

Multiscale Simulation of Carbon Nanotube Nucleation and Growth: Electronic Structure Calculations*#

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Abstract

To understand fundamental aspects of the nucleation and growth of carbon nanotubes, several different types of first principles surface and bulk electronic structure calculations have been carried out based on density-functional theory (DFT).

A 38-atom Ni cluster and several low-index Ni surfaces have been studied. The binding energies of a C atom on various Ni surfaces and the corresponding facets on the Ni cluster have been obtained. In spite of the apparently large differences of these two types of substrate, the energetic ordering of the sites for C atom adsorption is the same. The Ni(100) facet is favored for C adsorption over the Ni(110) and Ni(111) surfaces.

A C cluster in the form of a flake containing fourteen atoms with an armchair type termination is chosen. This represents a segment of an "unrolled" carbon nanotube. The binding energies of C, Ni, Co, Fe, Cu, and Au atoms to this flake were then calculated in an effort to gain insight into the mechanism for the high catalytic activity of Ni, Co, and Fe and the lack of it in Cu and Au. In a suggested nucleation scenario, the role of the transition metal ions is to complete the dangling bonds of the flake and so counteract the strain energy introduced by deforming the flake into the nanotube caps. The calculations indicate that the binding energies of Cu and Au to the C flake are about an eV less than those of the three catalytic elements, the unfilled d shells clearly playing a role in this regard.

Electronic Structure Calculations

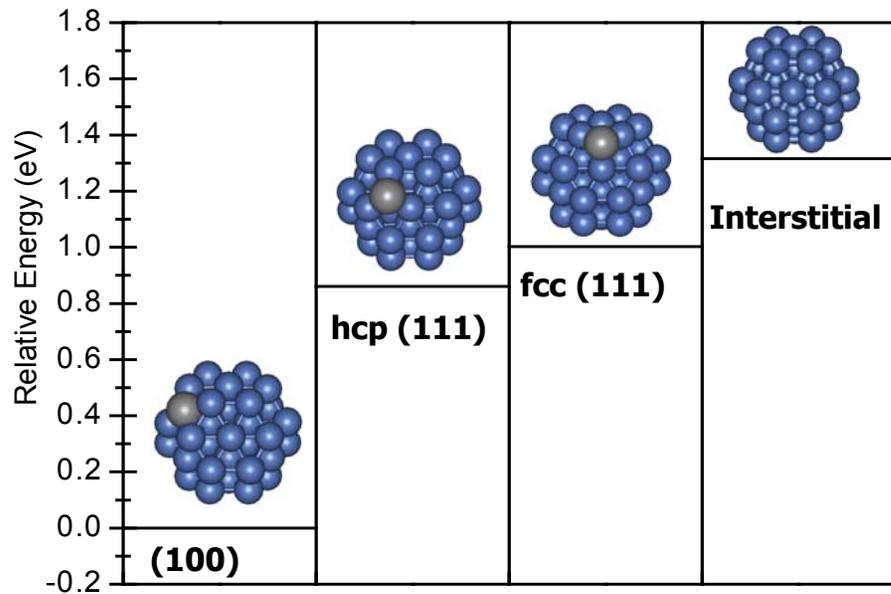
- Calculate diffusion coefficient of C in Ni as a function of T and C.
- Obtain insight into why Fe, Co, and Ni are good catalysts and Cu and Au are not.
- Calculate strain energy due to curvature and relate to pentagons.
- Determine energy of dangling bonds and relate to edge free energy.
- Use results from foregoing to calculate radius of critical nucleus via classical nucleation theory and compare to elasticity results.

