Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for "Structure and Dynamics of Metallic and Carburized Catalytic Ni Nanoparticles: Effects on Growth of Single-Walled Carbon Nanotubes" by Jose L. Gómez-Ballesteros and Perla B. Balbuena*

Monitoring of the Atom-pair Distances

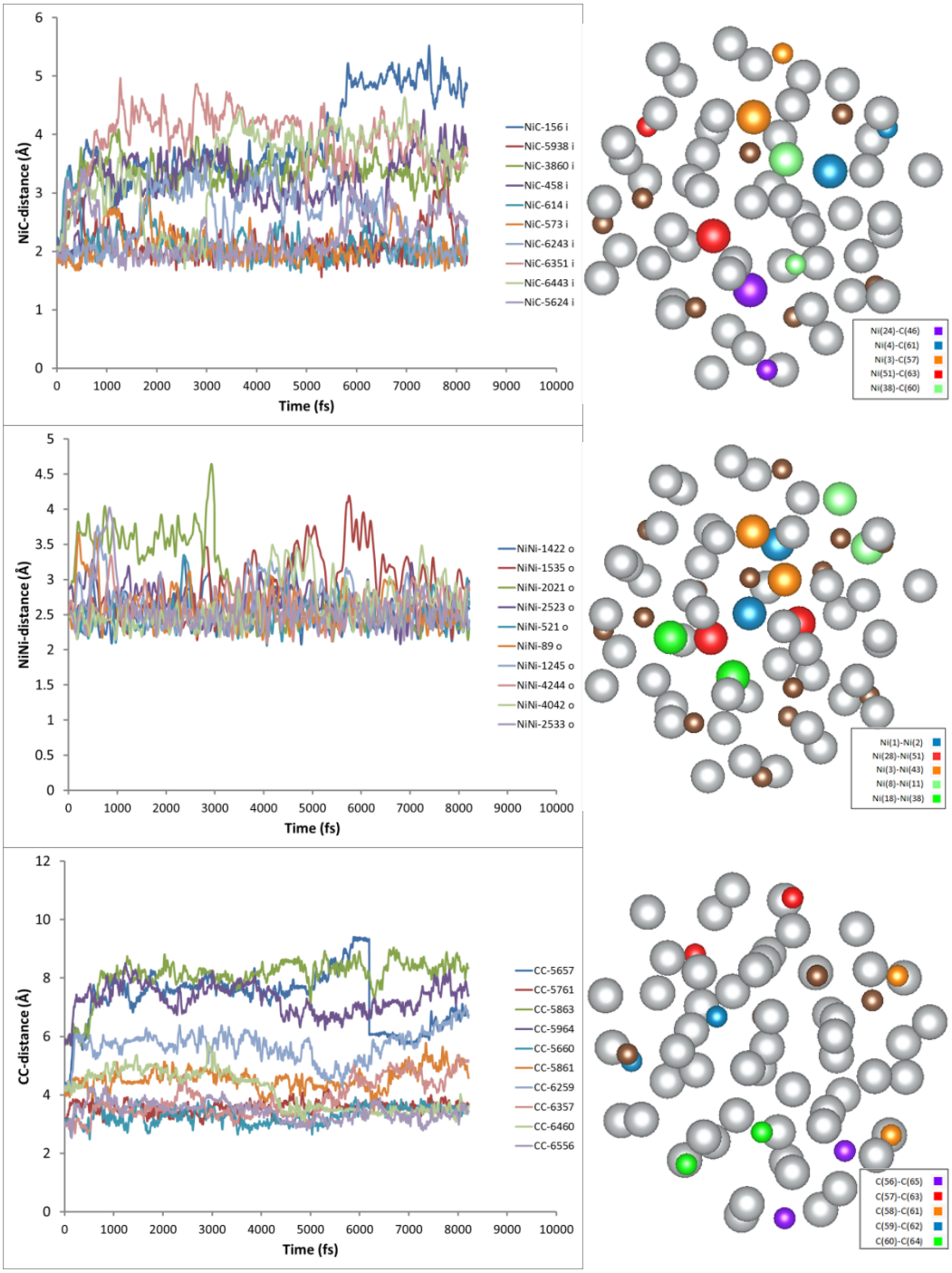

Figure S.1 Monitored distances for atom pairs in $Ni_{55}C_{14}$. Colors in pairs of atoms correspond with colors in lines. Ni and C atoms are represented by gray and brown spheres respectively.

Distances of atom pairs in consideration and their graphical representation are portrayed as purple, red, orange, blue and green lines and spheres, respectively.

