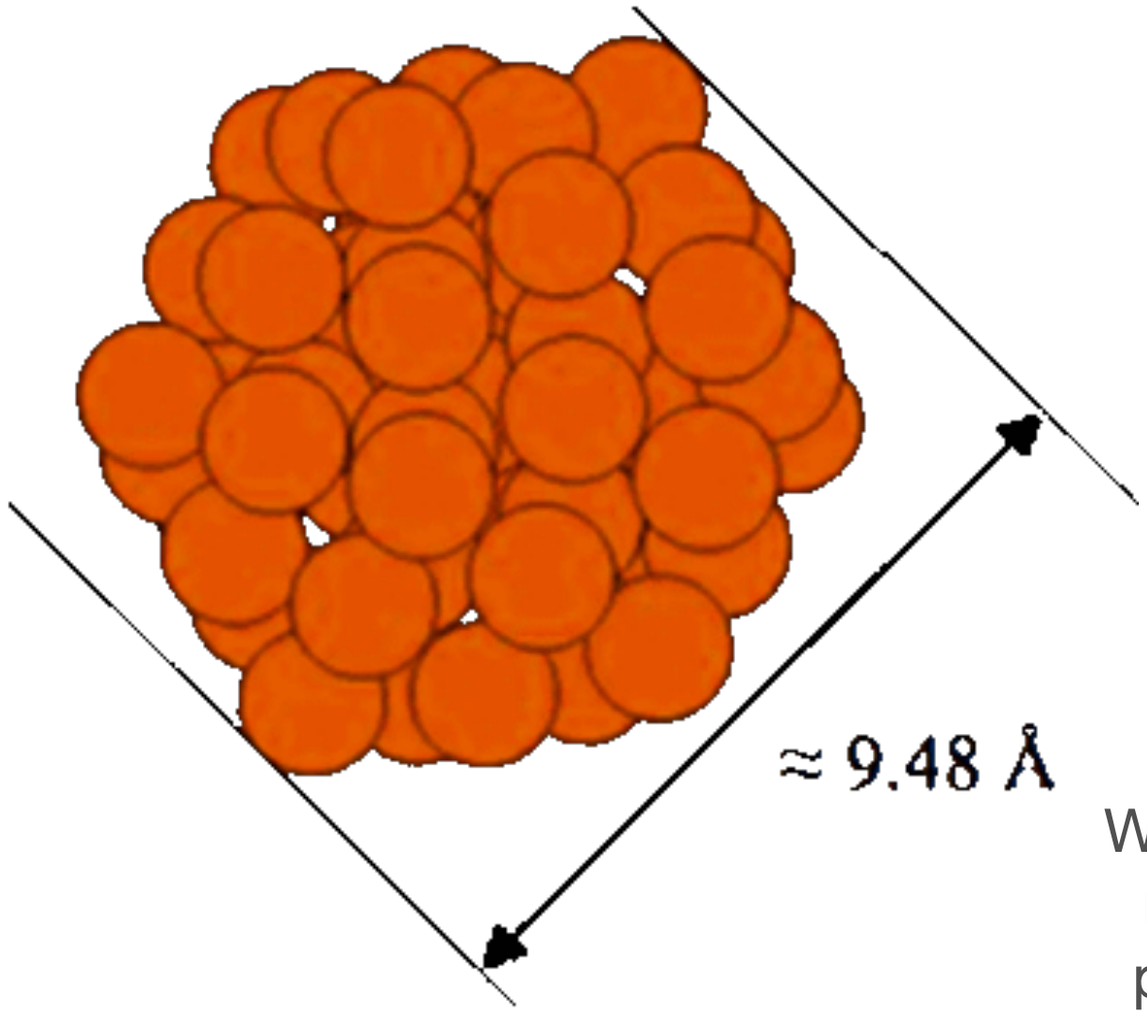
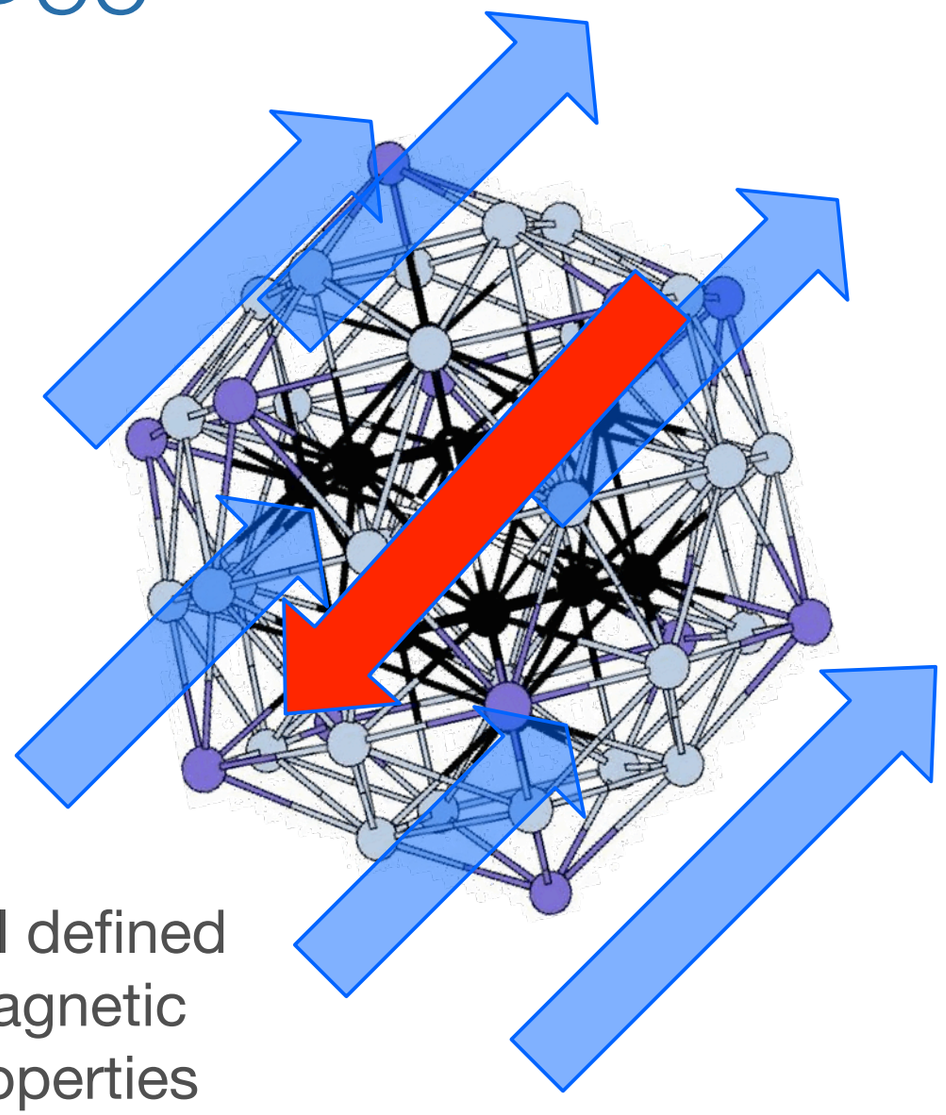
DFT study: Fe_{55}





Well defined magnetic properties

The best candidate for our study (biggest that we can use) is Fe_{55} in a supercell of 21 Å x 21 Å x 21 Å. μ_{tot}= 136 μB (almost on Z axis).

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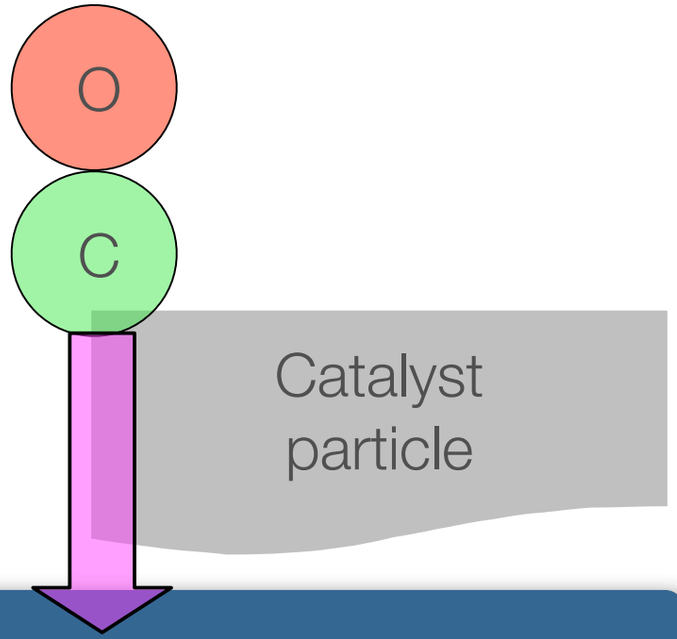
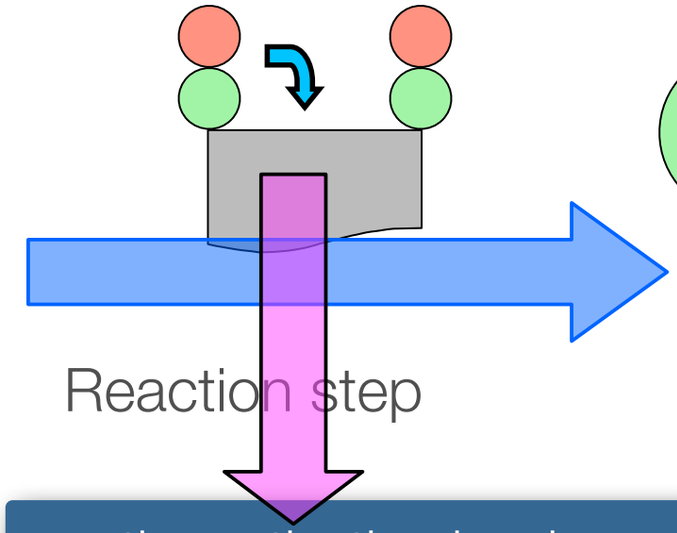
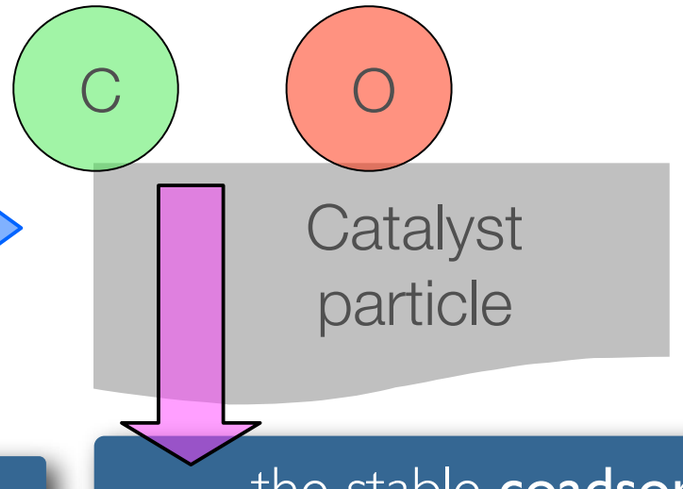


To obtain a full description of the reactivity we need to know the **stable adsorption geometries** of reactants ....



.... the activation barrier....



...the stable **coadsorption** geometries **of the products.**

NEB calculations (VASP/GPAW codes) has been used to calculate the activation barrier.

Geometry optimization (VASP/GPAW codes) has been used to study adsorption geometry of products and reactants on a icosahedral Fe_{55}.

J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, PRB 71 (2005)
S. R. Bahn and K. W. Jacobsen, Comput. Sci. Eng. 4 (2002)
G. Henkelman and H. Jonsson, JCP 113 (2000)
G. Kresse and J. Furthmuler, PRB 54 (1996)

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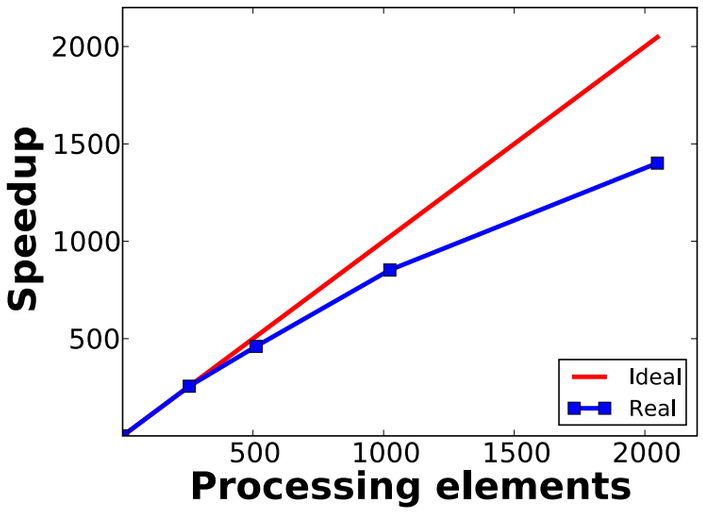
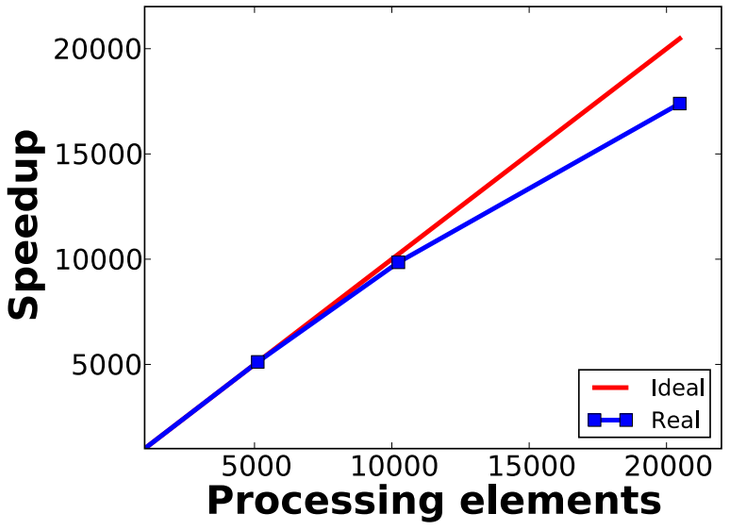
Ground state



Time propagation



GPAW

- Grid-based projector-augmented plane wave DFT Python code[1,2]
- Real-space uniform grids and multigrid methods, parallelization over k-points, spins, bands + domain-decomposition
  - $O(N^3)$, scales efficiently[2]
- Nudged elastic band method[3,4] to estimate the reaction barriers
  - Neglects entropy contribution
- Catalyst assumed static (=solid)

[1] J. J. Mortensen et al., Phys. Rev. B 71 (2005) 035109
[2] J. Enkovaara et al., J. Phys.: Condens. Matter 22 (2010) 253202
[3] G. Henkelman et al., J. Chem. Phys. 113 (2000) 9901
[4] G. Henkelman, and H. Jónsson, J. Chem. Phys. 113 (2000) 9978