Computational Approach: Plane-wave Basis

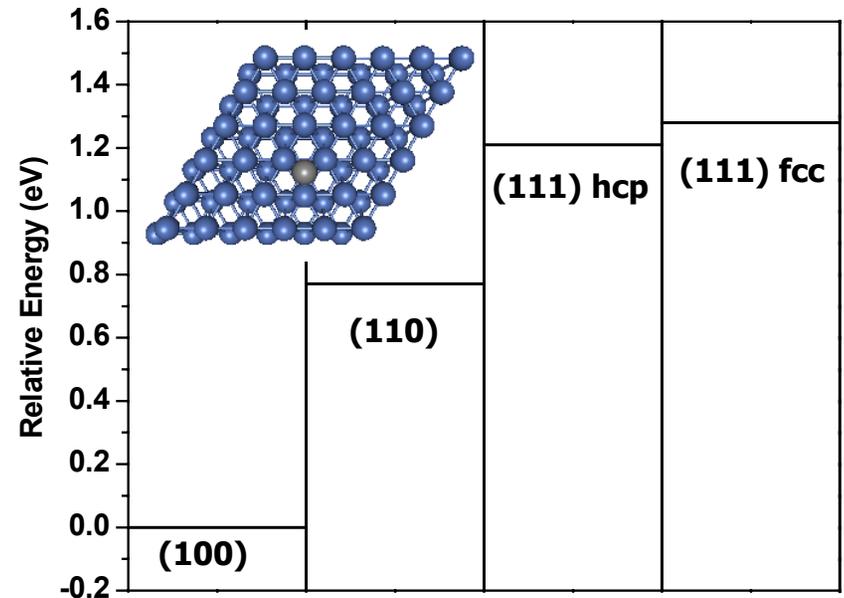
- Car-Parrinello method
- DFT + GGA(PW91)
- Plane wave (PW) basis
- Super cell geometry
- Vanderbilt ultra soft pseudopotentials
- Valence electrons: 2s2p for C, 3d4s for Ni
- Ni as a paradigm
- PW Cut-off:
 - 20 Ry for wave functions.
 - 150 Ry for augmented electronic charge density.

Carbon Adsorption on Clusters and Surfaces

- Fundamental, new predictions on small Ni_xC_y clusters and Ni surfaces.
- Insight into adsorption, nucleation for large clusters in CVD growth.



- 3 sites for adsorption on Ni_{38} .
–(100), (111) hcp, and (111) fcc.
- Localized relaxation of Ni_{38} at site.
- C will remain on cluster surface.

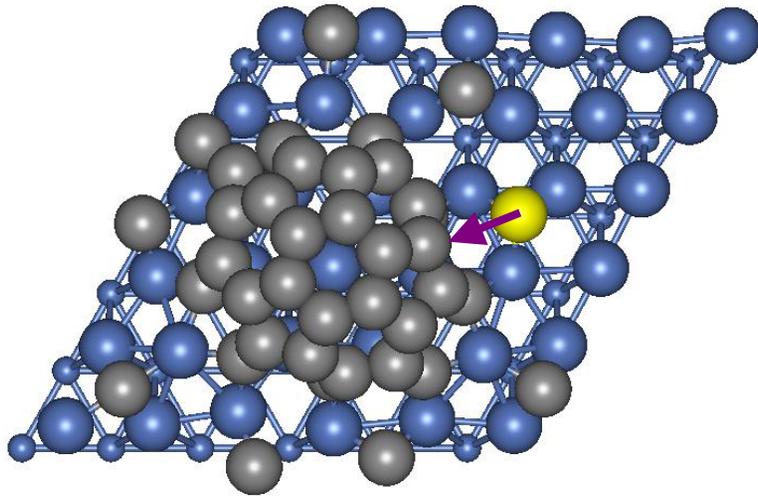


- Stable sites:
–(100), (110), (111) hcp and fcc.
- Adsorption Energetics order in same sequence on surface and Ni_{38} .

Growth of Baby Tubes on Ni(111) Surface

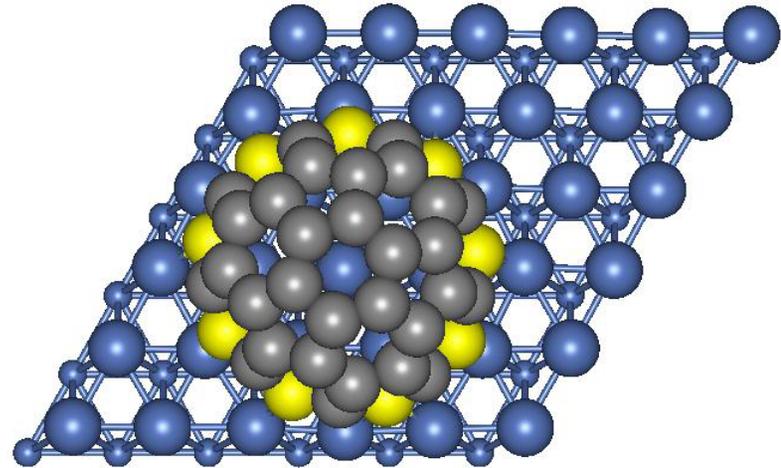
Questions: How are C-atoms incorporated into the tube?

