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Supplementary information

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

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Supplementary information

First-principles DFT calculations were used to study CO, NH₃, NH₂, NH, atomic C and N adsorption on icosahedral Fe₅₅ cluster. The geometry optimization was started from the high symmetry adsorption sites of one the 20 triangular face of the cluster. The high symmetry adsorption sites are the top site, octahedral hollow site and tetrahedral bridge sites. In our simulation, the bridge and top site can be in-plane on the cluster face or on its edge/vertices. For CO, interaction geometries presenting the molecular bond both coplanar (=) and perpendicular ($\perp$) to the cluster surface were considered. When the CO molecule is placed flat on the cluster, during the geometry optimizations oxygen atoms are not bonding to the surface and the molecule flips up.

Perpendicular adsorption is not favorable when oxygen is toward the surface ($\perp$ OC). During the relaxations with the molecule adsorbed through the carbon ($\perp$ CO), it spontaneously moves, migrating on the B, D and F sites (Fig. S1) of the surface. To describe quantitatively the energetics of the adsorbed species on the surface, we introduce the interaction energy term (I.E.), defined as

$$\text{I.E.} = E_{\text{Fe}_{55}/\text{CO}} - (E_{\text{Fe}_{55}} + E_{\text{CO}}), \quad (1)$$

where $E_{\text{Fe}_{55}/\text{CO}}$ is the total energy of the adsorbate-substrate system, $E_{\text{Fe}_{55}}$ of the Fe₅₅ cluster, and E_{CO} of the free CO molecule. I.E. describes the strength of the adsorbate-substrate interaction. In Fig. S1 the I.E. values are reported for the optimized geometries.

The stability of NH₃ on the cluster was considered as well. The molecule was set on the vertices, on the edge and on the centre of the icosahedral face of the cluster. For every adsorption site the possible effect of the orientation was considered, though only the interaction N-Fe was favorable, and only the top sites are stable ($-0.73 \text{ eV} < \text{B.E.}(\text{NH}_3) < -0.60 \text{ eV}$). The obtained stable geometries and I.E.s (calculated with respect to E_{NH_3}) are reported in Fig. S2.

In order to study CO and NH₃ dissociation with the CI-NEB method, we need to know the preferred adsorption sites for NH₂, NH, N, C and O atoms on the cluster. Considering NH₂, during relaxation the molecule spontaneously moves, migrating to the bridge sites on the facet of the surface ($-3.10 \text{ eV} < \text{B.E.}(\text{NH}_2) < -2.52 \text{ eV}$) (Fig. S3). The arrangement presenting the nitrogen

tetrahedrally coordinated to two hydrogens and two irons atoms is clearly preferred. Similar behavior has been observed considering the interaction of NH at the high symmetry adsorption site ($-4.64 \text{ eV} < \text{B.E.}(\text{NH}_2) < -3.18 \text{ eV}$) (Fig. S4). During geometry optimization, the fragment rearranges, moving to the hollow site, where N can easily interact with three metal atoms.

Considering atomic carbon and nitrogen, all possible adsorption sites on the surface (Figs. S5 and S6) and below (Figs. S7 and S8) were considered, but only few stable sites for individually adsorbed C and N were located. Both of the atoms present similar behavior: the hollow sites on and below the surface are most stable. I.E. values are reported in the figures; for comparisons remember that the reference energy for a non-adsorbed carbon is that of the isolated atom.

Fig. S9 shows a possible formation path for HCN was calculated with the NEB method. The obtained reaction barrier is 1.65 eV. Fig. S10 shows an Arrhenius plot of the mole fraction of HCN as a function of reactor wall temperature. A fit to the linear region yields a slope of -15689.7 K, which corresponds to an activation energy of 1.35 eV.