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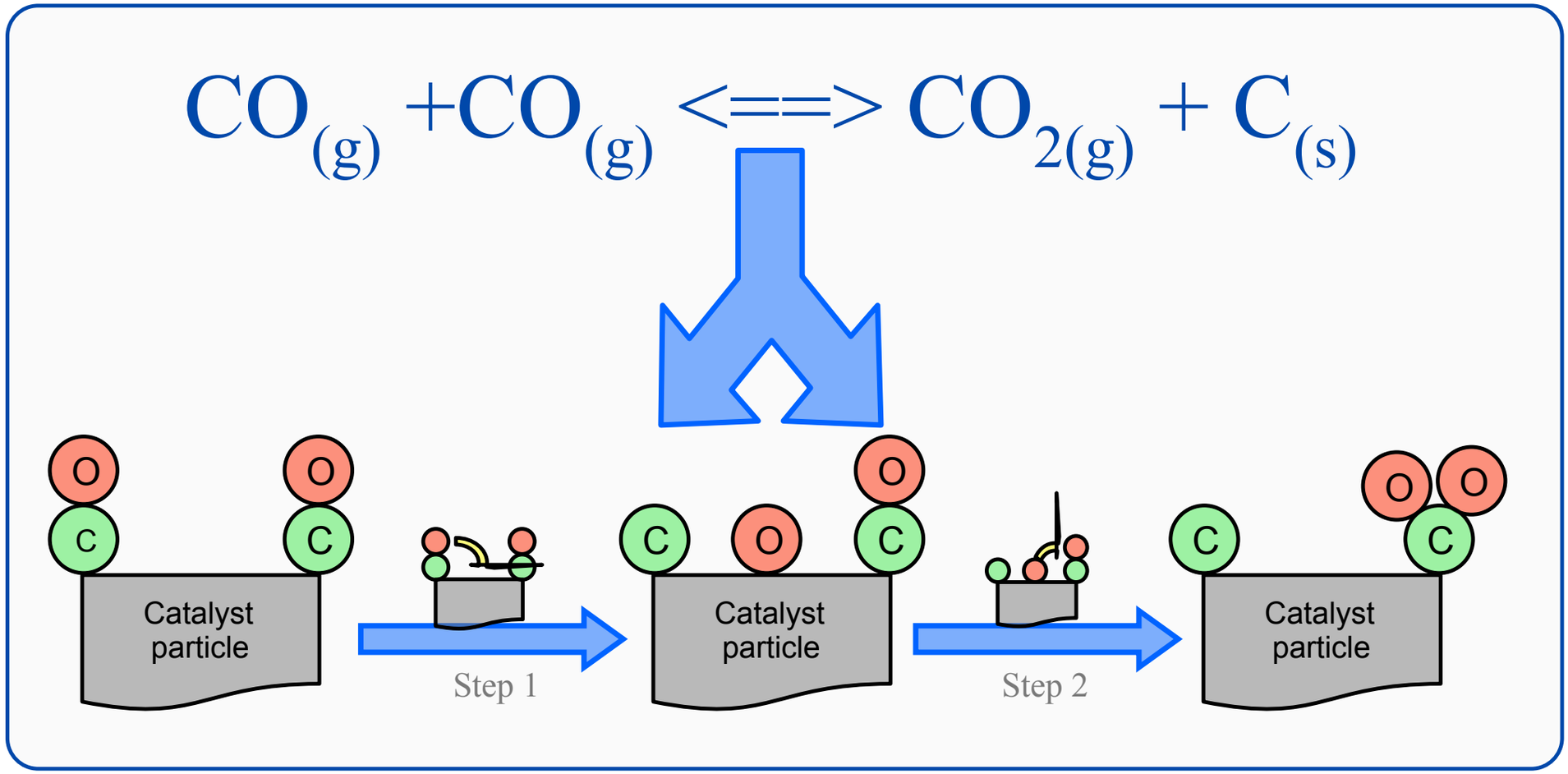
CO disproportionation



The hypothesis come from analogous study on the flat surface:

- D. Borthwick et al, Surf. Sci 602 (2008) 2325;
- M.P. Andersson et al, J. of Catal. 255 (2008);
- X.Y. Liao et al, Catal. 269 (2007) 169;
- D.E. Jiang et al, Surf. Sci 570 (2004) 167.

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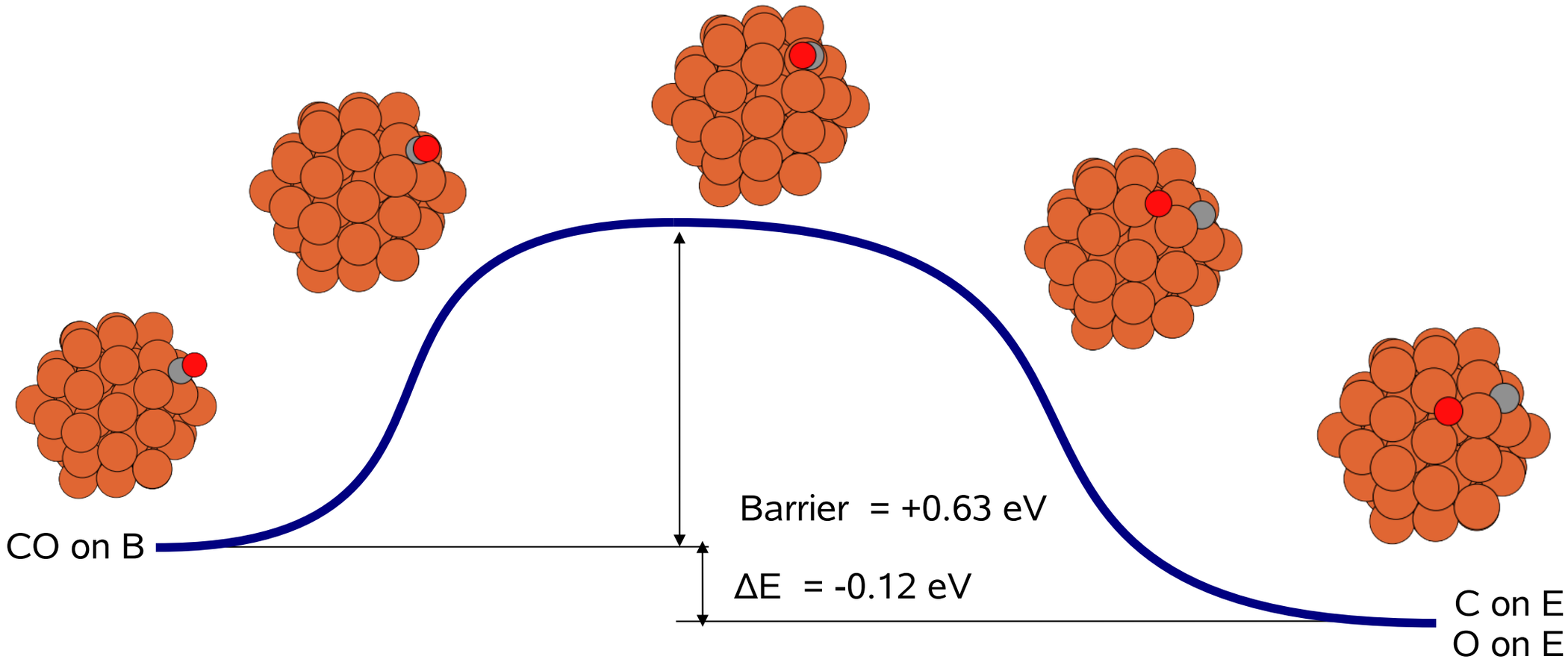
CO dissociation



[1] G. Lanzani et al., PSSb 247 (2010) 2708

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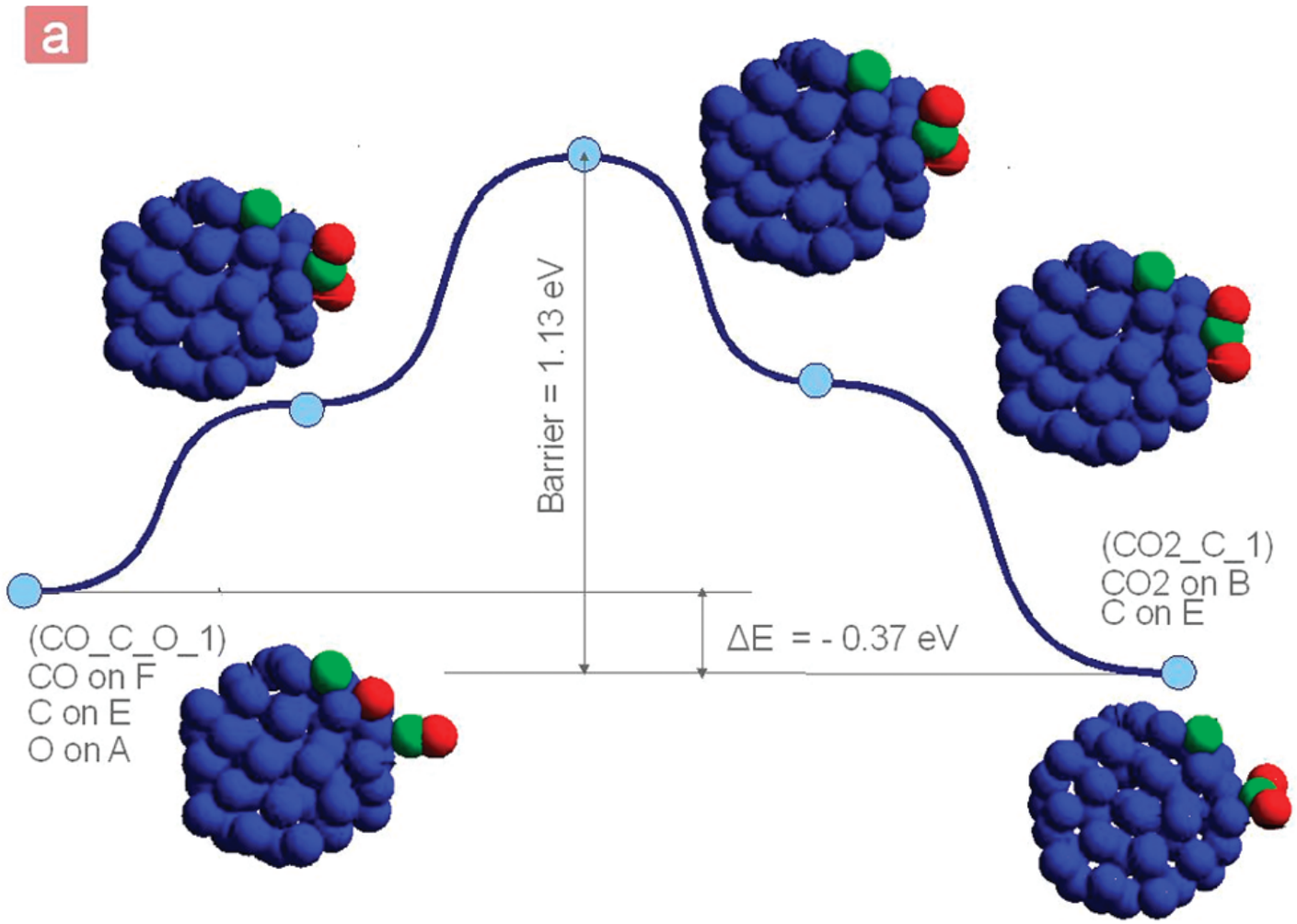
CO dissociation



[1] G. Lanzani et al., PSSb 247 (2010) 2708
[2] G. Lanzani et al., J. Phys. Chem. C 113 (2009) 12939

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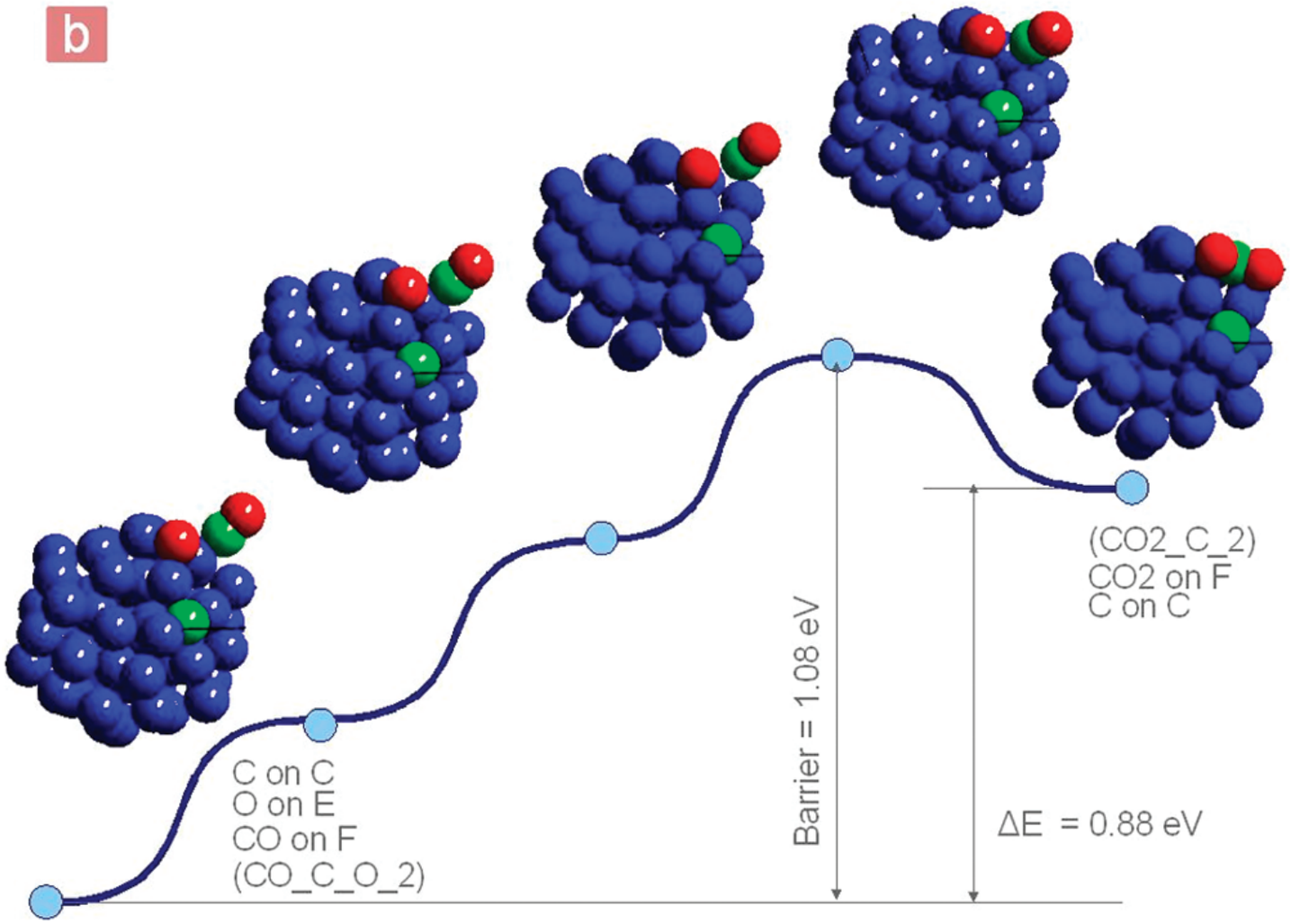
CO dissociation



[1] G. Lanzani et al., PSSb 247 (2010) 2708
[2] G. Lanzani et al., J. Phys. Chem. C 113 (2009) 12939