Single Atom Addition



- Surface diffusion barrier (bridge site) between hcp-fcc hollow:
– $\Delta E = 0.26$ eV.
- 3 different entries for single C:
–2 hexagon, $\Delta E = -1.26$ eV
–1 pentagon, $\Delta E = +0.63$ eV
- Diffusion barriers under investigation.

Concerted motion, ring-by-ring growth



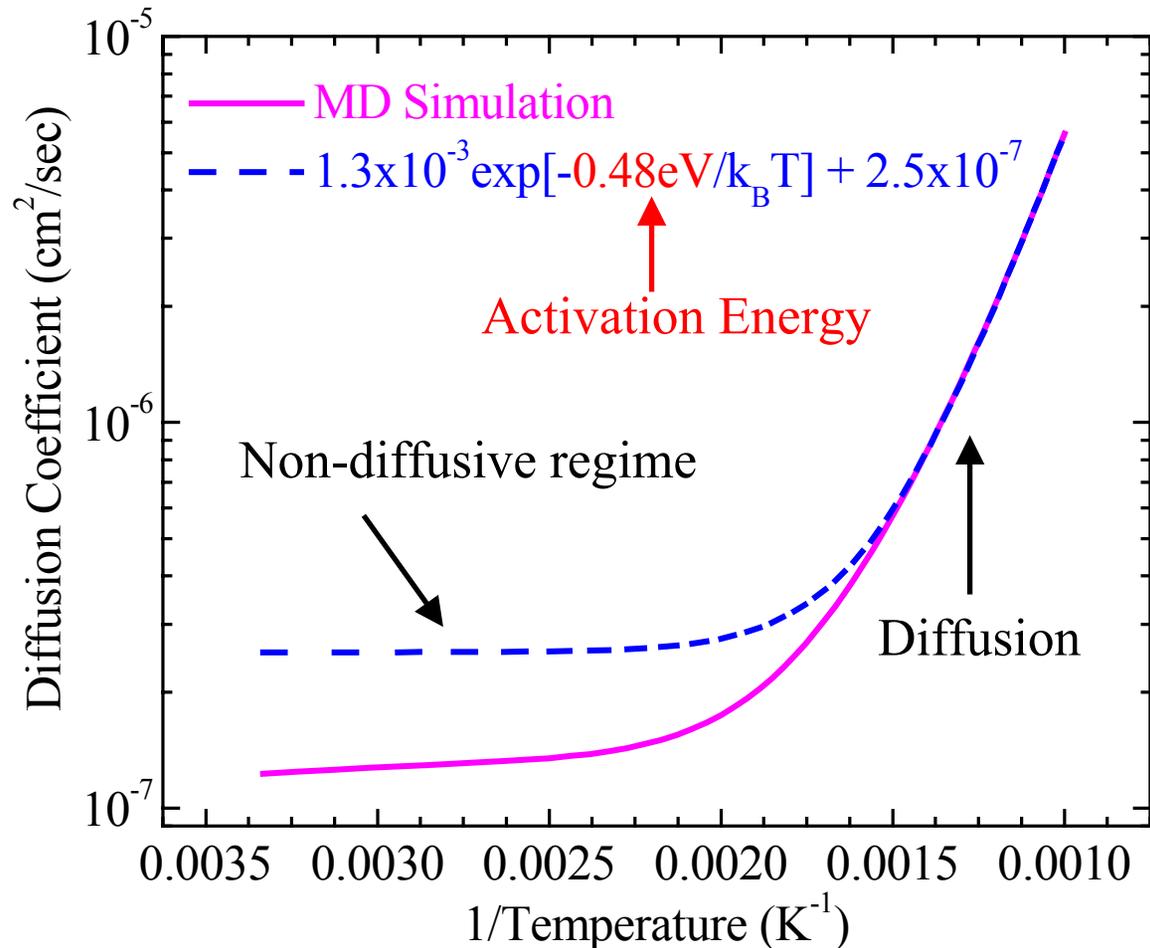
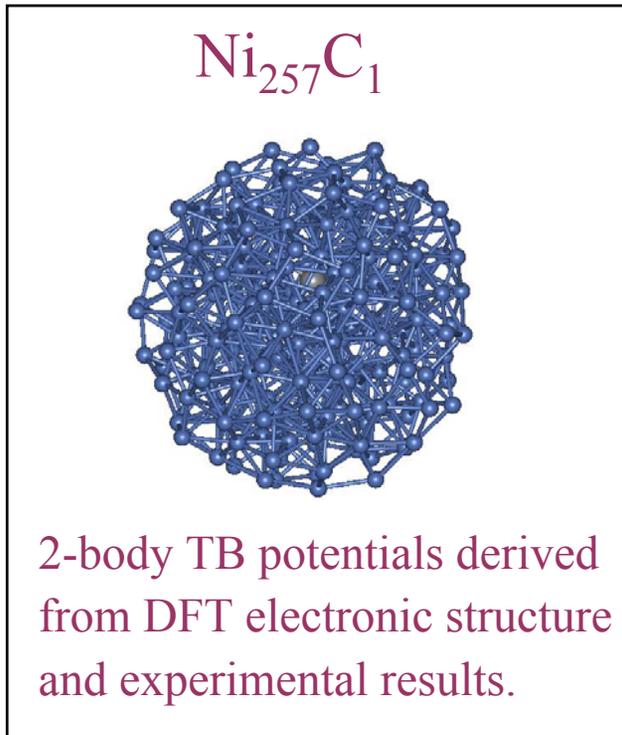
- “Ring”(9 C’s) grows into the tube.
- Energy:
–Against 9 remote/ separate C’s: -12.69 eV
–Against 9 adjacent C’s: ~ -9 eV