Ab initio molecular dynamics simulations (AIMD) were run for the carburized Ni nanoparticles $Ni_{55}C_{10}$ and $Ni_{55}C_{14}$ for 8 ps at 750 K and 1000 K without cap and $Ni_{55}C_{14}$ in contact with four different nanotube caps with chiral indexes: (8,7), (9,6), (11,5) and (13,0) for 3 ps. We followed the distances of selected pairs of atoms throughout the extension of the simulation. A minimum of ten pairs of atoms were randomly selected from the beginning of the simulations within one of five categories in the case of the carburized nanoparticle, namely, NiNi-o, NiNi-i, NiC-o, NiC-i, and CC. The name convention is the first three or four letters represent each of the two species being considered for the distance analysis (nickel and/or carbon) followed by numbers that identify each atom in particular. The final part of the name is a hyphen followed by either i or o, which indicates whether the Ni atoms are located at the inner core of the nanoparticle or the outer layer, respectively. One additional category is considered for the cases with nanotube caps to identify distances between dissolved C and C from the nanotubes, C-CN.

The graph and the corresponding images in Figure S1 depict the monitored distances between pairs of atoms in the $Ni_{55}C_{14}$ nanoparticle at 1000 K. Fewer colored atoms in the images than the number of atom pairs in the graphs are shown for illustration purposes. The images correspond to the final state of the nanoparticle after 8 ps of AIMD simulation. Each set of graph-image correspond to different sets of distances for a. Ni-C, b. Ni-Ni and c. C-C pairs. Throughout the simulation, distances for the selected pairs may span across a relatively wide range, being subject to variations as temperature and composition in the nanoparticle are varied. In order to synthesize the information provided in these graphs, bar diagrams as the ones shown in Fig. 4 were constructed. Each category in the bar diagram summarizes one of the graphs shown here, thus each bar diagram condenses information from 5 (or 6 for the capped nanoparticles) graphs of monitored distances. The procedure for building the bar diagrams consisted in counting the absolute frequency of atom pairs of a particular category falling within a small distance range (0.2 Å).

Pair Radial Distribution Function

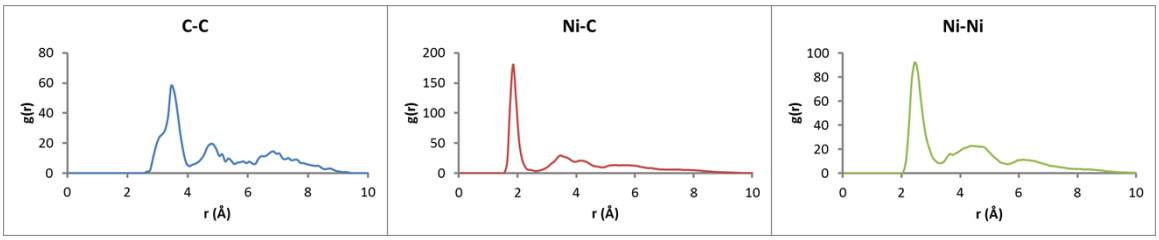

Figure S2. Pair radial distribution functions (RDF) for C-C (blue), Ni-C(red) and Ni-Ni(green) for atoms in the $Ni_{44}C_{14}$ nanoparticle at 1000 K.

RDF functions help describe the average structure of the system throughout the simulation time. The peaks indicate the most likely location of neighboring atoms of a certain type with respect to a reference atom. Sharp peaks are indicative of a well-defined structure and wider peaks reflect some degree of flexibility of the structure. Both Ni-Ni and Ni-C show a sharp peak located at 2.45 Å and 1.85 Å respectively, showing structural ordering between first nearest-neighbors and a longer range structure that is not very well defined due to fluctuations in the structure at the temperature of the system. A sharp, wider peak is observed for C-C at 3.45 Å as some of the C atoms migrate to the nanoparticle subsurface while maintaining a relative order.

Diffusion Coefficients of C Atoms

$D(\cdot 10^9$ $m^2/s)$	Temperature (K)	
	750	1000
$Ni_{55}C_{10}$	0.098333	0.448333
$Ni_{55}C_{14}$	0.208333	1.698333

Table S1. Diffusion coefficient of C atoms in the carburized Ni nanoparticle calculated for two different compositions and temperatures.