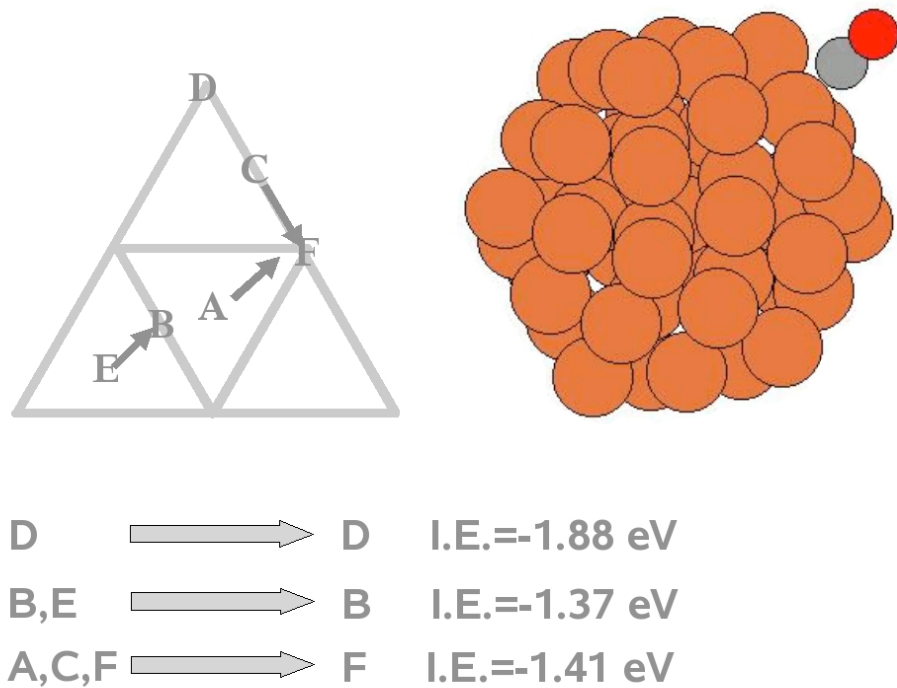


Fig. S1 Behavior observed during geometry relaxation of CO, started from the molecule adsorbed perpendicular at the cluster surface. During optimization, the molecule spontaneously moves to the edge of the facet or to the border of the hollow cavity.

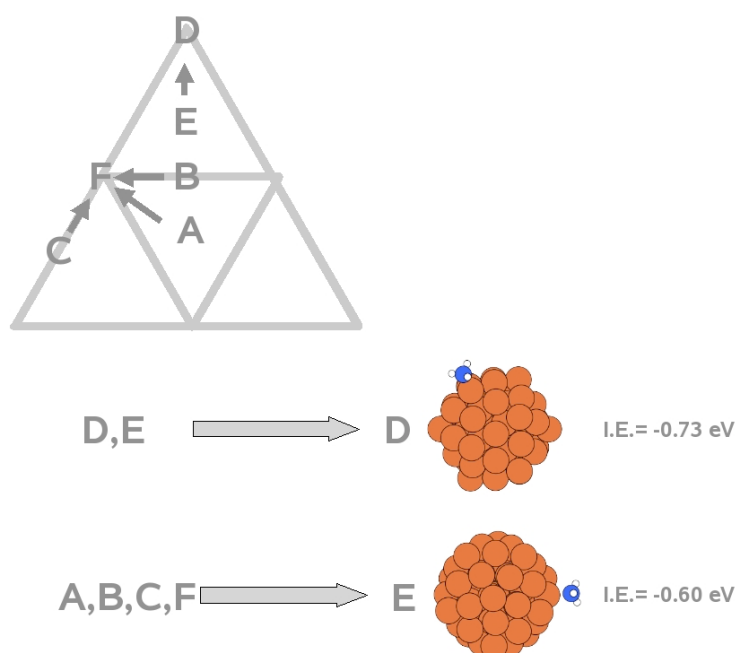


Fig. S2 Behavior observed during geometry relaxation of NH_3 , started from the molecule adsorbed on the cluster surface. NH_3 prefers to interact with the most exposed metal atoms, and after the first H dissociation, the molecule spontaneously moves to the top sites during geometry optimization.