Reaction-limited growth.

Need to compute Barriers, Dynamics.

Bulk Diffusion: MD Calculations

- Diffusion coefficient for C in Ni_xC_y clusters vs. Temperature
 - Diffusion is function of C fraction: Decreases with larger C fraction.
 - Non-exponential function of cluster size. Approaching bulk for large clusters.
 - Input into continuum calculations.



Computational Approach: Gaussian Orbitals

- NWChem*

- www.emsl.pnl.gov:2080/docs/nwchem/

- Local Spin-Density (LSD) Approximation

- Slater Exchange Functional

- VWN-V Correlation Functional

- Gaussian-type orbitals

- 6-311G for C

- Effective-Core Potentials (CRENBL)

- Core Electrons Cu(10), Au(60), Ni(10), Co(10), Fe(10)

- Isolated system

*R. J. Harrison, J. A. Nichols, T. P. Straatsma, M. Dupuis, E. J. Bylaska, G. I. Fann, T. L. Windus, E. Apra, W. de Jong, S. Hirata, M. T. Hackler, J. Anchell, D. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsel, M. Deegan, K. Dyall, D. Elwood, H. Fruchtl, E. Glendening, M. Gutowski, K. Hirao, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kendall, R. Kobayashi, R. Kutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, T. Nakajima, J. Nieplocha, S. Niu, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G. Thomas, J. van Lenthe, K. Wolinski, A. Wong, and Z. Zhang, "NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.1" (2002), Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA.

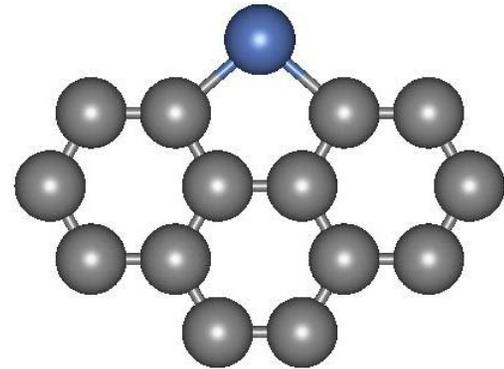
Pentagon Binding Energies

Definitions: $E(A)$ - energy of isolated A atom
 $E(C_N)$ - energy a “flake” with N carbon atoms
 $E(C_N + A)$ - energy of C_N flake plus 1 A atom

Binding energy of A atom (s) to carbon flake;

$$E_b(A, N) = E(C_N + A) - \{E(C_N) + E(A)\}$$

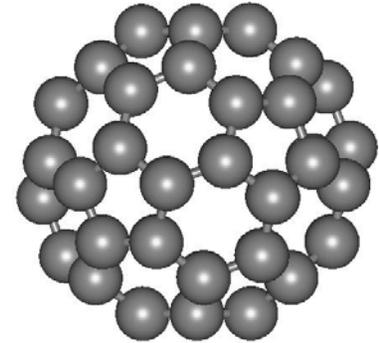
Atom A	$E_b(A, 14)$ (eV)
C	6.33
Fe	5.86
Co	5.94
Ni	5.87
Cu	5.05
Au	4.84



14 C atoms + 1 atom (A)

Energy of a Dangling Bond

- Binding energy of 60 atoms in C_{60} buckyball (bb).
 - $E_b(\text{bb}) = E_{\text{tot}}(\text{bb}) - 60 * E(\text{C}) = \underline{8.26 \text{ eV/atom.}}$
 - N. B., no dangling bonds.
- $E_b(1/2 \text{ bb}) = 7.16 \text{ eV/atom}$, 10 dangling bonds (DB).