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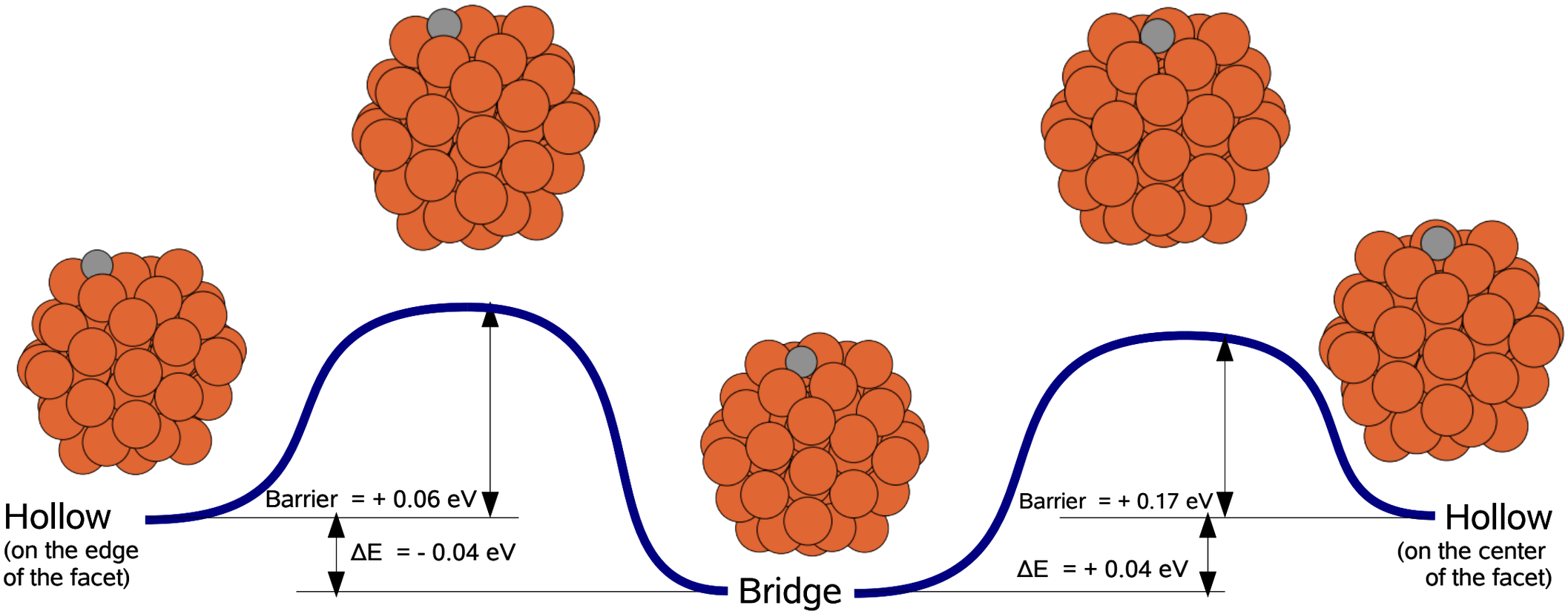
CO dissociation & mobility



[1] G. Lanzani et al., PSSb 247 (2010) 2708
[2] G. Lanzani et al., J. Phys. Chem. C 113 (2009) 12939

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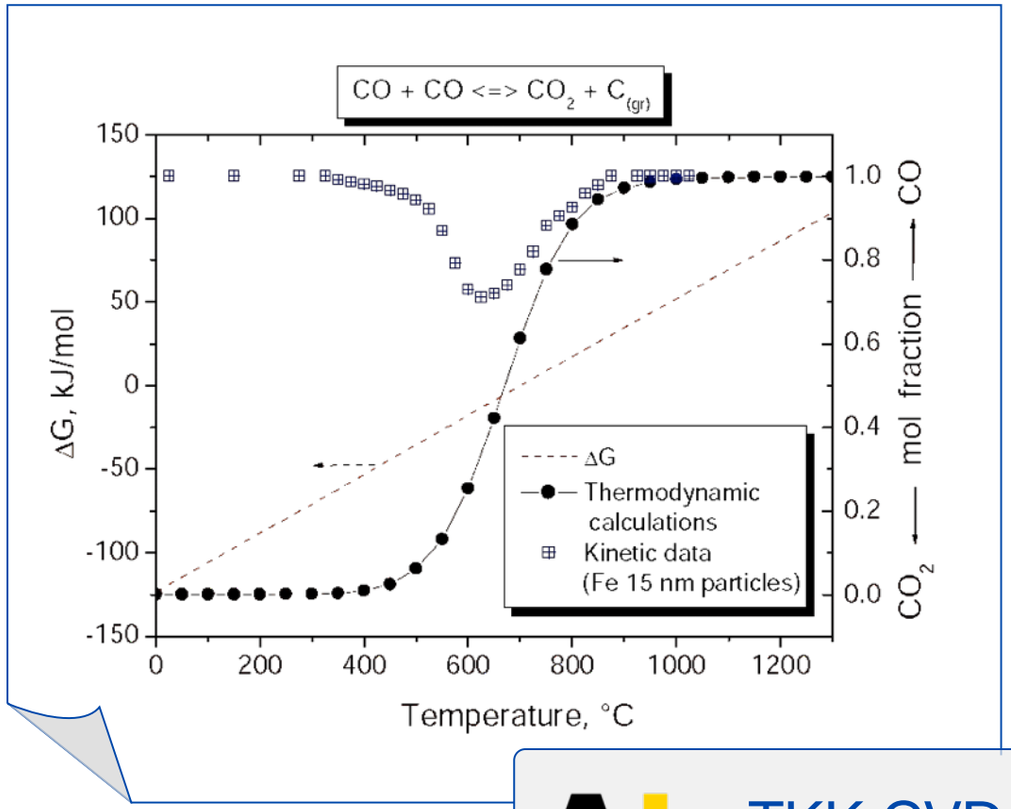

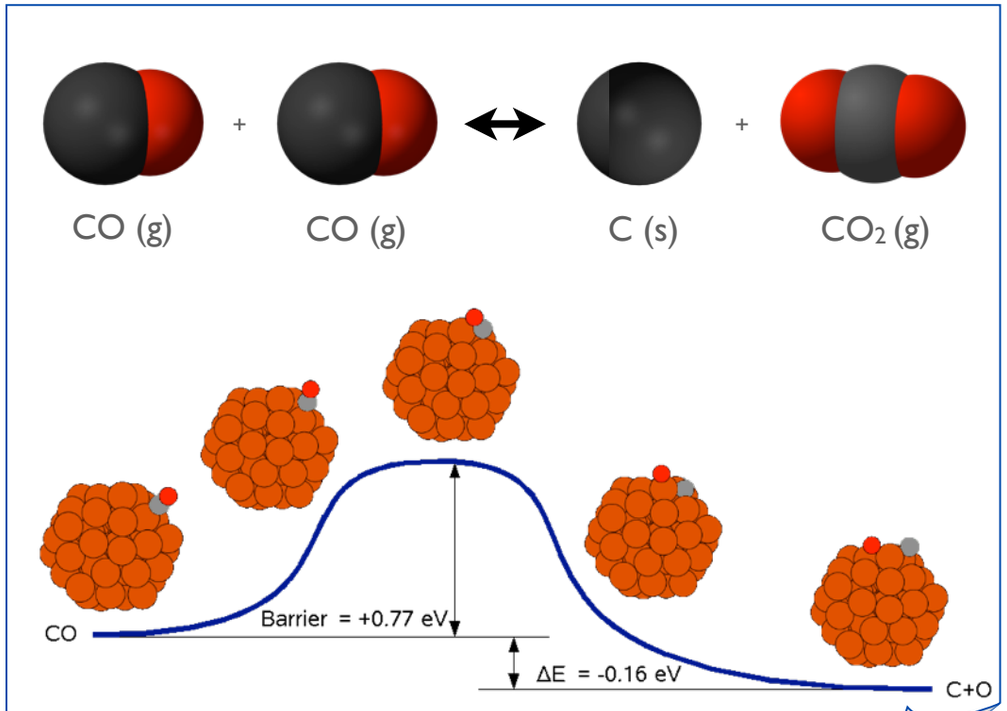

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TKK CVD REACTOR

OULU DFT CALCULATIONS

OULUN YLIOPISTO

GPAW!

The Arrhenius equation given in the form:

$$k = Ae^{-E_a/RT}$$

can be written equivalently as:

$$\ln(k) = \ln(A) - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

Where:

k = Rate constant

A = Pre-exponential factor

E_a = Activation energy

R = Gas constant

T = Absolute temperature, K

Activation barrier for CO dissociation:
Calculated: **0.63** eV

Activation barrier for CO disproportionation:
1.08 eV < Calculated [1] < **1.13 eV**
Experimental [1]: **0.65 eV** (~15 nm particles)

[1] G. Lanzani et al. J. Phys. Chem. Lett. 113 (2009) 12939

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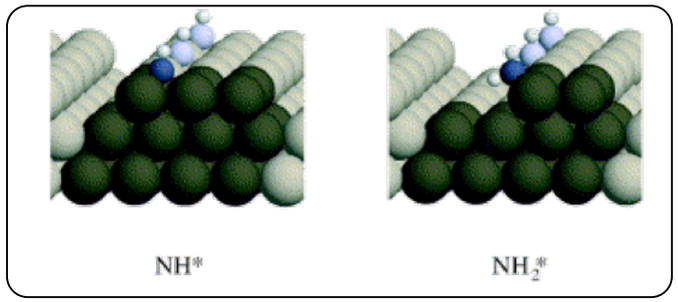
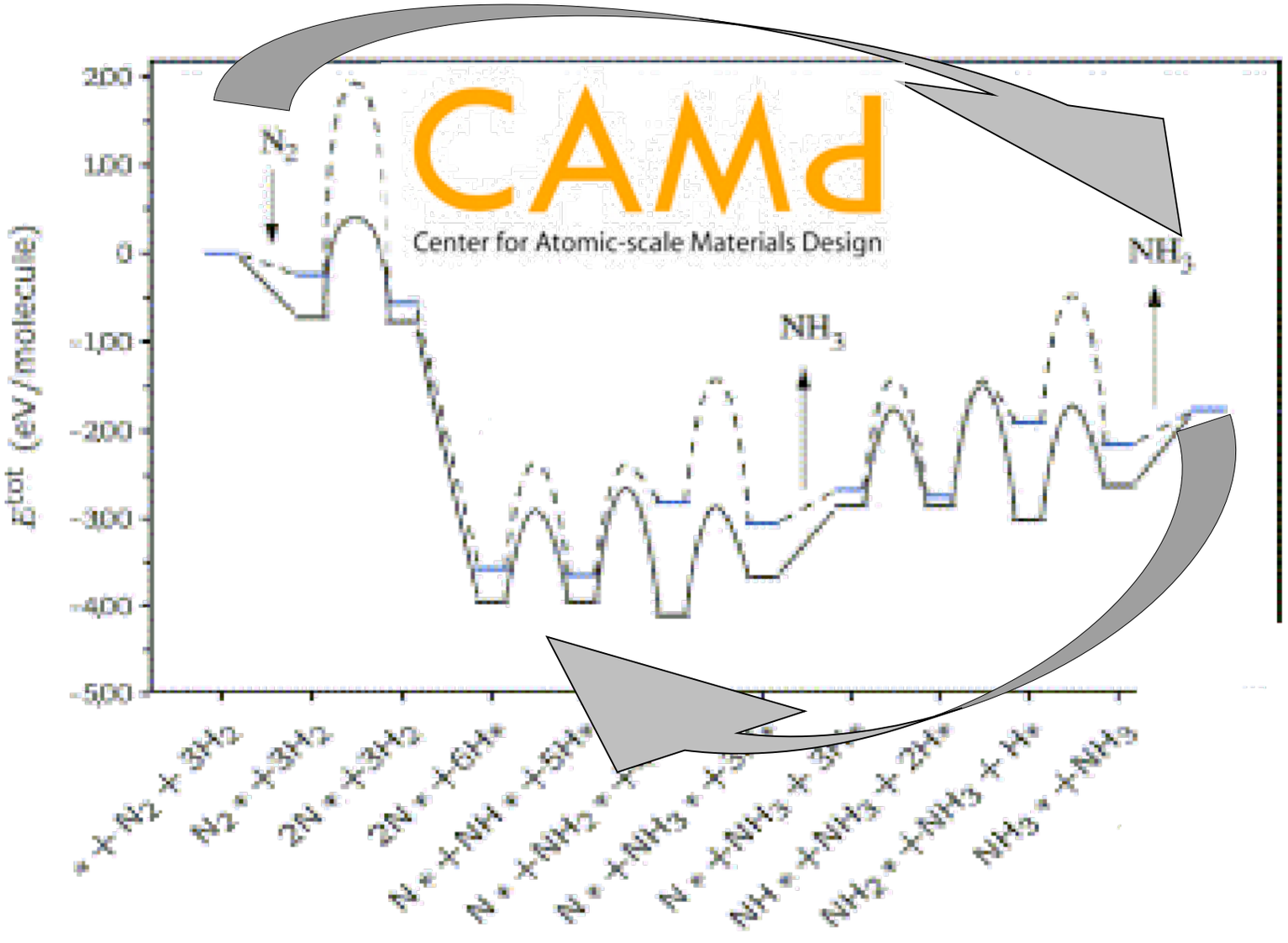
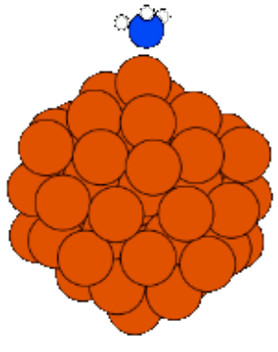
NH_3 reactivity



This reactivity is already well studied on flat surfaces:

- G. Ertl in Catalytic Ammonia Synthesis, Plenum, New York (1991), p. 109.
- P. Stoltze and J.K. Nørskov. Phys. Rev. Lett. 55 (1985), p. 2502.
- Á. Logadóttir and J. K. Nørskov J. Catalysis 220 (2003), p. 273.





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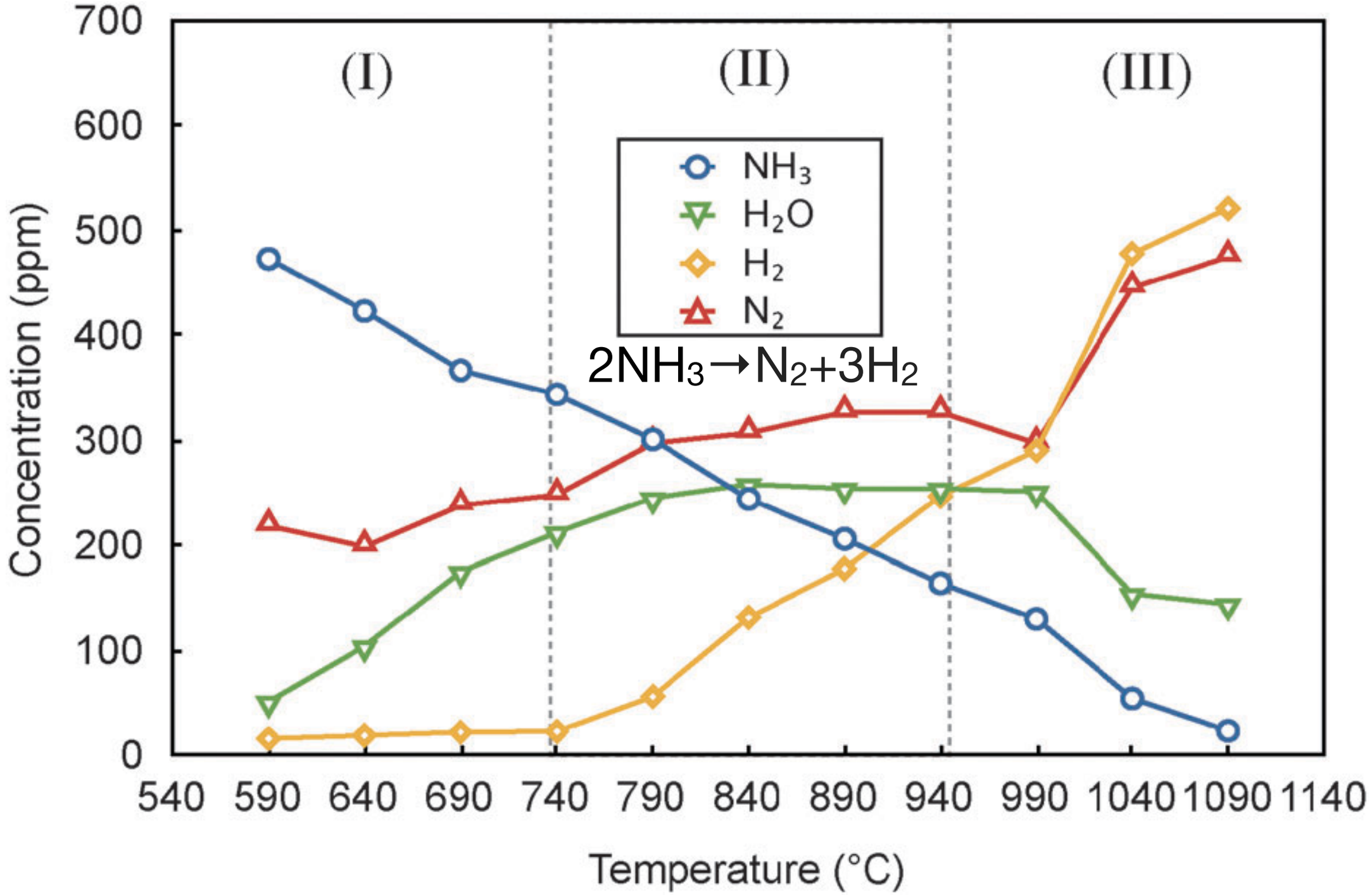
Input: 500 ppm NH_3