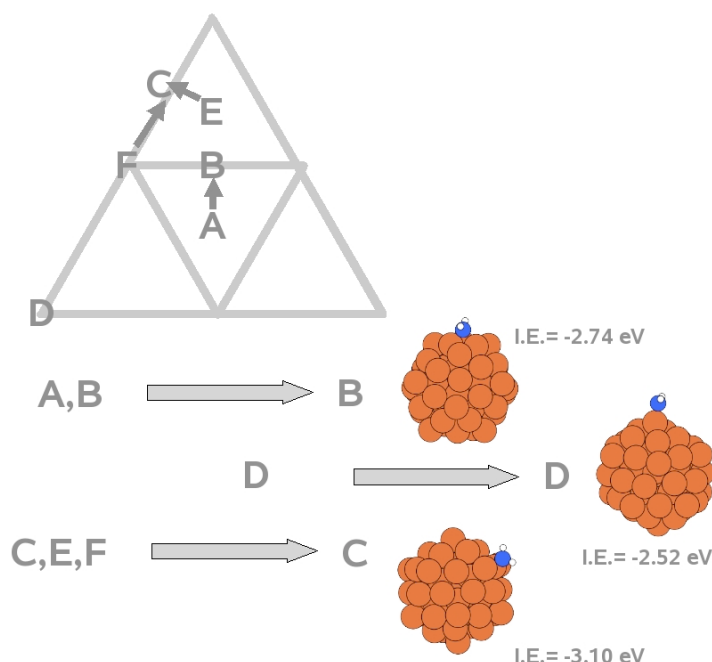


Fig. S3 Behavior observed during geometry relaxation of NH_2 , started from the molecule adsorbed on the cluster surface. In order to optimize the interaction with the surface and maintain tetrahedral coordination, NH_2 spontaneously move to the bridge sites (C and B) during the optimization.

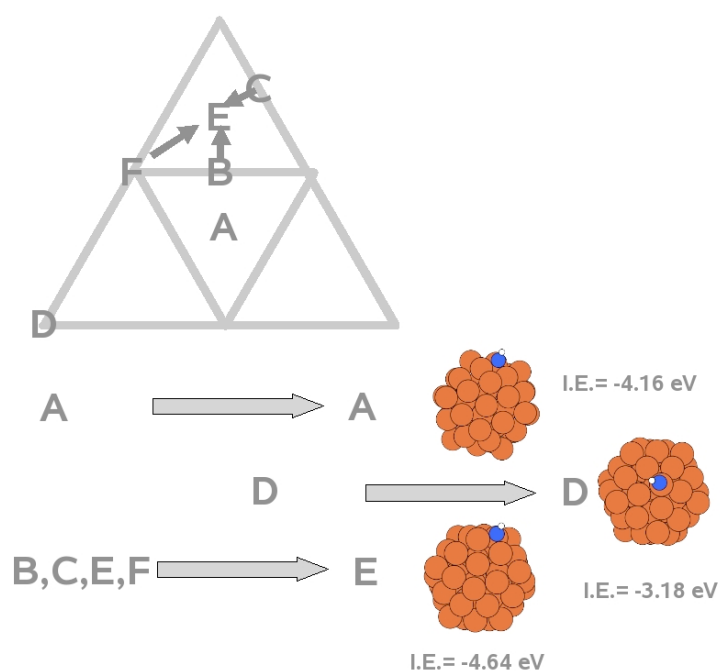


Fig. S4 Behavior observed during geometry relaxation of NH, started from the molecule adsorbed on the cluster surface. In order to optimize interaction with the surface and maintain tetrahedral coordination, NH spontaneously moves to the hollow sites (A and E) during the optimization.