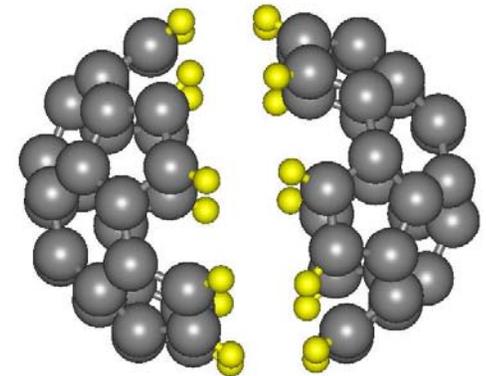
- Two halves of a C_{60} molecule are bound together by $\Delta E = E_b(\text{bb}) - 2E_b(1/2 \text{ bb})$.
 $= 65.9 \text{ eV}$ or 6.59 eV/bond .

Therefore, $E_{\text{DB}} = 3.30 \text{ eV/electron}$.

- For CNT with diameter ($d \sim 1.3 \text{ nm}$), edge energies.

$E_{\text{edge}} = (10 E_{\text{DB}} / \pi d)$ are for C-C bonding = 0.81 eV/\AA ;

C-Ni, C-Fe, C-Co = 0.72 eV/\AA ; C-Cu and C-Au = 0.60 eV/\AA .



Strain Energy Due To Pentagon Formation

- Calculate binding energy of 30 atom flat flake and compare with energy of 1/2 bb (also 30 atoms!). We find

$$E_b(30 \text{ flat}) = 216.02 \text{ eV}, \text{ or } 7.20 \text{ eV/atom}$$

- There are 14 DBs in this structure and 10 in a 1/2 bb. To calculate strain energy E_S , the energies of these DBs must be added in and the resulting energies compared. We find

$$E_S = 14.31 \text{ eV}, \text{ or an average of } 0.48 \text{ eV/atom}$$

- To estimate if the CNT will nucleate, calculate minimum radius of a stable nucleus from classical, continuum, nucleation theory (see V. L. Kuznetsov et al, PRB 64, 235401 (2001)). It is given by $R_{\min} \sim E_{\text{edge}} - E_S$

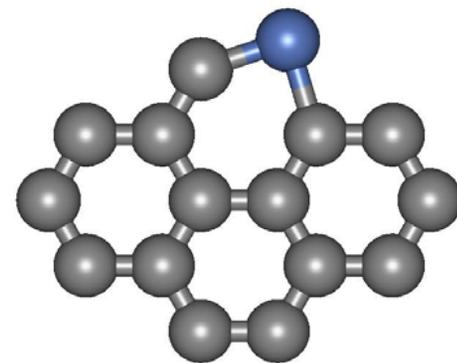
$$\begin{aligned} E_{\text{edge}} - E_S &= 0.33 \text{ eV for C-C,} \\ &= 0.24 \text{ eV for M-C with M= Ni, Fe, and Co} \\ &= 0.12 \text{ eV with M= Cu, Au} \end{aligned}$$

Therefore, this simple calculation suggests nucleation for all metals, but Cu and Au are borderline. Connects continuum and ab initio calculations.