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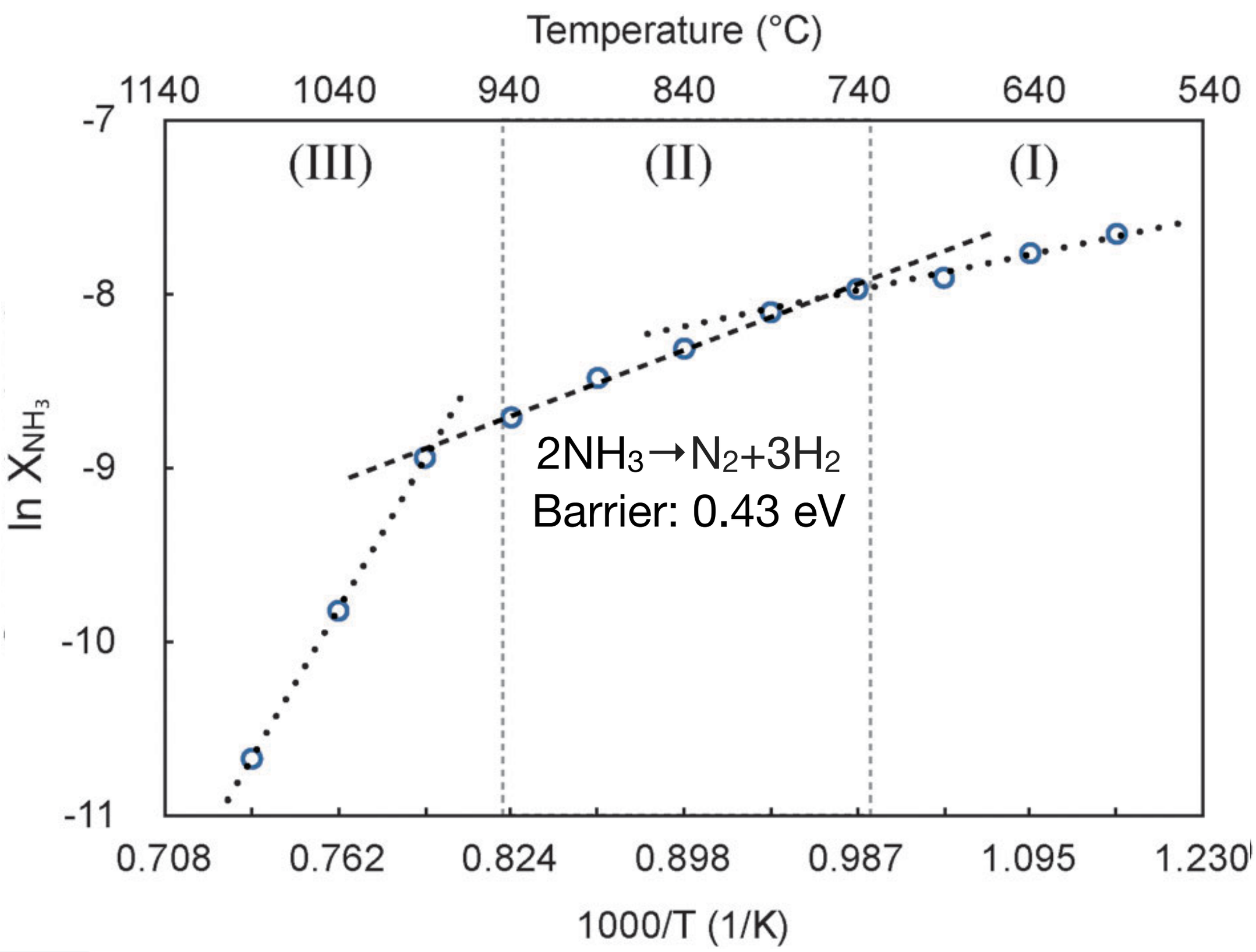

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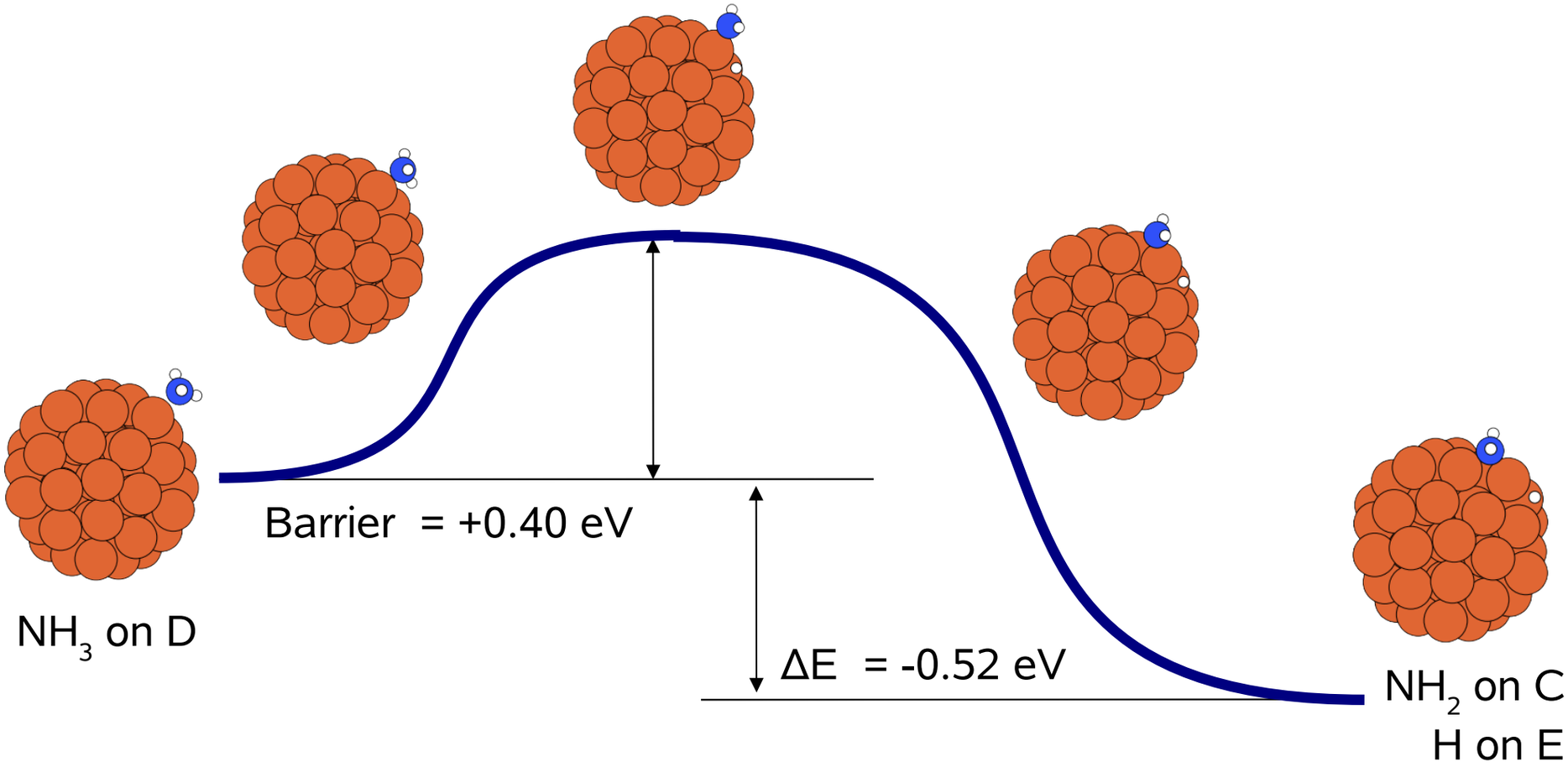
NH_3 dissociation



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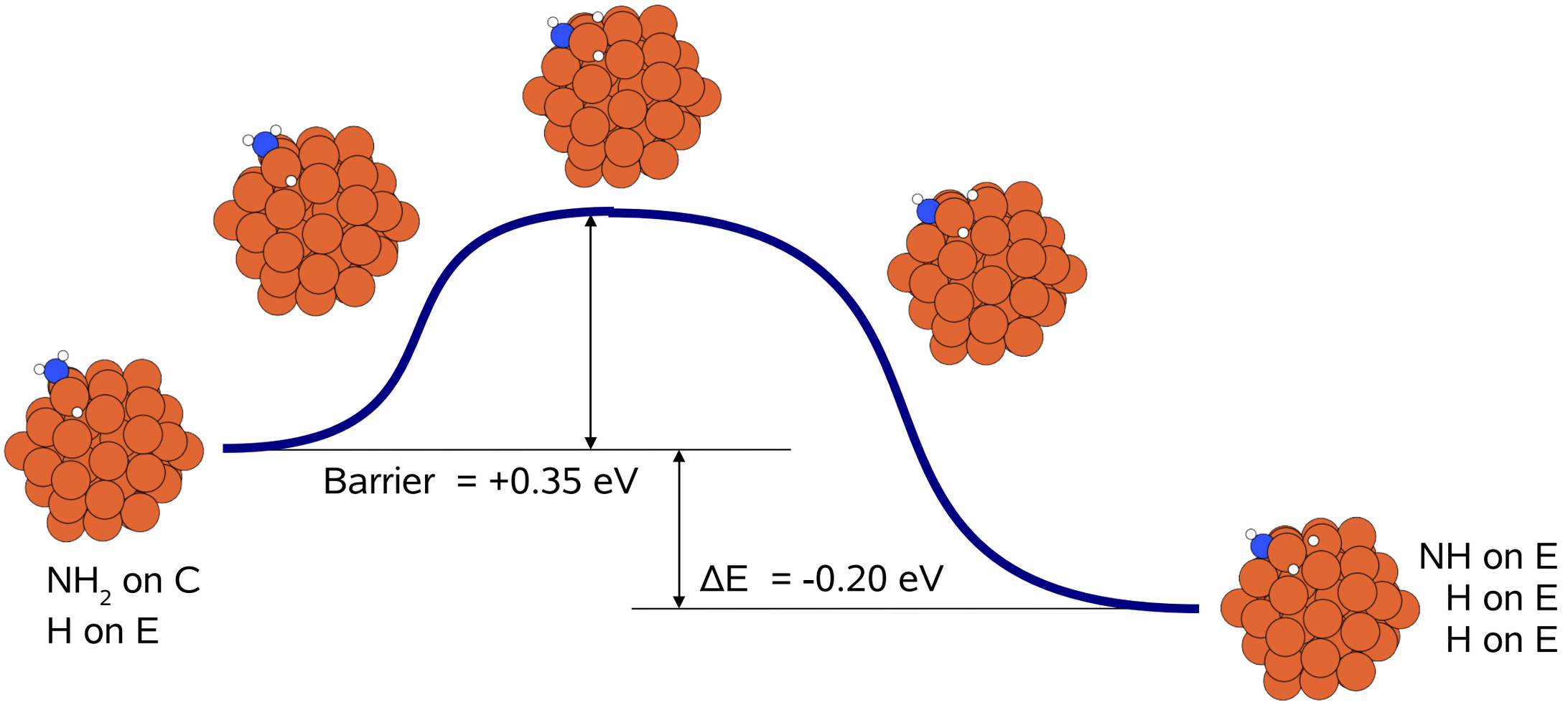
NH_3 dissociation



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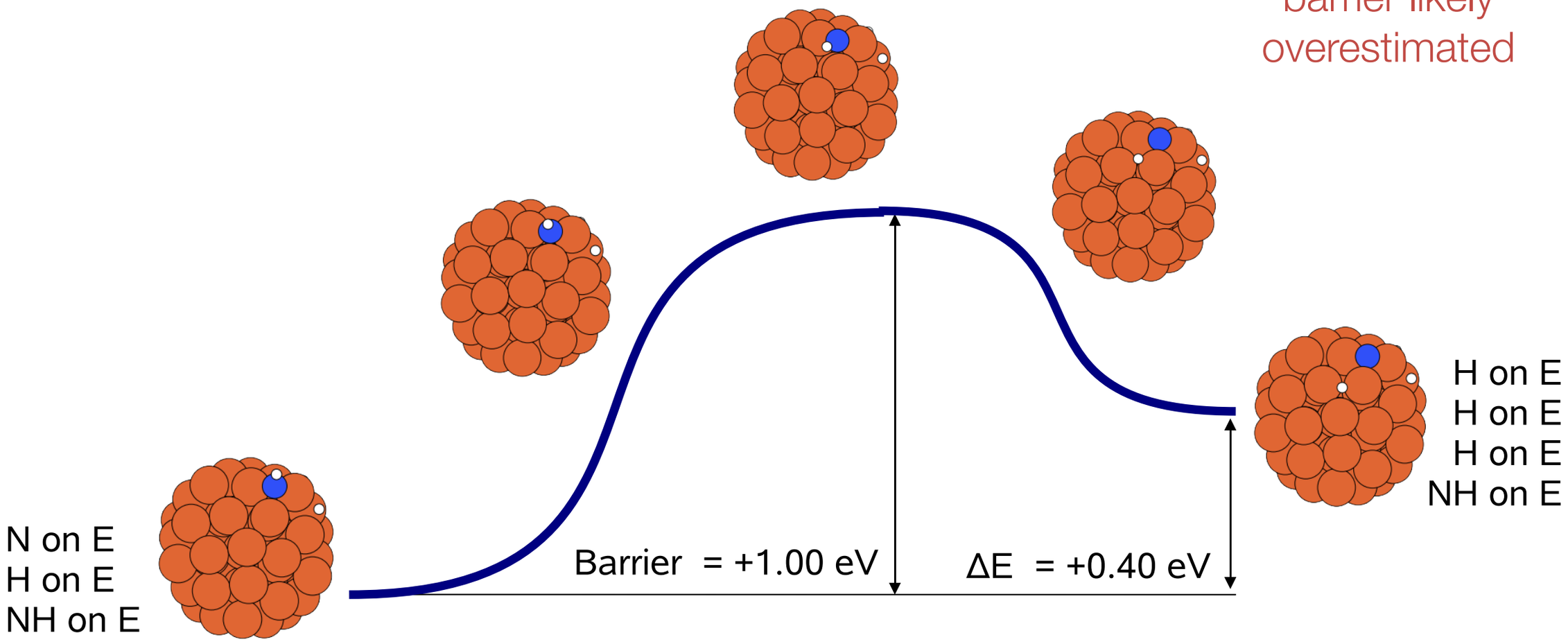
NH_3 dissociation

Final H cleavage barrier likely overestimated



Experimentally: 0.43 eV (tandem mass spec & FTIR)
T. Susi et al., PCCP 13 (2011) 11303

