Carbon Cluster on Ni (111) Surface: A Density Functional Theory Study

Jingde Li, Eric Croiset, Luis Ricardez-Sandoval*

Department of Chemical Engineering, University of Waterloo, Waterloo, ON, Canada N2L 3G1

Supplementary Information

Procedures for searching the transition states

i) A geometry for the transition state is proposed based on the geometries of the reactant and the product in a particular elementary step.

ii) Frequency calculations are conducted at the proposed geometric point. The lowest vibrational mode in the direction of the transition state (TS) is sought from the frequency calculations. The search for the TS is performed starting from this point (lowest vibrational mode) using the hessian of this frequency run.

iii) Frequency calculations are performed on the transition state obtained from the previous step. The TS is confirmed if there is only one imaginary frequency corresponding to a single negative vibrational mode. The TS can be further verified by slightly perturbating the TS along the reaction coordinate, corresponding to the normal mode with imaginary frequency, in the direction of the product or reactant. The optimization of this perturbed transition state geometry will end up with the geometry of the product or the reactant in a particular elementary step. Otherwise, a new geometry for the TS needs to be proposed for the current system, i.e., go back to step i). This procedure continues up until the TS with only one negative vibrational mode is identified.

Adsorption of Carbon Atom and Clusters (C₂~C₆) on Ni (111)

The carbon coverage θ_C is defined as the ratio between the number of deposited C atoms, n_C , and the number of surface (upper layer) Ni atoms, n_{Ni} , per unit cell, i.e.,

$$\theta_c = n_c / n_{\rm Ni} \tag{3}$$

Thus, one layer that contains more carbon atoms than the surface Ni atoms is characterized by $\theta_C > 1$ monolayer (ML).

S1 shows the adsorption energies for a single C on different unit cells equivalent to a surface coverage θ_c from 1/9 to 1/4 ML. For the different θ_c investigated here, the 3-fold hollow hcp and fcc sites were found to be more energetically stable than the bridge and the top sites. This is because the 3-fold hollow sites have a higher coordination number than the bridge and top site. The results in S1 also indicate that there is no a clear correlation between θ_c and E_{ads} . However, the results show that C on the hcp site is slightly more stable than on the fcc site for every θ_c tested.

S1: Adsorption energies, E_{ads} , (eV), of a single C atom at different surface sites of Ni (111) as obtained with different surface unit cells and carbon coverages, θ_C : on top of a surface Ni atom (top), bridging two surface Ni atoms (bri), at an fcc or hcp three-fold hollow site.

Unit cell	θ_{C}, ML	fcc	hcp	bri	top	
(2 × 2)	1/4	-6.12	-6.22	-5.74	-4.18	
(2 × 3)	¹ / ₆	-6.13	-6.16	-5.80	-4.07	

(3 × 3)	¹ /9	-6.13	-6.17	-5.69	-4.34	

The adsorption of C₂ dimer and two single C atoms with different separation distances were studied on a 2 × 2 unit cell of Ni (111) surface, which is equivalent to a surface coverage $\theta_c = 1/2$ ML. As shown in S2, the most stable adsorption state is the C2 dimer adsorbed on nearest neighboring hcp and fcc sites (S4), with a C-C distance of 133 pm. The adsorption energy per C atom for this system is -6.40eV, and the calculated interaction energy between the dimer and the Ni surface is -2.96eV. As shown in S2, the adsorption of two single C atoms has been found to be much less stable than that obtained for the dimer. This result indicates that, at the carbon coverage $\theta_c = 1/2$ ML, the formation of C₂ dimers is thermodynamically favored. The C₂ dimer and two single C atoms' adsorption behavior at lower carbon coverage $\theta_C = 1/3$ and 2/9 ML have also been studied and reported on S3. The results show that the C2 dimers are still more stable than the adsorbed two single C atoms at $\theta_C = 1/3$. That table also shows that, at low coverage (2/9), the single C has an adsorption energy of -6.15eV. As the two single C atoms approach each other at a surface coverage of 1/2, the corresponding adsorption energy becomes -5.55eV. This indicates that the single carbon atoms become more unstable as the surface coverage increases, due to the strong repulsive interactions between these isolated carbon atoms. Thus, as more carbon is deposited on the Ni (111) surface, the carbon atoms thermodynamically tend to aggregate together. S3 also shows that the adsorption energy of a carbon dimer on Ni (111) is independent of the surface coverage, indicating that the formation of C-C covalent bonds on Ni surfaces can reduce the repulsion at higher coverages.