Carbon +Metal Hexagon Binding

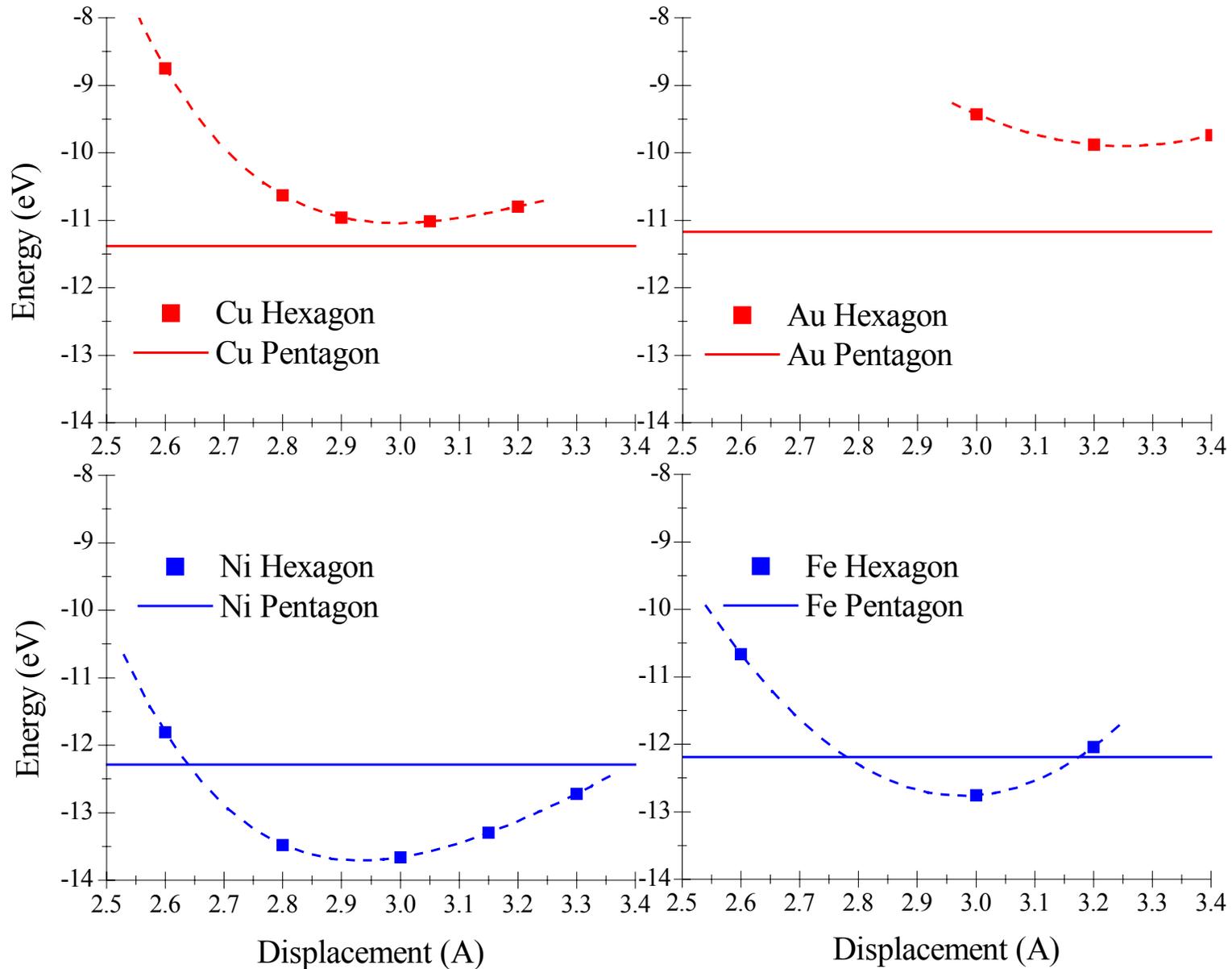
Compare binding energies of a carbon and a metal atom in a hexagon to the binding energies in separated pentagons. $\Delta E > 0$ means C-M hexagon is stable against break-up into two pentagons.

	<u>C+M hexagon (eV)</u>	<u>C+M pentagons</u>	<u>ΔE</u>
C	-15.75	-12.66	+3.09
Cu	-10.96	-11.38	- 0.42
Au	-9.88	-11.17	-1.29
Ni	-13.66	-12.29	+1.37
Co		-12.27	
Fe	-12.76	-12.19	+ 0.57



14 C atoms
+ 1 C atom
+ 1 metal atom (M)

Comparison of Hexagons and Pentagons



Summary & Conclusions

- Binding C adatom on various Ni surfaces and Ni Cluster facets.
 - Small clusters yield the same results as larger clusters and extended surfaces.
 - Ni(100) facet is favored over the Ni(110) and Ni(111) surfaces.
- Growth of Baby Tubes on Ni(111) Surface:
 - Energetics indicate that growth is reaction limited.
 - Concerted motion may be important for incorporation of C into nanotubes.
- Calculation of input parameters for continuum calculations.
 - Calculate strain energy due to curvature and relate to pentagons.
 - Determine energy of dangling bonds and relate to edge free energy.
- Why are Fe, Co, and Ni are good catalysts and Cu and Au are not?
 - BE of Cu and Au to Fullerene flake are ~ 1 eV less than Ni, Co, and Fe.
 - Comparison of BE of a carbon and a metal atom in a hexagon to the BE in separated pentagons indicates that, for the catalytic metals, the hexagon is stable against break-up into two pentagons.