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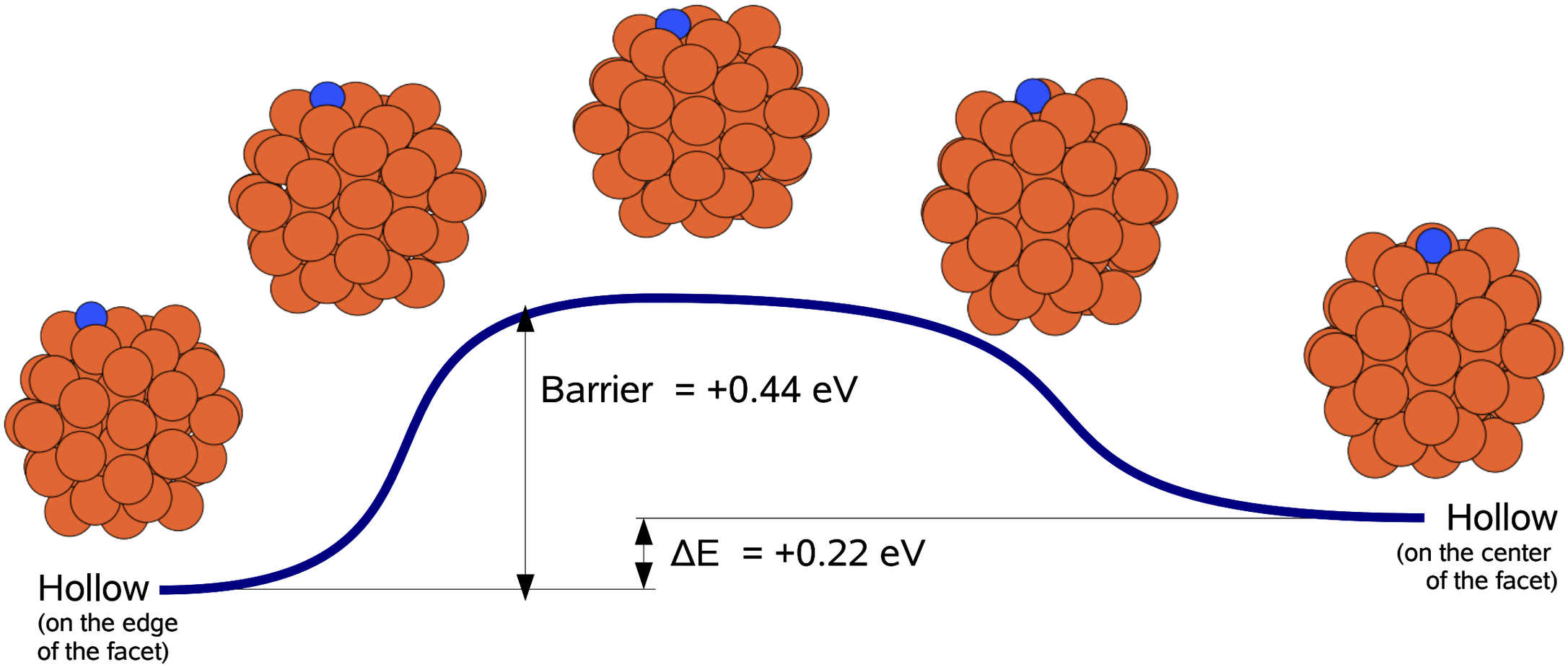
NH_3 dissociation & mobility



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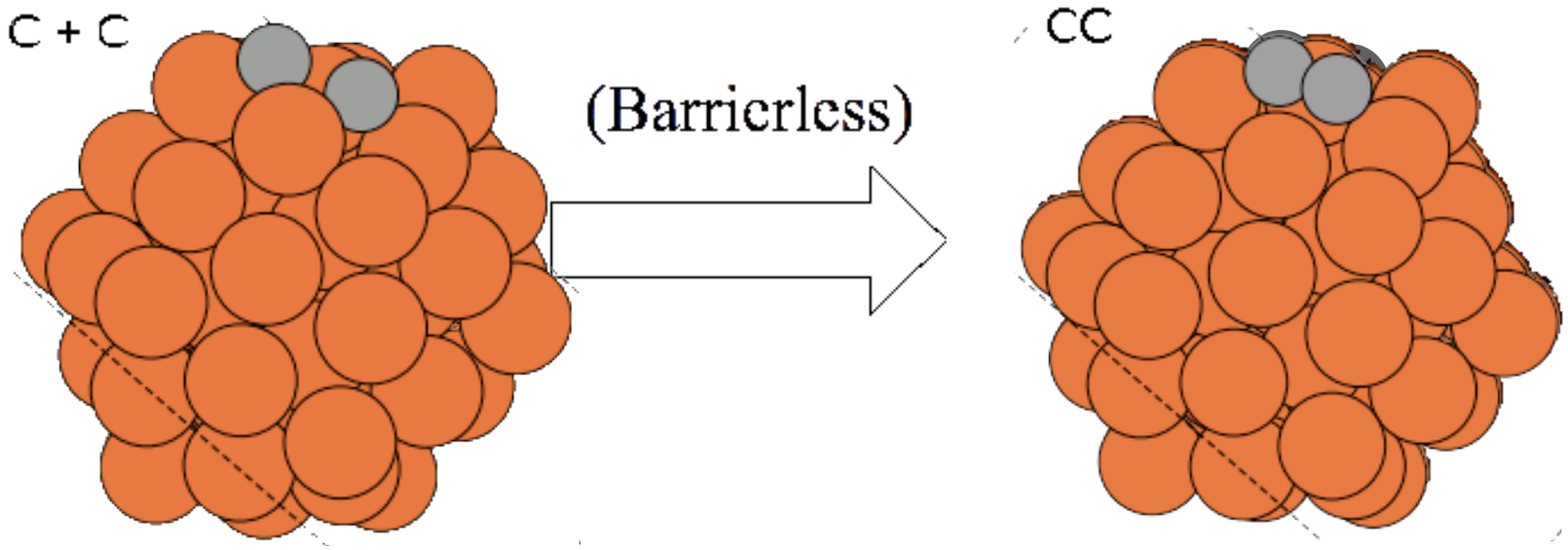

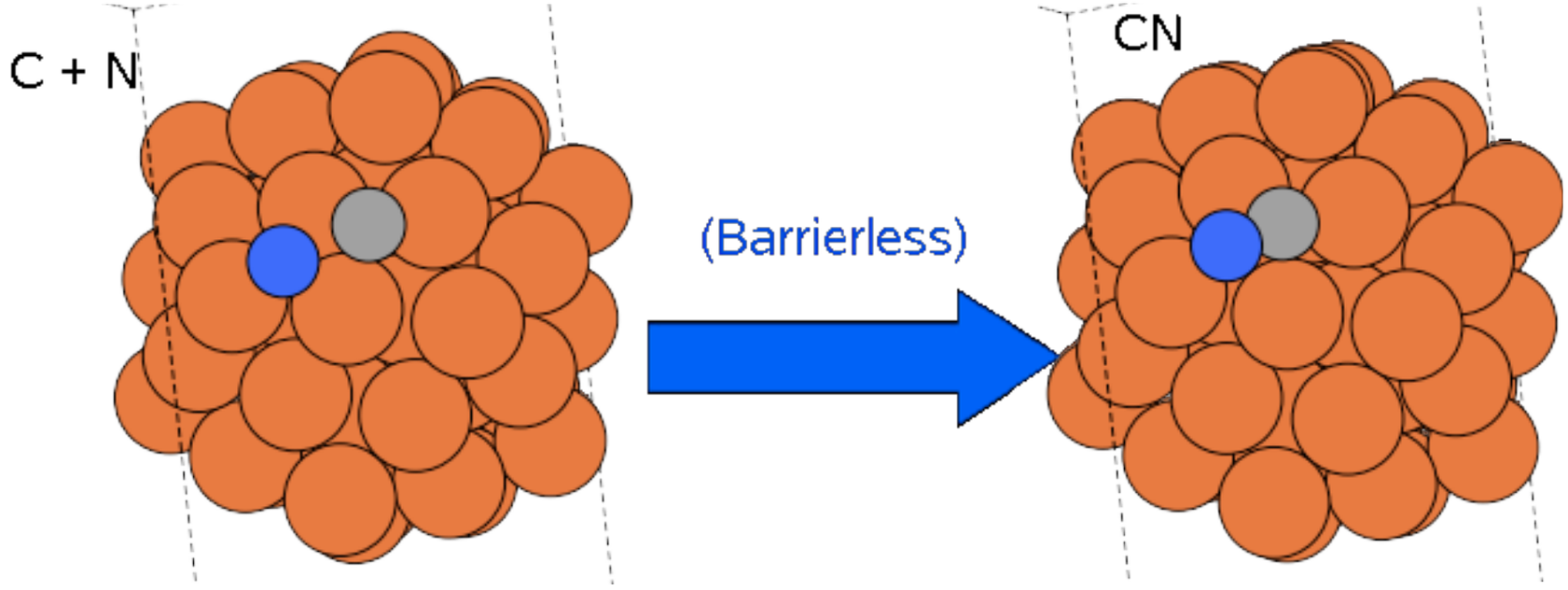

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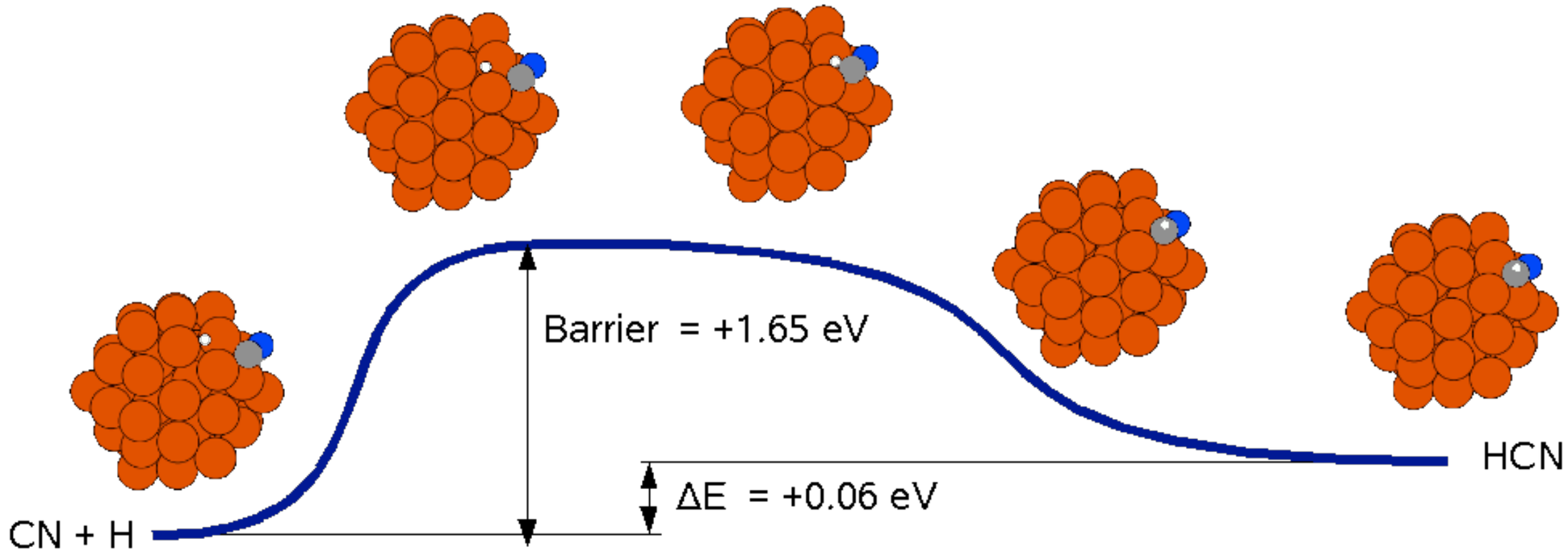
HCN formation on Fe_{55}



Experimentally: 1.51 eV (tandem mass spec & FTIR)
T. Susi et al., PCCP 13 (2011) 11303

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THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

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Initial Stages of Growth of Nitrogen-Doped Single-Walled Carbon Nanotubes

Stefan Taubert and Kari Laasonen*

DFTB MD simulation study

Background

Experimental

DFT mechanism study

DFTB MD simulation

Conclusions

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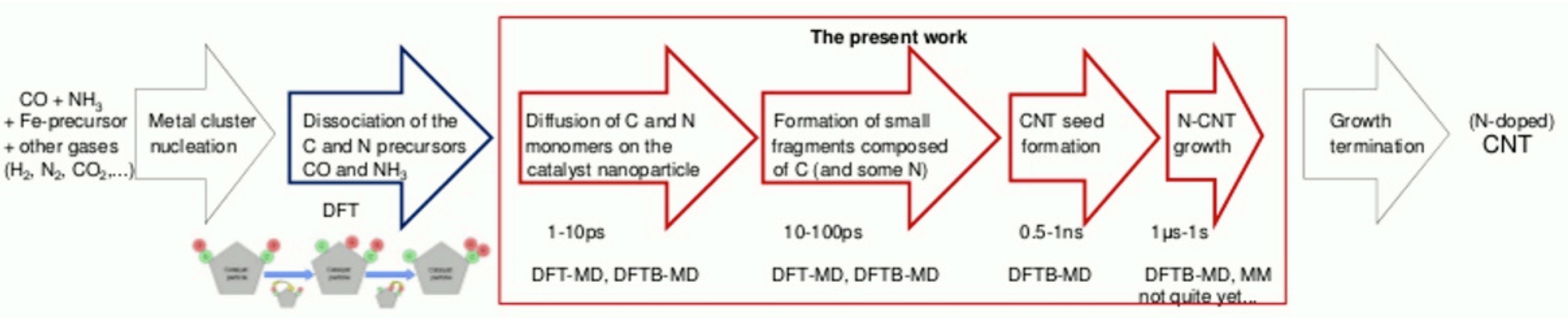
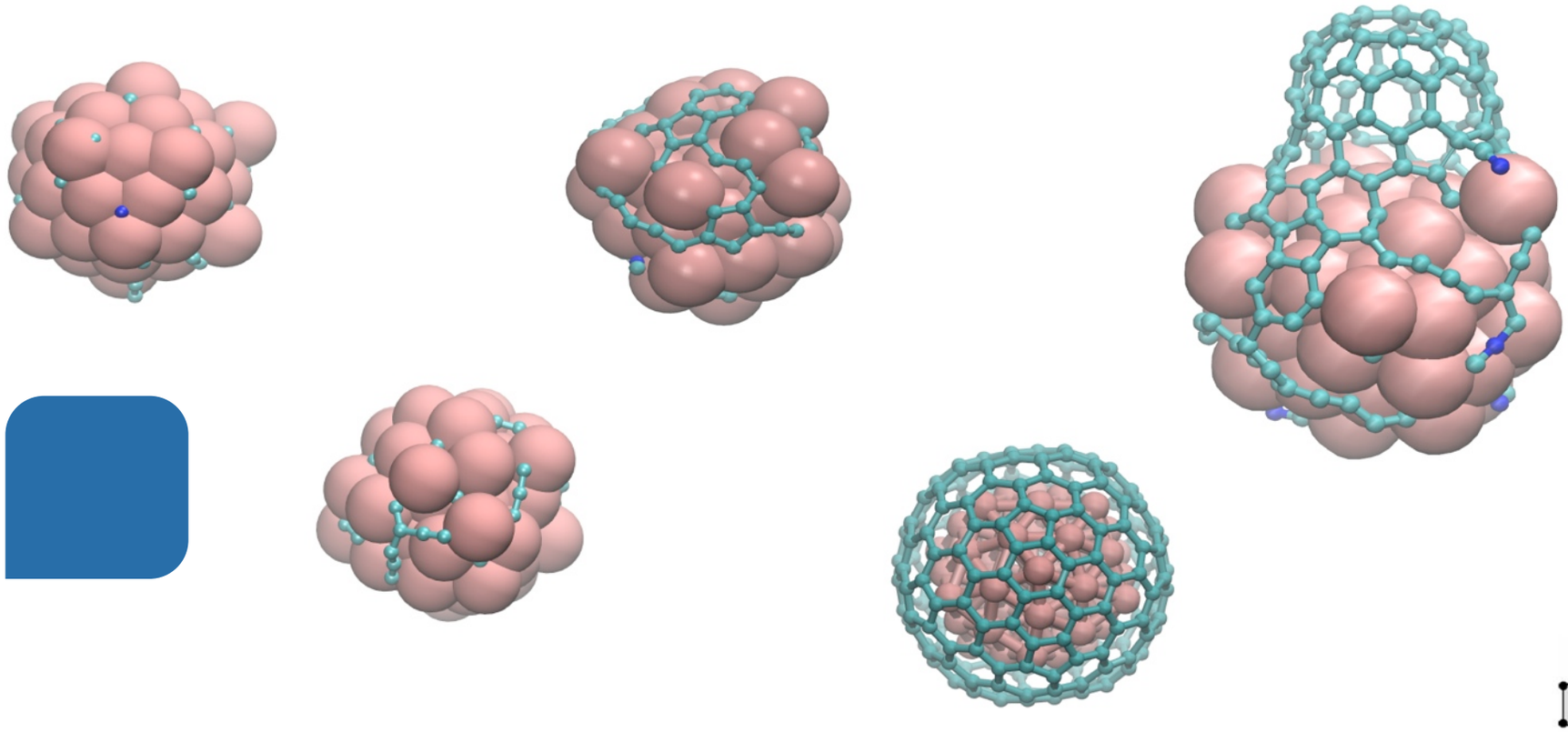
Method





