ENERGETICS OF CARBON DEPOSITION ON METALLIC SURFACES

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Abstract: Density functional theory (DFT) calculations are carried out to investigate the energetics of carbon adsorption on conventional Cu and Ni metal surfaces. The source of carbon for adsorption is based on the dissociation of hydrocarbon fuels (methane) and CO (Bouduard reaction) similar to the processes representative of anode surface in solid oxide fuel cells (SOFCs). The most stable adsorption sites on (111) surface of Cu and Ni are identified and a comparative adsorption behavior of carbon clusters on two surfaces is studied. The DFT results predict a higher stability of carbon clusters on a Ni surface as compared to on a Cu surface. The current efforts to investigate the role of temperature and partial pressures on the stability of these structures using first principles thermodynamics are presented.
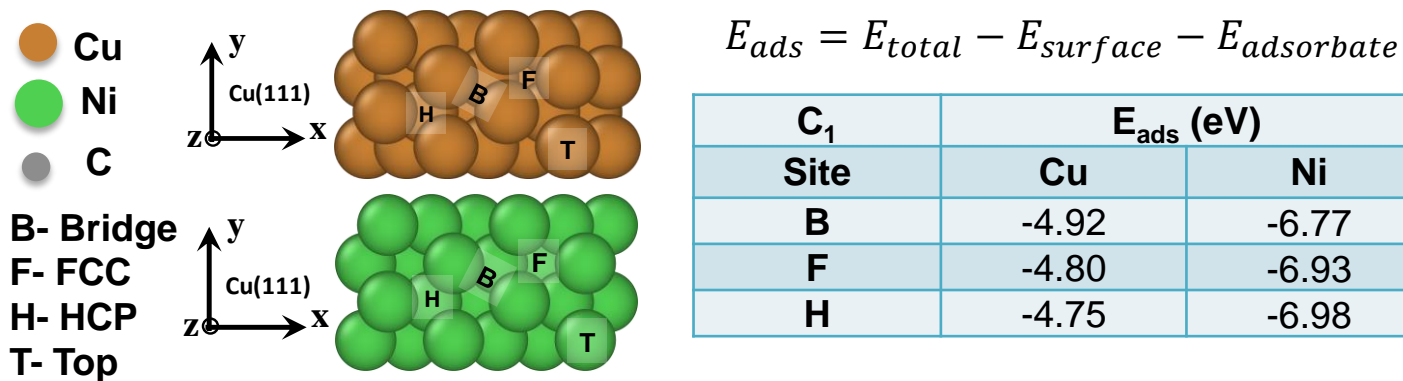
Background: Carbon deposition over anode (Ni catalyst) has been a challenging problem in hydrocarbon fueled SOFCs. Use of less reactive metals such as Cu can avoid carbon deposition [1], however their catalytic performance is not enough for efficient operation of SOFCs. The current understanding of the comparative behavior of carbon adsorption on Cu and Ni surfaces that results in or avoids carbon deposition is still in an infancy. Such kind of study is very essential for the efficient and optimum design of anode chemistry.

Objective:
- Calculate the adsorption energy of various carbon structures on Cu and Ni (111) surfaces.
- Predict the relative stability of carbon over Cu and Ni (111) surfaces based on carbon adsorption energetics.
- Extend the stability regime of adsorption structures for experimental temperatures and pressure conditions.

Energetics of Carbon Adsorption on Cu and Ni (111) Surface

- DFT calculations are carried out using VASP [2] using GGA by Perdew-Burke-Ernzerhof (PBE),
- Adsorption energetics is considered for carbon clusters with size ranging from 1 to 10 carbon atoms (C_1, C_2, C_6, C_{10}) on (111) surfaces of Cu and Ni

Cu
Ni
C

B- Bridge
F- FCC
H- HCP
T- Top

$$E_{ads} = E_{total} - E_{surface} - E_{adsorbate}$$

C_1	E_{ads} (eV)	
Site	Cu	Ni
B	-4.92	-6.77
F	-4.80	-6.93
H	-4.75	-6.98

- Single carbon (C_1) has the lowest energy of adsorption at bridge and HCP sites for Cu and Ni (111) surfaces, respectively.