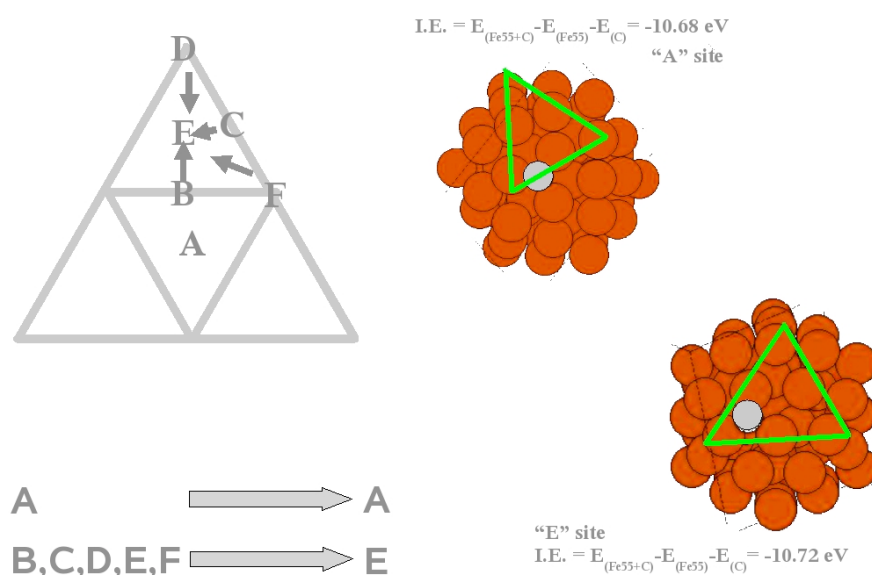


Fig. S5 Behavior observed during geometry relaxation of atomic C adsorbed on the high symmetry adsorption sites of the cluster surface. The hollow sites (A and E) are the only stable ones, and from the others, the adsorbed C migrates to the nearest hollow site.

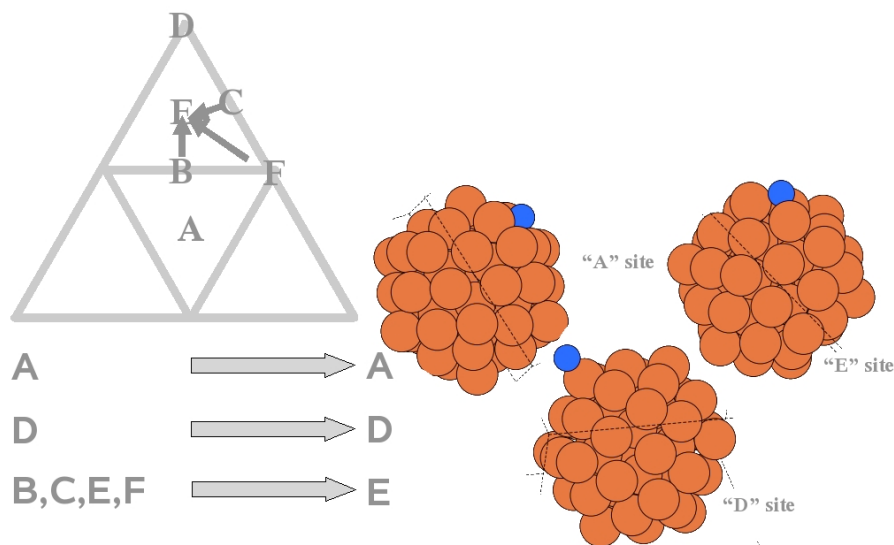


Fig. S6 Behavior observed during geometry relaxation of atomic N adsorbed on the high symmetry adsorption sites of the cluster surface. The hollow sites (A and E) are the only stable ones, and from the bridge sites, the adsorbed N migrates on the nearest hollow site.