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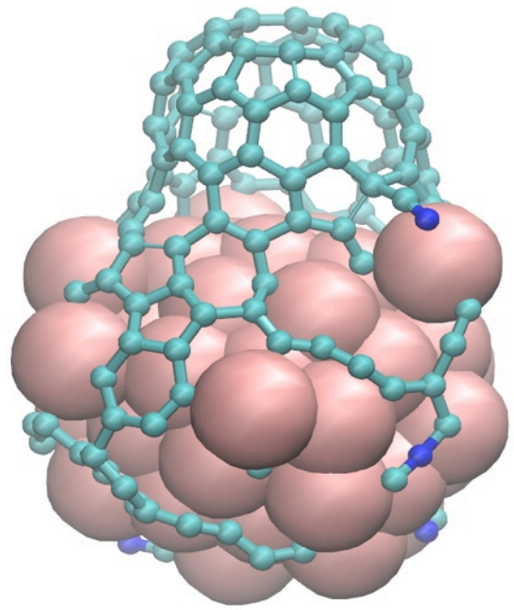
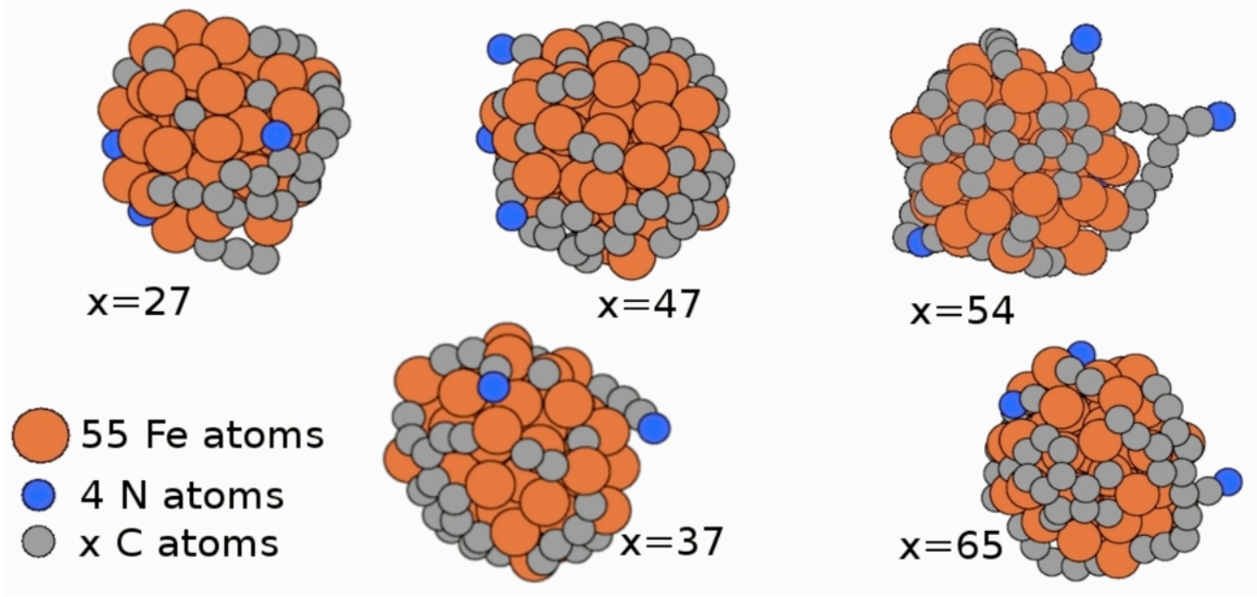
What did they do?

- DFTB/MD simulations*
  (collinear magnetic moments)
- Dissociated N and C atoms on Fe_{55}
  - 4 N atoms, and
    27, 37, 47, 54, 65 C atoms



- Short CNT models
  - 4, 5, 6, 7 N atoms,
    and
    137, 147 C atoms



* SCC-DFTB with DftbPlus Program, NVT, velocity-Verlet, time step 2 fs
T=1000 K (Berendsen thermostat), simulated time 0.1-0.4 ns

Very short (~1ps) DFT/MD to confirm qualitatively the DFTB picture
(GPAW program, PBE functional, NVT, 1000 K, 2 fs time step)

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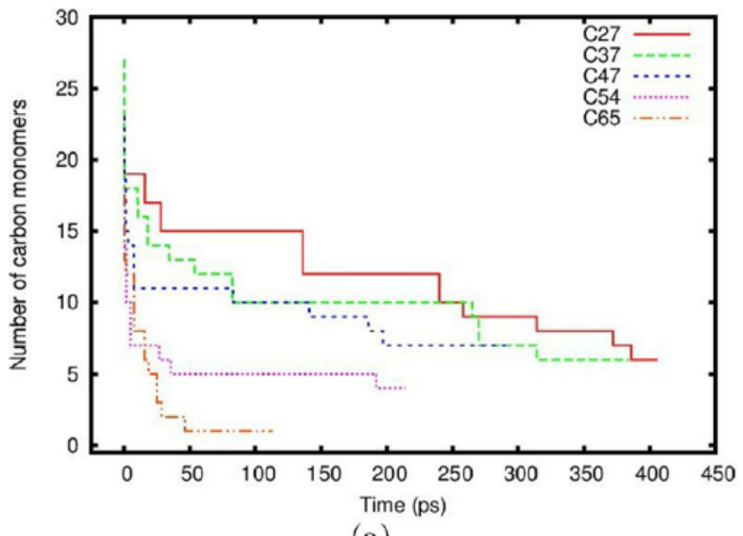
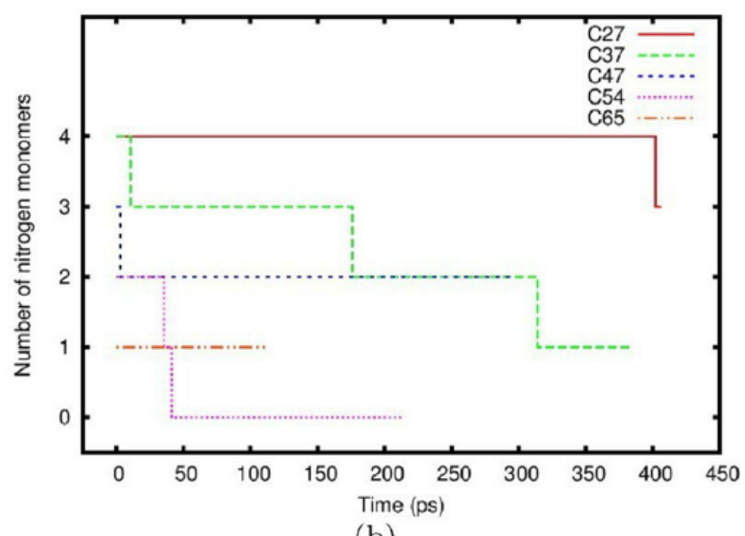
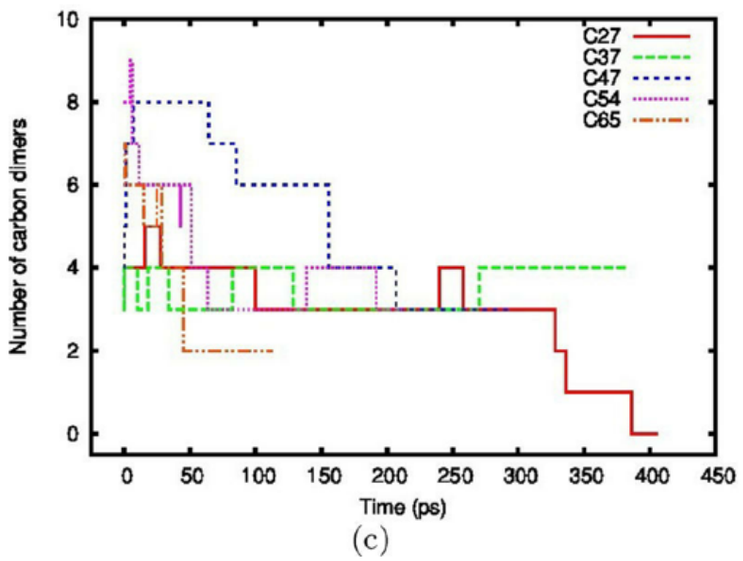
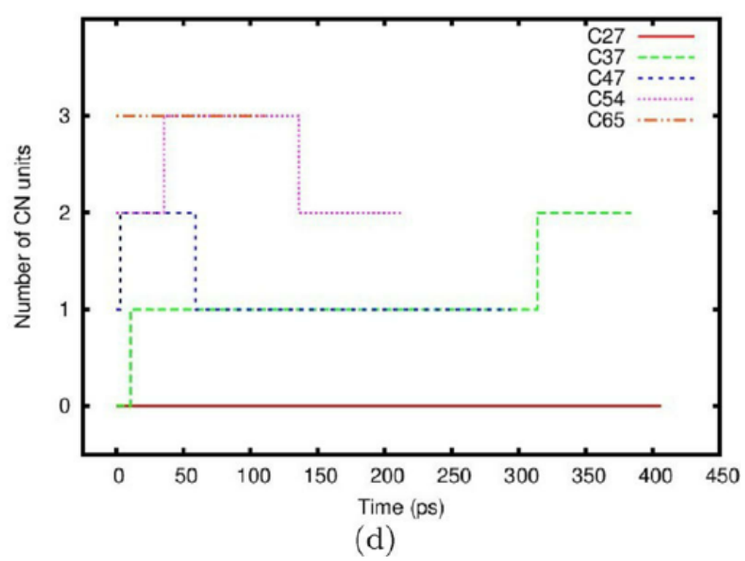
Monomers and small fragments

- Small fragments short-lived especially at high adatom coverage
- Site change freq:
  - C atom 35-70 ps
  - N atom 40-70 ps
  - C_2 dimer 10-22 ps
  - CN unit 6-14 ps









Time-evolution of the number of small fragments

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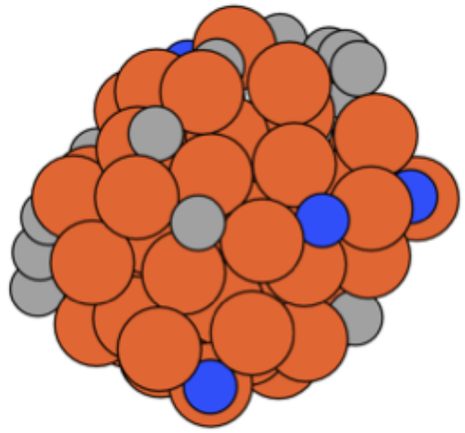
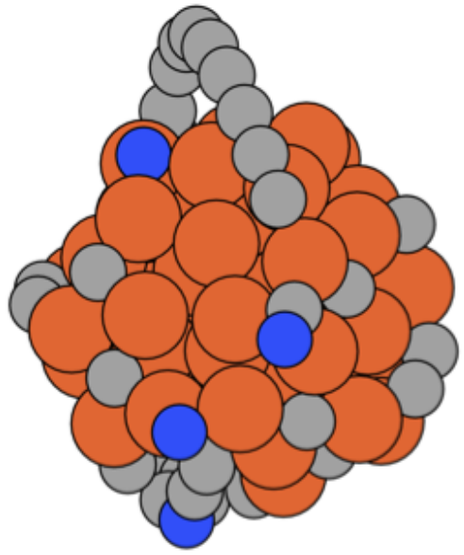
Monomers and small fragments

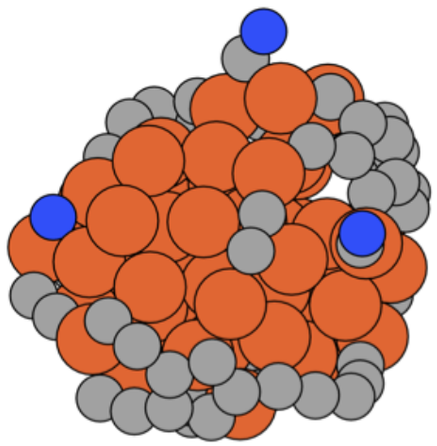
- Structures DFT-optimized
- N monomers reside at deep sites, 3- and 4-coordinated
- CN units point out of surface, C_2 align along it
- Longer chains attach to surface at terminal C, mid chain released from surface