The self-diffusion coefficient of C atoms dissolved into the Ni_{55} nanoparticle for two different compositions ($Ni_{55}C_{10}$ and $Ni_{55}C_{14}$) at 750 K and 1000K were obtained by calculating the mean square displacement and applying Einstein's diffusivity equation shown below.

$$D_s = \lim_{t\to\infty} \frac{1}{6t}\left\langle \frac{1}{N}\sum_{j=1}^{N} \left\| r_j(t) - r_j(t_0) \right\|^2 \right\rangle \qquad (S1)$$

The terms in brackets represent the ensemble average of squared displacements of the species of interest, calculated over multiple time origins (t0) for a time (t) sufficiently long to assume that the system is equilibrated. The calculated self-diffusivities are shown in table SI. Higher diffusivities are found at higher temperatures due to the faster dynamics effect on the mobility of C atoms. At higher carbon content, diffusivities are higher as C atoms move faster motivated by a greater overall repulsion inside the nanoparticle due to an increase in the charge magnitudes as mentioned in the charge analysis.

Energy of Adhesion Nanotube Cap-Nanoparticle

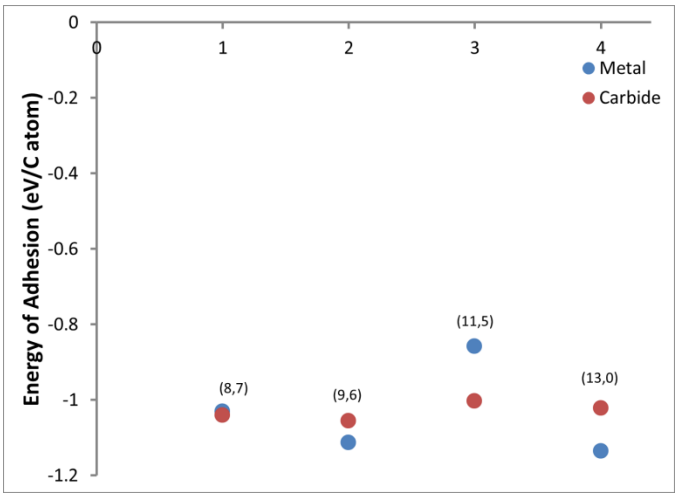

Figure S3. Energy of adhesion of nanotube caps to pure metal (blue) and carbide (red) nanoparticles.

Electron Density of States

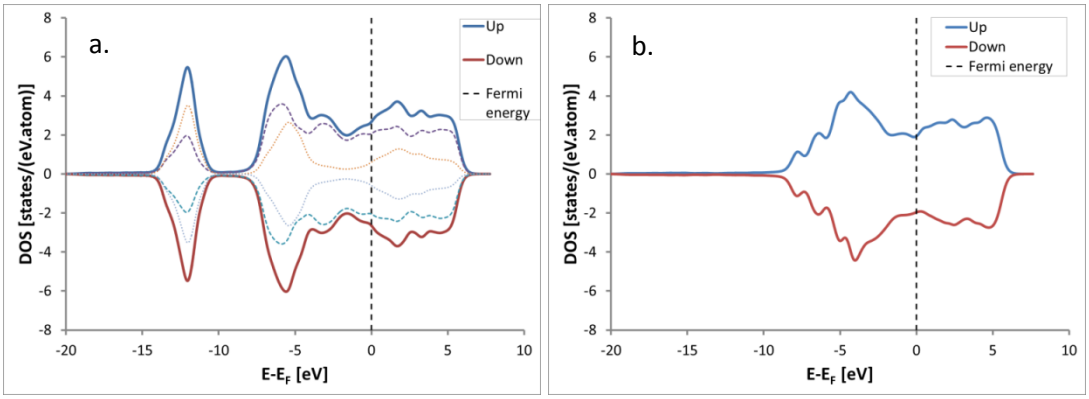

Figure S4. Electronic density of states for the carburized a. $Ni_{55}C_{14}$ nanoparticle and the metallic b. Ni_{55} nanoparticle. Continuous blue and red lines represents total up and down density of states, dashed purple and light blue lines represent up and down contributions from C atoms, and orange and purple represent contributions from Ni atoms.

The density of states of Ni_{55} exhibits a population of electronic states concentrated in a smaller range of energies than $Ni_{55}C_{14}$, and a lower density of unoccupied states above the Fermi level, which is considered and indicator of a higher reactivity of the latter and supports the reasoning presented in the results and discussion section with respect to electron accumulation and depletion. The density of states shows a continuous population for the metal nanoparticle whereas the presence of a new set of inner orbitals is observed below the Fermi level for the carburized nanoparticle as a consequence of adding C atoms into the nanoparticle. Equivalent trends are observed for the other nanotube caps.