$C2$	E_{ads} (eV)	
Site	Cu	Ni
FCC + HCP	-12.94	-14.28
E_{ads}/atom	-6.47	-7.14

Cu
Ni
C
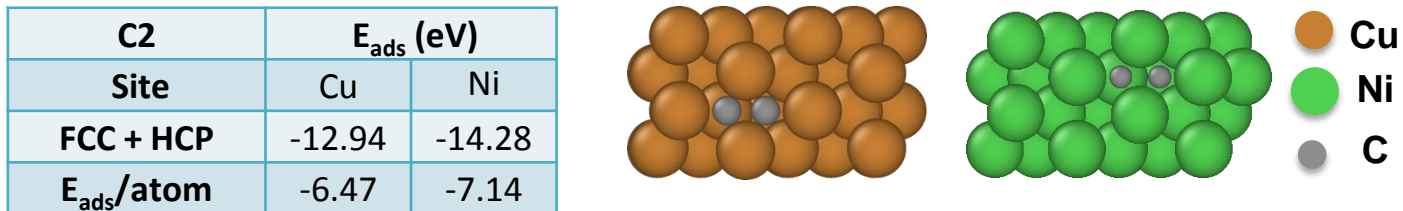
- A combination of H+F site is found more stable than others like F+F or H+H on Ni and Cu (111) surfaces.
- Comparatively, H+F is also more energetically stable in Ni than Cu.

	Cu				Ni			
(eV)	C_1	C_2	C_6	C_{10}	C_1	C_2	C_6	C_{10}
E_{ads}	-4.92	-12.94	-39.07	-67.20	-6.98	-14.76	-41.83	-70.65
E_{ads}/atom	-4.92	-6.47	-6.51	-6.72	-6.98	-7.14	-6.97	-7.07

Cu
Ni
C

C_6, Ni C_6, Cu C_{10}, Ni C_{10}, Cu
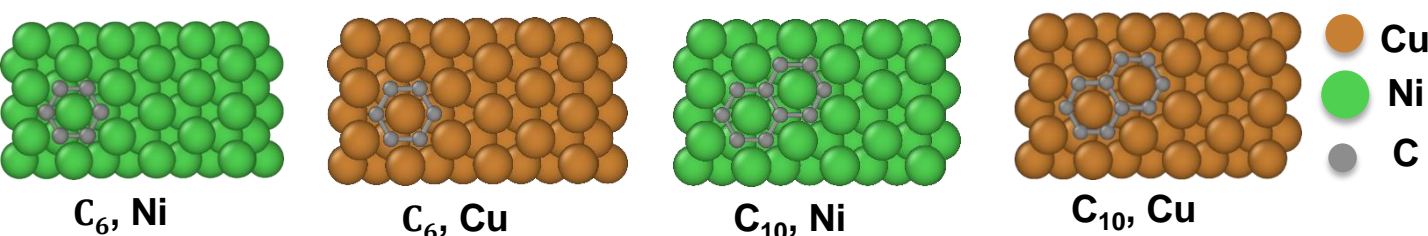
- Larger carbon clusters have lower adsorption energy on Cu surface; This trend is not observed for Ni.

Ab Initio Thermodynamics, Effects of Pressure/Temperature

$$\Delta G^{ads} = \frac{1}{A}\left(G(T,p,N_C,N_M) - G(T,p,0,N_M) - N_C\mu_C(T,p)\right) \quad [3]$$

ΔG^{ads} = Surface free energy, N_C/N_M = No. of carbon/metal atoms, T, p = Temperature, pressure, μ_C = Carbon chemical potential