$Fe_{55}N_4C_{27}$, t=412 ps



$Fe_{55}N_4C_{47}$, t=294 ps



$Fe_{55}N_4C_{65}$, t=98 ps

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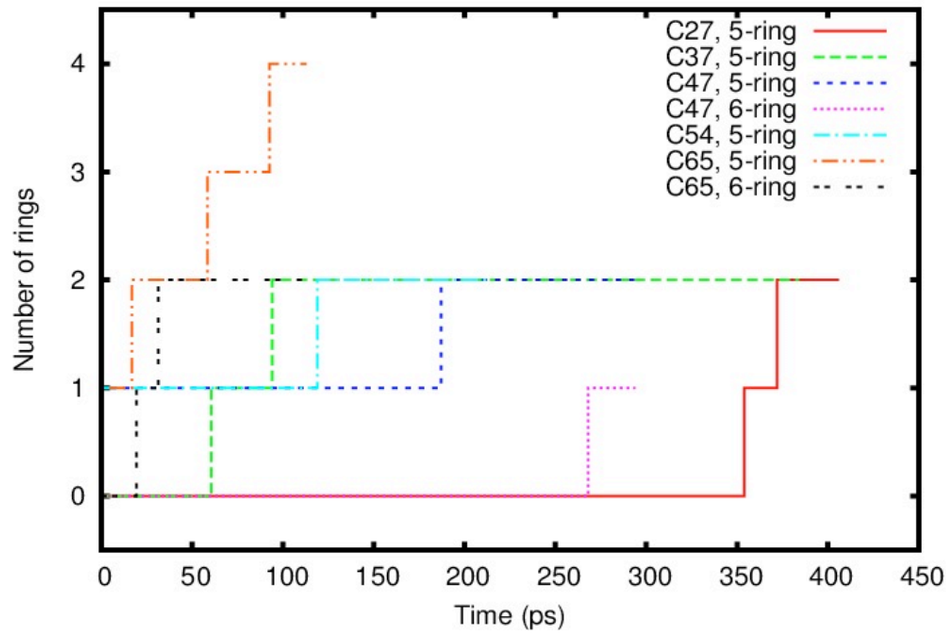
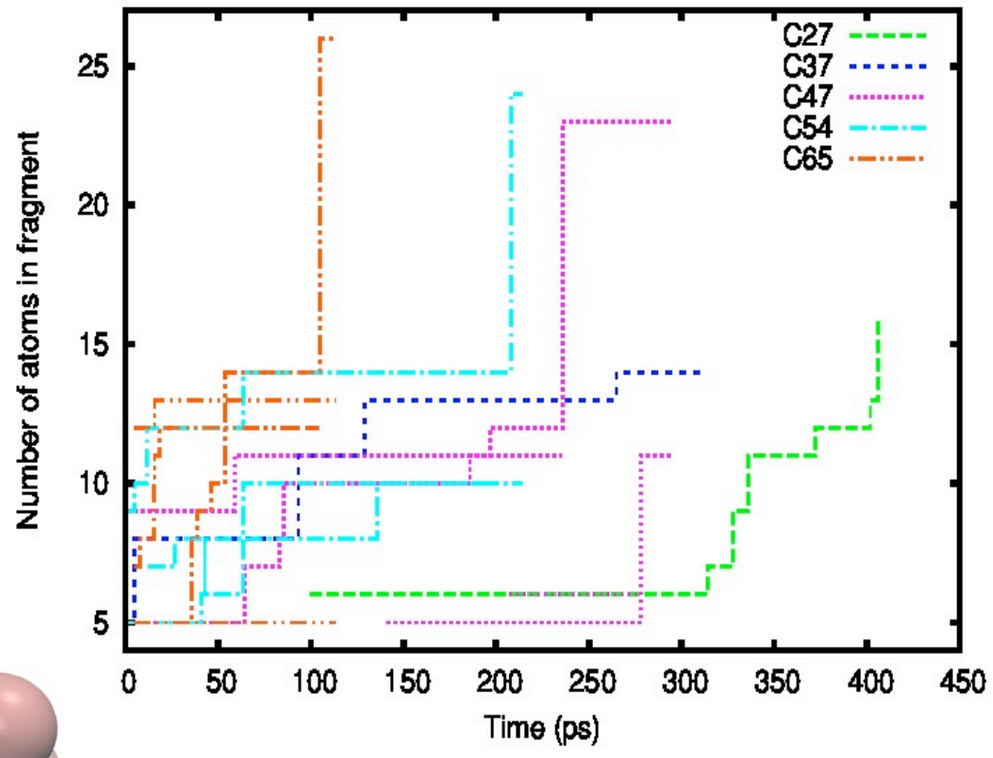
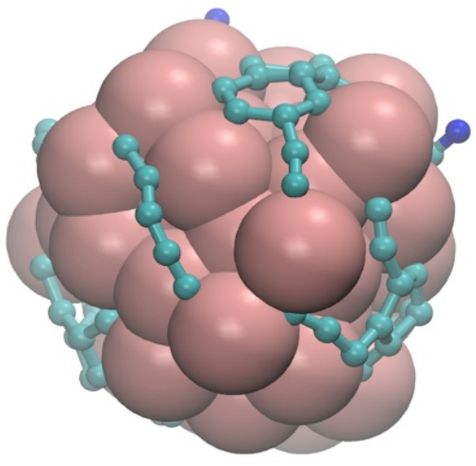
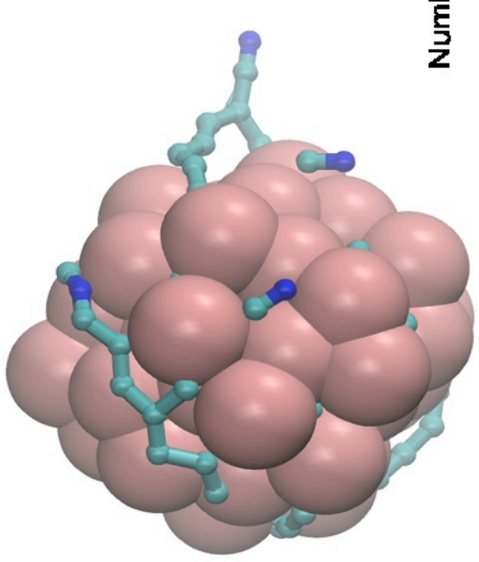
Large fragments

- Large fragments modify the particle surface strongly
- Fragment growth is fast when the adatom coverage is large
- 5-membered rings formed first
- N orient out of the surface when terminal atoms









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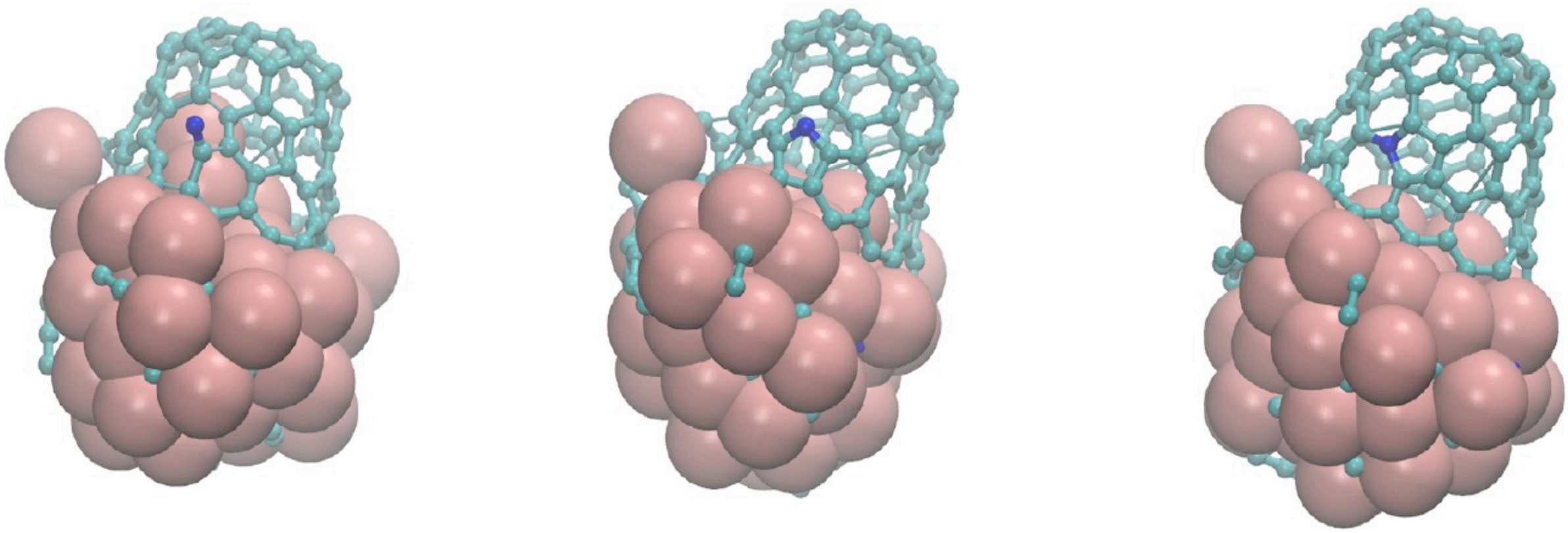
Role of nitrogen



(a) (b) (c)

N atom introduces a (7,7,5) defect

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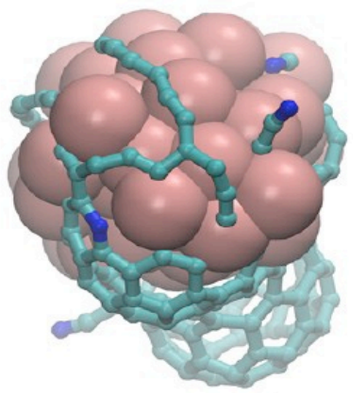
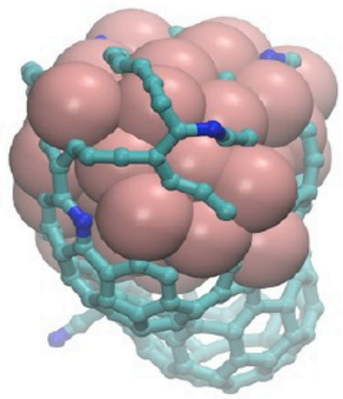
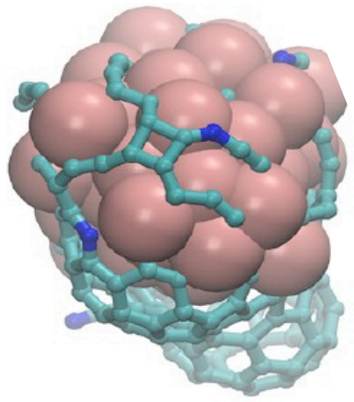
Role of N in ring formation



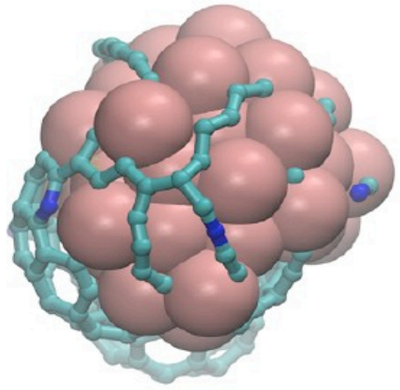
(a) 69.5ps



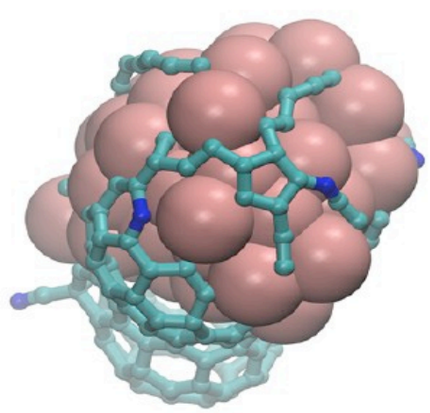
(b) 70.6ps



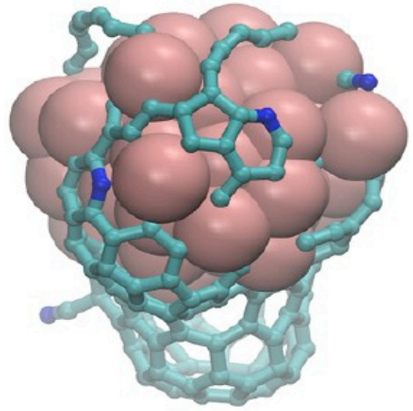
(c) 71.2ps



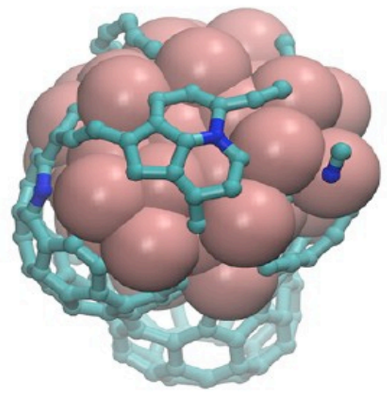
(d) 77.5ps



(e) 80.5ps



(f) 99.9ps



(g) 108.9ps

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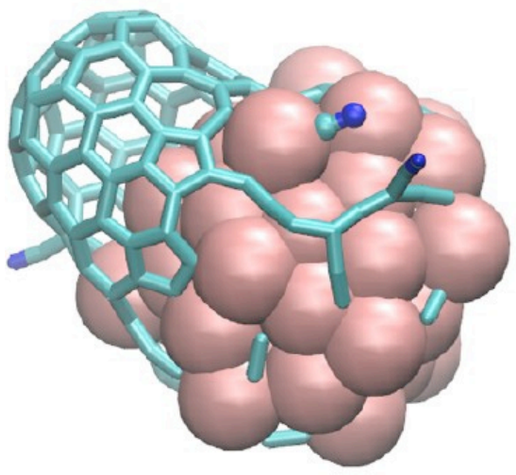
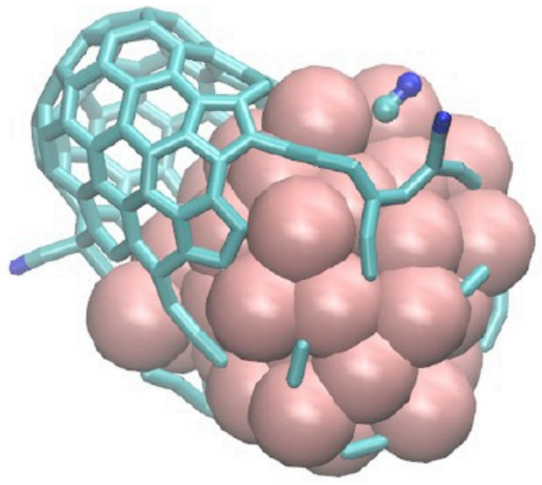
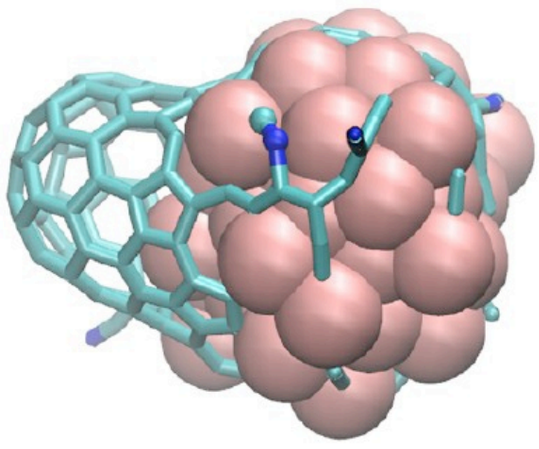
Role of nitrogen