S2: Adsorption energy per atom for the adsorption of two carbon atoms (named C^1 and C^2) on a (2×2) slab model ($\theta_C = 1/2$) (Site Occupation and the shortest distance between C atoms, d(C₁-C₂), are also shown)

adsorbate	Site C ¹	Site C ²	$d(C^1-C^2)$, pm	E _{ads} ,eV	E _{int} ,eV
single C	fcc	hcp	388	-5.27	
single C	hcp	hcp	250	-5.55	
single C	fcc	fcc	250	-5.51	
dimer C ₂	top	hcp	134	-5.87	-2.45
dimer C ₂	top	fcc	134	-5.83	-2.41
dimer C ₂	fcc	hcp	133	-6.40	-2.96

S3: Adsorption energies per carbon atom for a C_2 dimer formed at neighboring fcc and hcp sites and two single C Atoms (at the nearby hcp sites) for different $\theta_C [d(C^1-C^2)$ is the C-C distance]

		din	dimer C ₂		single C	
unit cell	θ_C ,ML	E _{ads} ,eV	$d(C^1-C^2)$, pm	E _{ads} ,eV	$d(C^1-C^2)$, pm	
(2 × 2)	¹ / ₂	-6.40	133	-5.55	250	
(2 × 3)	¹ / ₃	-6.40	134	-6.13	382	
(3 × 3)	² / ₉	-6.36	134	-6.15	431	



S4. Optimized geometries for selected carbon species on Ni (111): a) atomic carbon C@hcp; b) dimer C₂@hcp-fcc; c) trimer C₃@fcc-hcp-fcc; d) trimer C₃@hcp-fcc-hcp; e) three single carbon 3C@hcp-hcp-hcp; f three single carbon 3C@fcc-fcc-fcc.

Different arrangements of three carbon atoms on a (3×3) unit cell of Ni (111) surface were also optimized, i.e., C₃ trimer in a row (S4 c and d) or in a triangular shape, three single carbon atoms with different separation distance on different sites (S4 e and f). The resulting stable adsorption geometries are presented in Figure 1. The corresponding adsorption energies for C₃ are shown in S5. As in in the case of C₂ dimer adsorption, the results show that the C₃ trimer is more energetically stable than the three single adsorbed C atoms, indicating that the formation of C₃ trimer is also thermodynamically favored over the single C atoms. The most stable trimer is the one with its three carbon atoms adsorbed on next nearest neighboring hcp-fcc-hcp site with the middle carbon atom slightly lifted. S5: Adsorption and cluster-metal interaction energies per carbon atom for C₃ trimers formed around a Ni atom on the (111) surface at a coverage of 1/3 ML, [d(C-C) is the shortest C-C distance between two C atoms]

Adsorption Geometry	d(C–C), pm	E _{ads} ,eV	E _{int} ,eV	
trimer C ₃ @fcc-hcp-fcc	136	-6.42	-1.60	
trimer C ₃ @hcp-fcc-hcp	136	-6.44	-1.58	
single carbon 3C@hcp-hcp-hcp	328	-6.12		
single carbon 3C@fcc-fcc-fcc	320	-5.92		

For carbon aggregates larger than a trimer, the carbon clusters can form linear chains (C_x ,L), branched (C_x ,B) and/or ring (C_x ,R) configurations. The present DFT analysis shows that the carbon tetramer is most stable in a linear chain configuration, C_4 (L) since the two end atoms of the carbon's chain are strongly bonded at the hollow sites of the Ni (111) surface (S6), which stabilizes the chain configuration. As shown in S7, this structure has an adsorption energy of - 6.54eV/atom. The branched structure, C_4 (B), was found to be less stable by 0.27eV. Note that the calculated metal-cluster interaction energy shows that the most stable C_2 dimer on the Ni (111) surface has an interaction energy of -2.96eV whereas an interaction energy of -1.60eV was obtained for the trimer. For the C_4 (L), an even smaller metal-cluster interaction was observed (-1.23eV). This result shows that, as the size of the carbon chain cluster increases, the interaction between the cluster and the Ni decreases. As it is shown below, this decrease in the metal-cluster interaction energy also holds for the C_5 and C_6 clusters. Note that the C_4 (B) has a metal-cluster interaction of -2.33eV, indicating that the branched clusters are more strongly bonded with the metal support than the linear clusters.



S6. Optimized geometries for tetramer (C₄-chain; C₄-branch) and pentamer (C₅-chain; C₅-branch; C₅-ring) on Ni (111).

S7: Adsorption and cluster-metal interaction energies per carbon atom for selected small carbon clusters on the (111) surface.

Adsorption Geometry	E _{ads} ,eV	E _{int} ,eV	
C4(L)	-6.54	-1.23	
C4(B)	-6.27	-2.33	
C5(L)	-6.50	-1.01	
C5(B)	-6.36	-1.94	
C5(R)	-6.29	-1.94	
C6 (L)	-6.55	-1.08	
C6 (B)	-6.36	-2.06	
C6 (R)	-6.43	-1.18	

The results for carbon pentamer, C_5 , are similar to those observed for the tetramer C_4 . That is, the $C_5(L)$ was found to be the most stable configuration on the Ni (111) surface with an adsorption energy of -6.50eV whereas $C_5(B)$ and $C_5(R)$ are less stable by 0.14 and 0.21eV, respectively. Similar results were also obtained for C_6 clusters: $C_6(L)$ is more favored over $C_6(B)$ and $C_6(R)$

with an adsorption energy of -6.55eV. Moreover, a further decrease of the metal-cluster interaction was observed for these C_5 and C_6 clusters, as compared with that obtained for the tetramer. The stable C_6 configurations obtained by the present analysis are presented in S8.



S8. Optimized geometry for C₆ (C₆-chain; C₆-branch6; C₆-ring) on Ni (111).