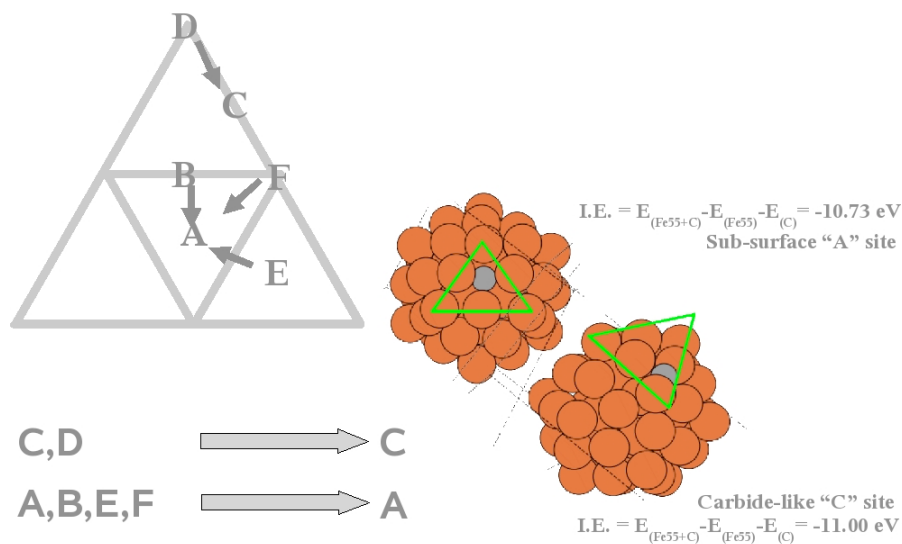


Fig. S7 Behavior observed during geometry relaxation of subsurface atomic C adsorbed on the high symmetry adsorption sites of the cluster surface. In the majority of cases, the C atom moves spontaneously to the octahedral cavity below the A site during the geometry optimization.

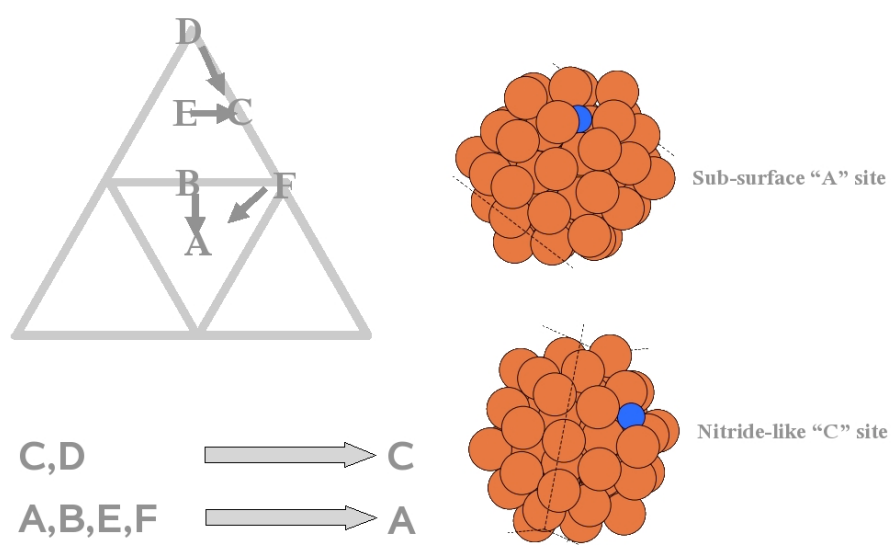


Fig. S8 Behavior observed during geometry relaxation of subsurface atomic N adsorbed on the high symmetry sites of the cluster surface. The behavior is similar to what is observed for atomic C.

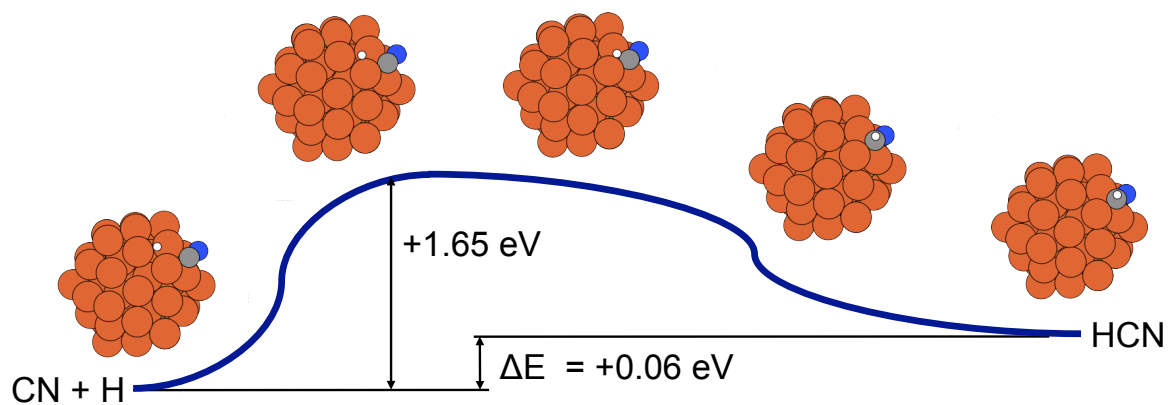


Fig. S9 Proposed reaction path for HCN formation reaction on the cluster.