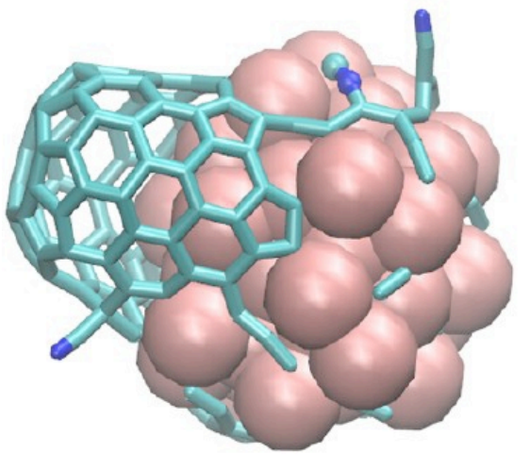
(a) 90.4ps



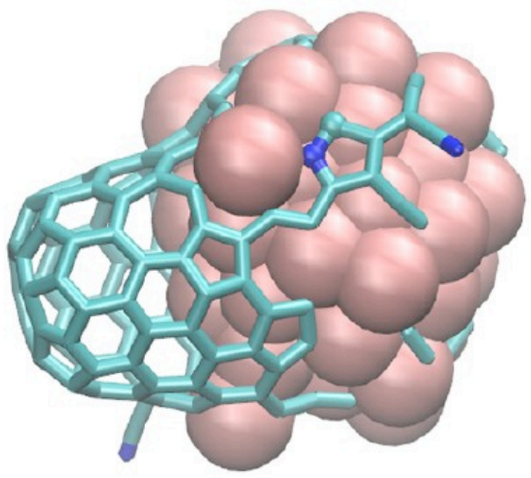
(b) 93.8ps



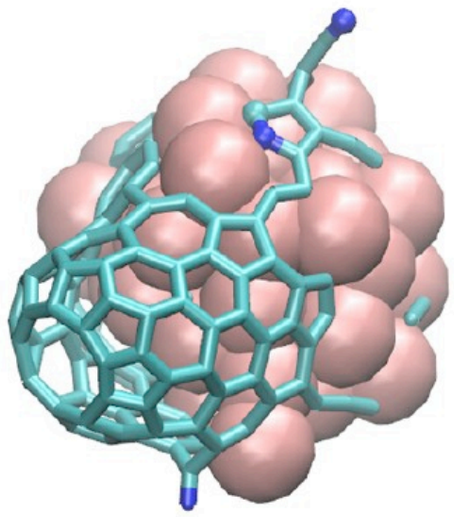
(c) 97.2ps



(d) 98.1ps



(e) 100.6ps



(f) 112.6ps

CN unit coupled via N (negative partial charge) to the carbon network

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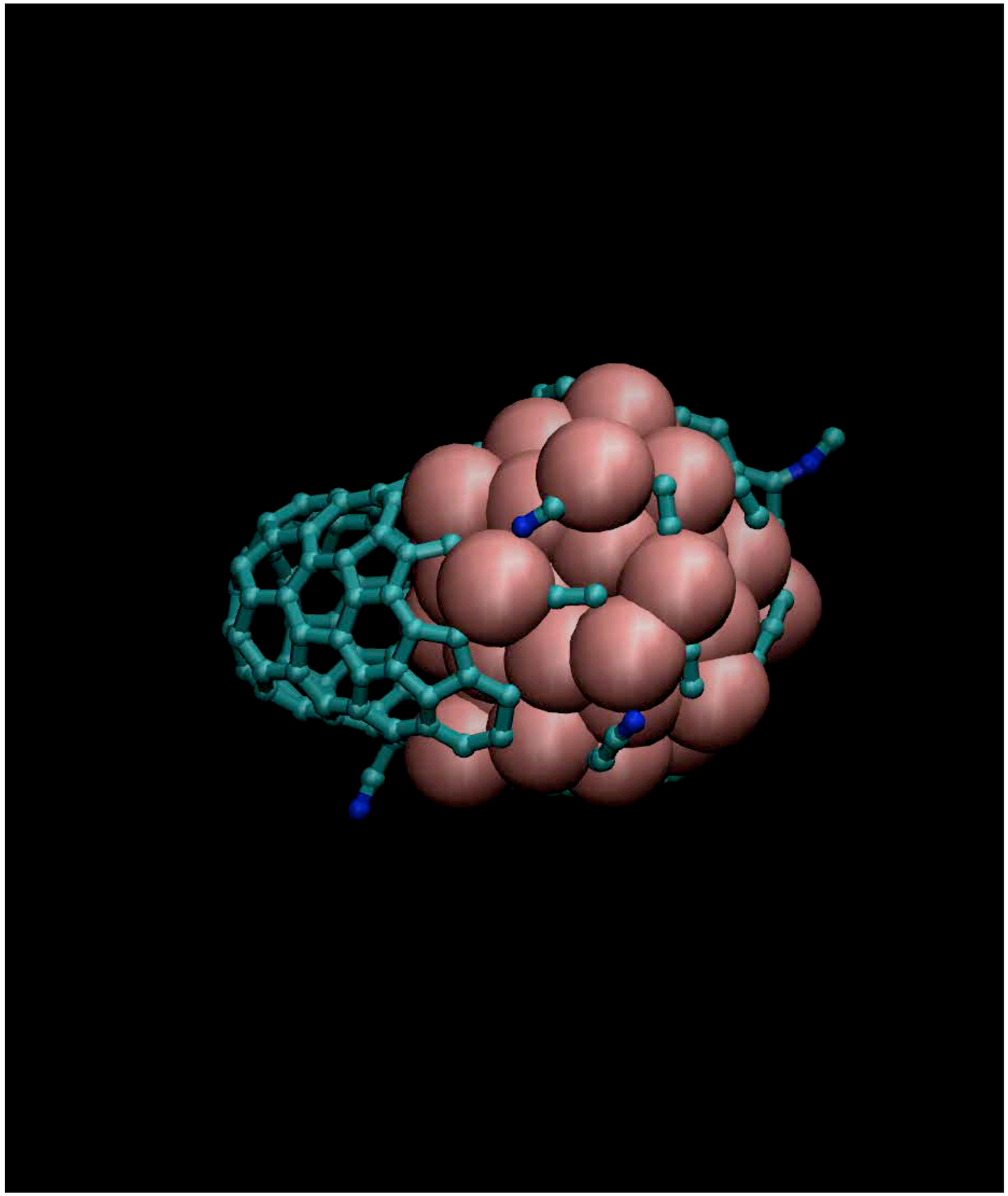
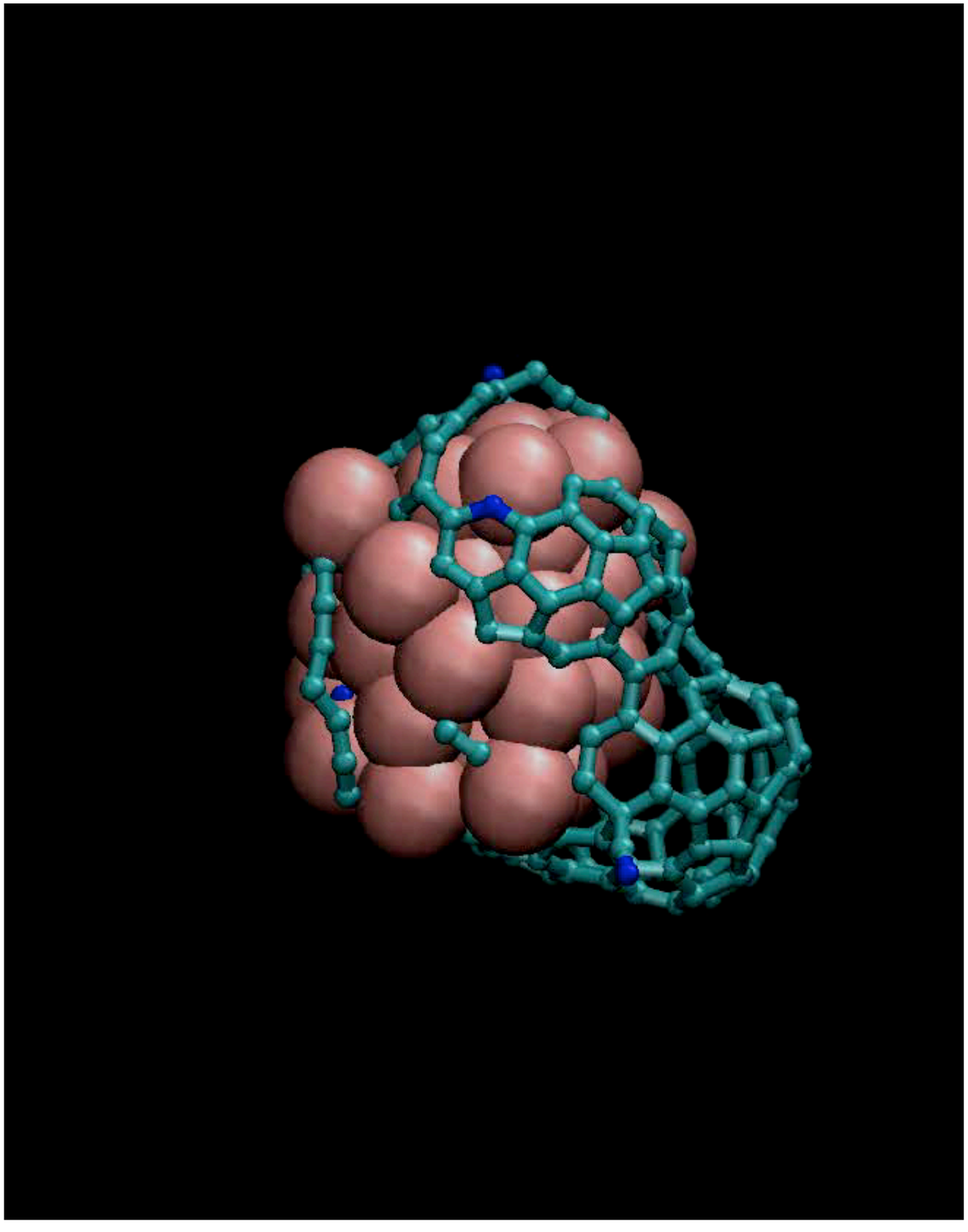
Mechanisms

- Behavior of N-containing fragment
  - N out of surface
  - Fragment added
  - 5-ring formed
  - sp^2 hybridization → planarity → N along surface

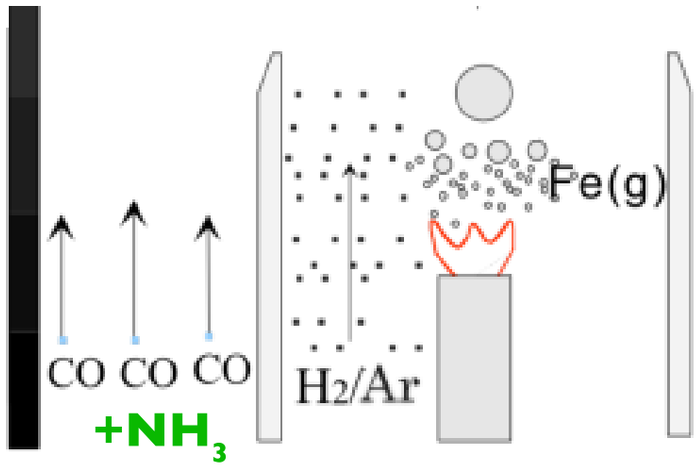


Mechanisms

- Ring formations
  - Unstable 4-ring → 5-ring; chain-to-chain condensation
  - N-containing 6-ring, end-to-chain condensation
  - Another 6-ring, end-to-chain cond.



Tentative growth model

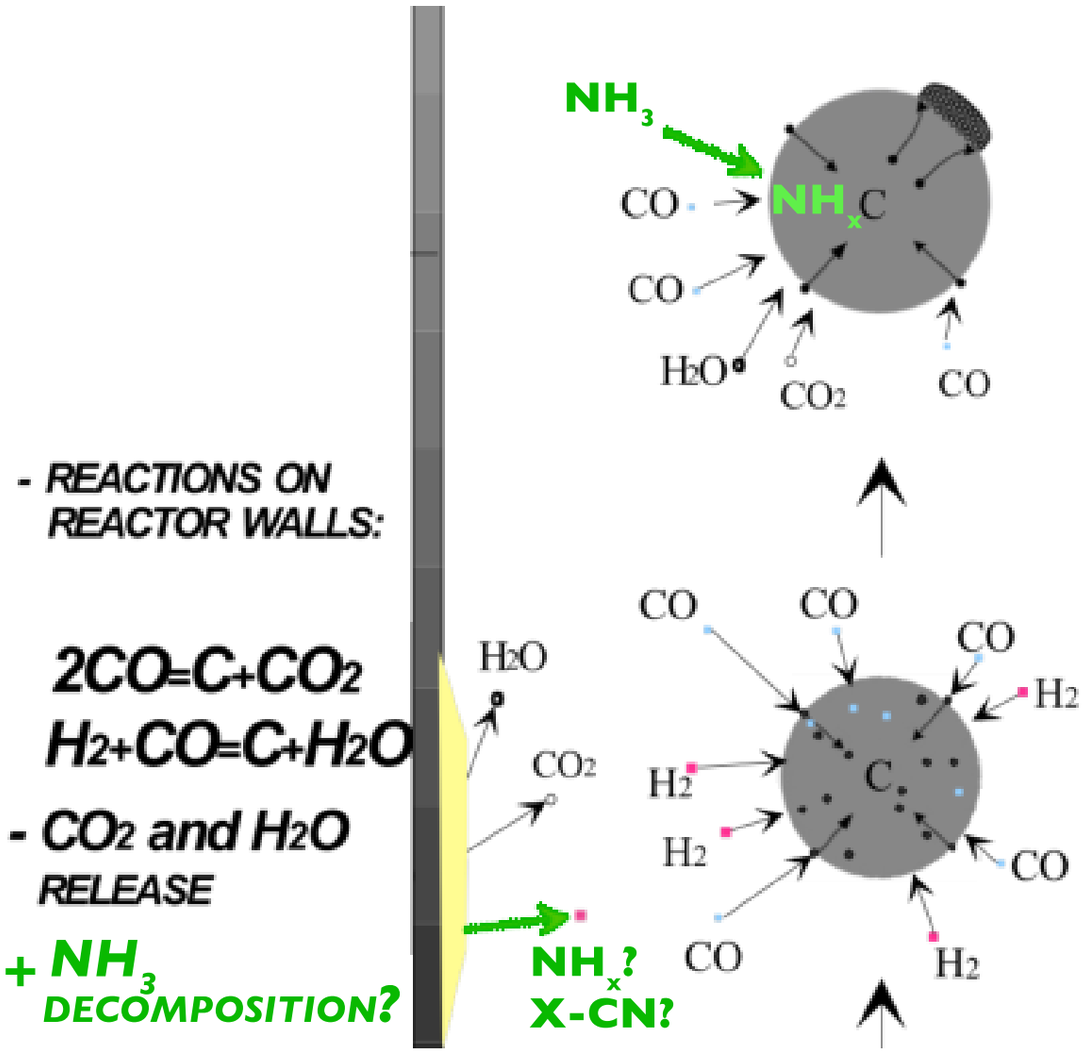


FE particle formation
- ***VAPOUR NUCLEATION***
- ***CONDENSATION***
- ***CLUSTER COAGULATION***

Adapted from Nasibulin et al, CPL 402 (2005)

Tentative growth model

Adapted from Nasibulin et al, CPL 402 (2005)



Formation of graphitic cap

- *HEXAGON AND PENTAGON FORMATION*
- *REACTIONS OF CARBON RELEASE AND ETCHING:*

$2CO \leftrightarrows C + CO_2$ AND $H_2 + CO \leftrightarrows C + H_2O$

+ NH_3 ADSORPTION
+ RELEASE OF ATOMIC N:

$NH_3 \rightarrow NH_2 + H \rightarrow$
$NH + 2H \rightarrow N + 3H$

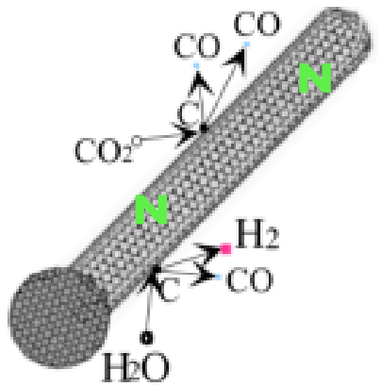
Particle saturation by C

- *REACTIONS:*
  $2CO = C + CO_2$ AND $H_2 + CO = C + H_2O$
- C RELEASE ON SURFACE
- C DISSOLUTION

Tentative growth model

Adapted from Nasibulin et al, CPL 402 (2005)

"growth window"



etching reactions:

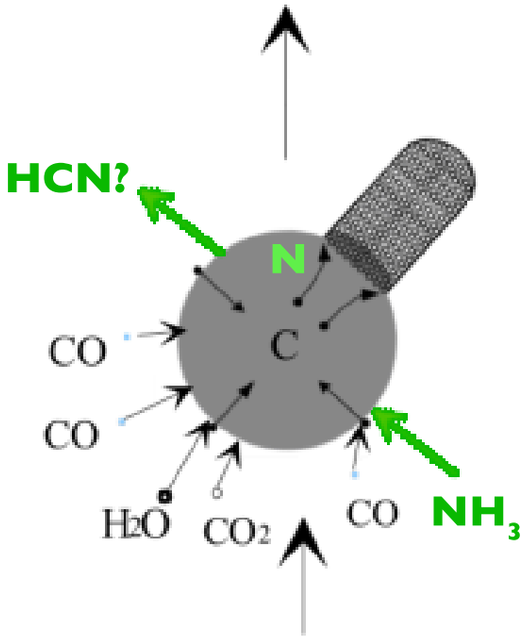
$C+CO_2 \Leftrightarrow 2CO$ *AND* $C+H_2O \Leftrightarrow CO+H_2$

- *CLEANING AMORPHOUS CARBON*
- *HEALING OF DEFECTS?*

+ *STABILITY OF DOPANTS?*

End of CNT growth

- *CO DISPROPORTIONATION AND HYDROGENATION ARE LIMITED*
- *CATALYST PARTICLE LEAVES ACTIVE ZONE OF REACTOR*



Steady-state growth of CNT

- *C DISSOLUTION AND SEGREGATOIN*
- *C INCORPORATION INTO GRAPHENE LAYER*
- *REACTIONS OF CARBON RELEASE AND ETCHING:*

$2CO \Leftrightarrow C+CO_2$ *AND* $H_2+CO \Leftrightarrow C+H_2O$

+ *INCORPORATION OF N AT ROOT*

+ *BONDING CONFIGURATION?*

+ *HCN FORMATION AS PARASITE REACTION (>1.5 eV BARRIER)*

+ *SLOWING OF GROWTH RATE DUE TO ETCHING/TERMINATION*

Acknowledgements

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Kari Laasonen (DFTB)

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Paola Ayala

Thank you.

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Center for Atomic-scale Materials Design

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Thomas Bligaard

Esko Kauppinen
Albert Nasibulin

Aalto University
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