For bulk solid/surface
$$G = E_{DFT} + E_{vib} + E_{conf} + pV$$

Based on Boudouard reaction $2CO \leftrightarrow CO_2 + C$ and CH_4 cracking reactions, the chemical potential of carbon is calculated via equations below:
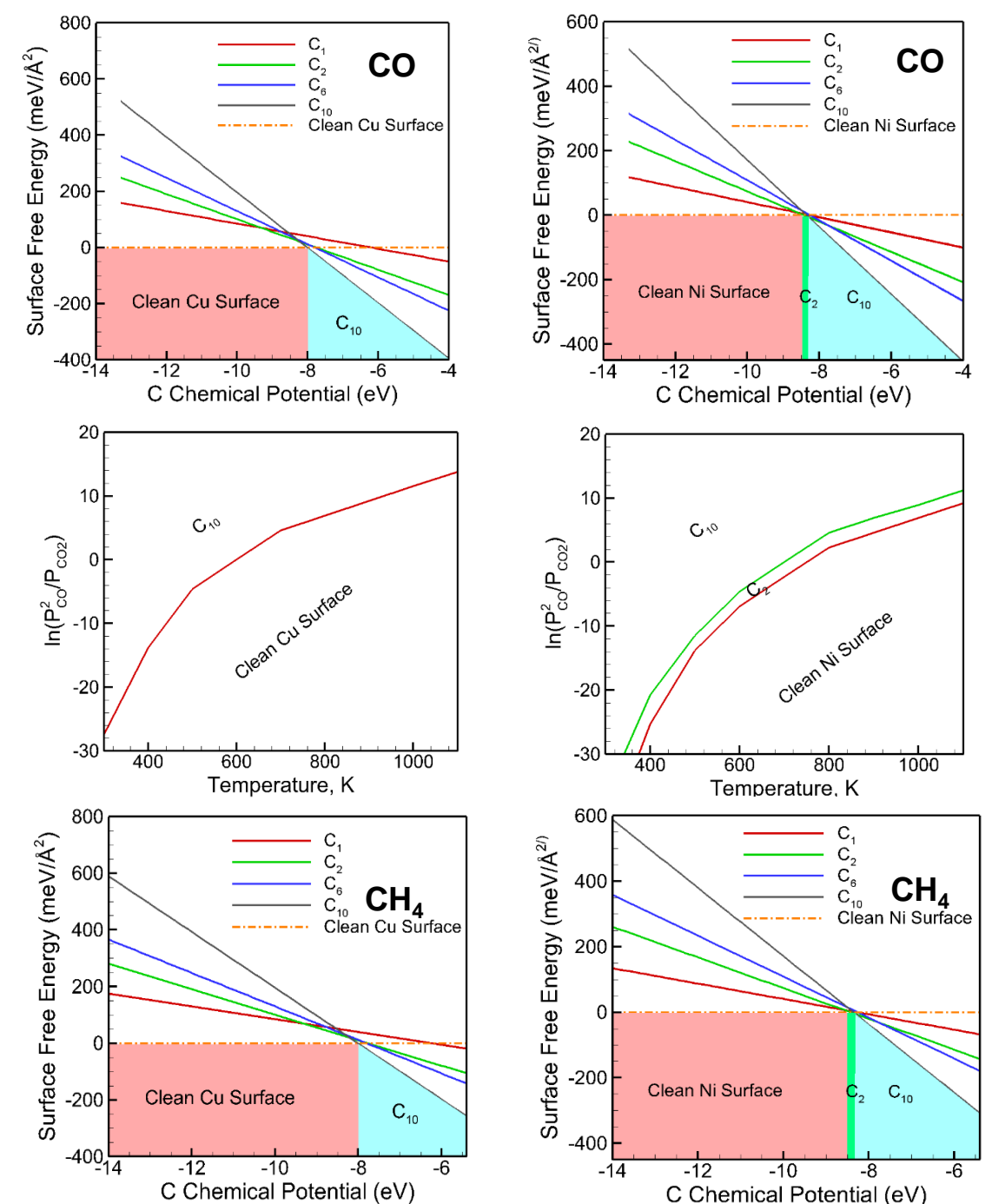
$$\mu_C = \boxed{2E_{DFT}^{CO} - E_{DFT}^{CO_2} + 2E_{ZPE}^{CO} - E_{ZPE}^{CO_2}} + \boxed{2\mu^{CO} - \mu^{CO_2}} + \boxed{k_BTln\left(\frac{p^2_{CO}}{p_{CO_2}}\right)}$$

$$\mu_C = \boxed{E_{DFT}^{CH_4} - 2E_{DFT}^{H_2} + E_{ZPE}^{CH_4} - 2E_{ZPE}^{H_2}} + \boxed{\mu^{CH_4} - 2\mu^{H_2}} + \boxed{k_BTln\left(\frac{p_{CH_4}}{p^2_{H_2}}\right)}$$

DFT Energy   Temperature Dependent   Pressure Dependent

Ab Initio Thermodynamics, Effects of Pressure/Temperature

- The data for chemical potential calculations is taken from JANAF tables [4]

$P^2_{CO_2}/P_{CO}=1$	Cu				Ni			
Surface Free Energy (meV/Å^2)	C_1	C_2	C_6	C_{10}	C_1	C_2	C_6	C_{10}
300 K	25.30	-18.98	-27.32	-66.09	-21.81	-51.13	-57.80	-105.89
600 K	41.87	14.14	16.26	6.55	-4.51	-16.53	-11.66	-28.99
900 K	57.21	44.83	56.64	73.85	11.52	15.53	31.08	42.25

- At three representative temperatures of 300 K, 600 K and 900 K, $P_{CO_2}/P_{CO}=1$, Ni surface is more stable. At 600 K, Cu surface is unstable while Ni is stable.
- Similar thermodynamic stability trends are observed for if C source is CH_4

Future Directions
- The stability of C1, C2, C6 and C10 carbon clusters will also be compared for (110), (100) and (112) Cu and Ni surfaces.

References
[1] Wei An, X. C. Zeng and C. Heath Turner J. Chem. Phys. **131**, 174702 (2009).
[2] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
[3] Rogal J and Reuter K. Ab Initio Atomistic Thermodynamics for Surfaces: A Primer.
[4] D.R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd edn., U.S. NBS, Washington, D.C. (1971).

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