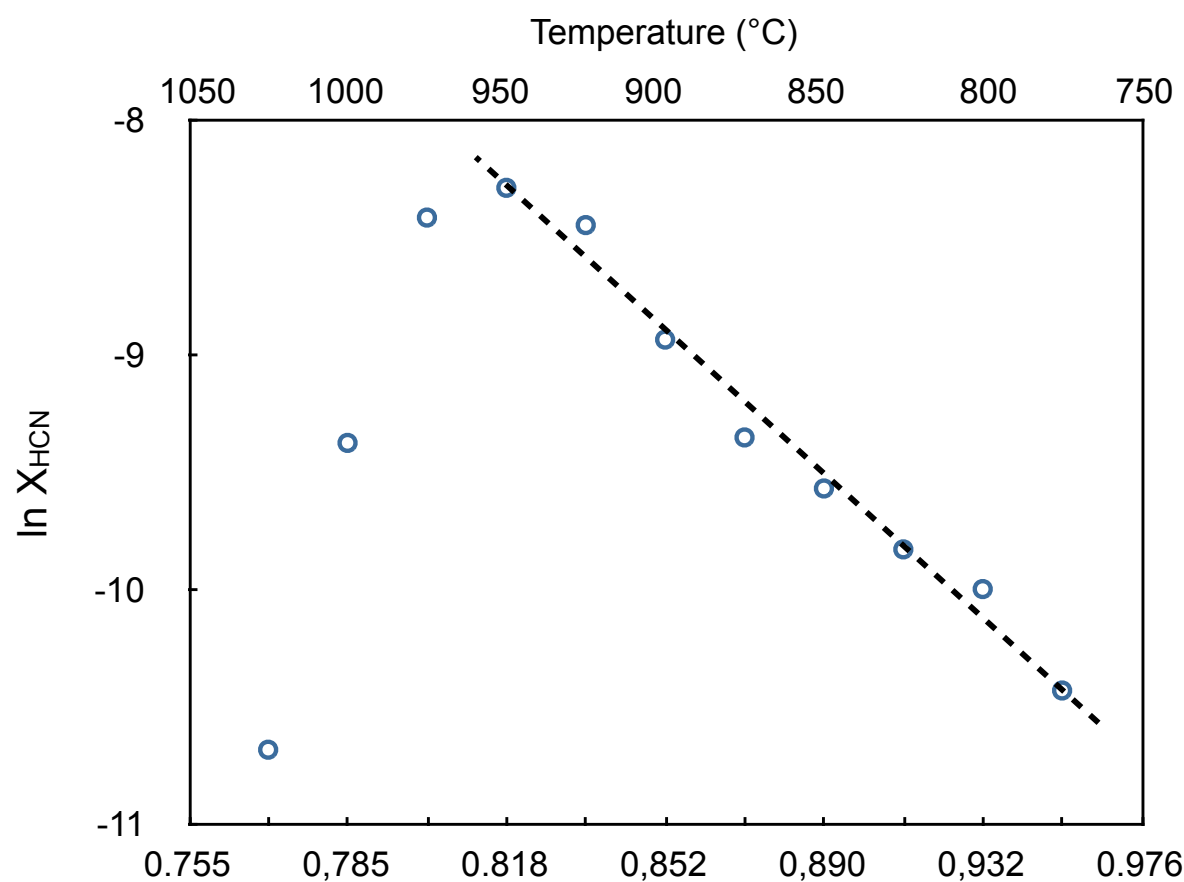


Fig. S10 Arrhenius plot of the mole fraction of HCN measured using FTIR as a function of reactor maximum wall temperature.