We interpret previously published C K edge CEELS and NEXAFS data for carbon on Ni between 500-700K. The C K CEELS data for CO/Ni at 500K reveal the presence of C-C bonding on the surface, i.e. horizontal C$_n$ (n=2,3,..). The CEELS data for carbon at 620K reveal that some of the C$_2$ species flip up at this temperature, while the others dissociate. Evidence for vertical C$_2$ is seen only at higher carbon coverages, suggesting that some of the C$_2$ are forced to flip up to make room for neighboring horizontal C$_n$'s to dissociate. These vertical C$_n$'s then apparently serve as the precursor for the nucleation of graphite, as it explains the lack of graphite formation at lower coverages when total dissolution into the bulk occurs. These results confirm recent effective medium theory calculations, which indicate that a nucleation step must be involved in the carbide to graphite transformation, and suggest that vertical C$_2$ may be a precursor to this nucleation step on Ni.
Evidence for Vertical C on Ni
as a Precursor for Graphite Nucleation

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Carbon is relatively unreactive with Ni. Thus Ni forms a relatively unstable carbide, which above 670K either undergoes dissolution into the bulk or at higher coverages forms a graphitic layer which sits high above the surface (e.g. 2.8 Å above a Ni(111) surface) [1]. Carbon is usually deposited on the surface by exposure to CO, ethylene, or acetylene. These molecular species decompose with heating, so that above 450K, SIMS data reveals all H and O has left the surface, leaving only C on the surface [2]. NEXAFS (near edge x-ray absorption fine structure) data have been very helpful in determining the various orientations of the molecular fragments below 450 K [3,4], but little new information from NEXAFS data has been reported for C/Ni above 450 K. In this work we utilize previously published [5,6] CEELS (core electron energy loss spectroscopy) and NEXAFS data [7] to obtain experimental verification that vertical C\(_2\) acts as a precursor for graphite nucleation on Ni. Comparison is made with the NEXAFS technique commonly utilized below 450K.

1. NEXAFS results below 450K

The expression for the differential cross section derived for a transition from an s initial state (e.g. a C 1s state) to any π state can be written [4]:

\[
\{1s \rightarrow \pi\} \propto (3\cos^2\beta - 1)(3\cos^2\theta - 1) + 2
\]  

(1)

where \(\theta\) is the angle between the surface normal and the electric field vector (or between the surface and the photon beam direction) and \(\beta\) is the angle between the surface normal and the molecular plane normal. A similar but approximate expression for excitation to a \(\sigma\) state can be written:

\[
\{1s \rightarrow \sigma\} \propto (3\cos^2\alpha - 1)(3\cos^2\theta - 1) + 2.
\]  

(2)

Here \(\alpha\) is the angle between the surface normal and the main molecular symmetry axis. When the ethylene is lying flat on the surface, \(\alpha\) is 90\(^\circ\) and \(\beta\) is 0\(^\circ\). In this case eqs. 1 and 2 reduce to 3sin\(^2\theta\) and 6cos\(^2\theta\). On the other hand, when the ethylene axis stands perpendicular to the surface, \(\alpha\) is 0\(^\circ\) and \(\beta\) is
In this case, eqs. 1 and 2 reduce to $6\cos^2\theta$ and $3\sin^2\theta$, respectively. The latter more specific expressions are apparently qualitatively valid for most other molecules as well [7].

Fig. 1 summarizes the data [3,4] for ethylene on Pt(111) or Ni(100) at various temperatures and coverages. These data for all four adsorbed species reveal the characteristic $\pi^*_{CC}$ and $\sigma^*_{CC}$ peaks and the opposite variation with $\theta$ for nearly vertical and horizontal orientations of the adsorbates, as anticipated by eq. 1 and 2. We have given the initial bound state feature the label $\pi^*_{CM}$, in Fig. 1, i.e. carbon-metal antibonding rather than $\pi^*_{CC}$, since for most of the four cases this is more appropriate. These data were utilized previously to quantitatively determine the orientation angles for the four different adsorbate orientations on the surface [3,4]. Fig. 1 also shows our assignments for some of the smaller peaks such as the $\pi^*_{CH}$ and $\sigma^*_{CH}$ peaks as well as Rydberg or atomic-like np features. Our assignments are based on comparison with other NEXAFS data and theoretical calculations [8].

A combination of HREELS, NEXAFS, and PES data and theoretical calculations have been utilized to previously determine the orientation and bonding of ethylenic species to metal surfaces as schematically indicated in Fig. 1. For C$_2$H$_4$/Pt(111) at 90K, the molecule is believed to be di-$\sigma$-bonded to the Pt surface, i.e. the molecule lies flat on the surface ($\alpha = 90^0$ and $\beta = 0^0$). Here the molecule is apparently only partially rehybridized, leaving the molecule somewhere between an sp$^2$ and sp$^3$ type structure. At 300K, Fig. 1b, the molecule stands erect ($\alpha = 0^0$ and $\beta = 90^0$) forming an ethylidyne species, i.e. sp$^3$ hybridized with 3 C-Pt bonds and 3 C-H bonds [3]. On Ni(100) at 130K, ethylene is $\pi$-bonded to the surface (i.e. more fully sp$^3$ hybridized); however, the molecule is not lying completely flat ($\alpha = 0^0$ and $\beta = 50^0$) [4]. Finally on Ni(100) at 180K, a more erect ($\alpha = 30^0$ and $\beta = 65^0$) vinyl species
is present [4]. The molecule is still essentially sp² hybridized, but a full σ C-M bond is formed in place of one C-H bond. In summary, the adsorbates at lower temperature lie more horizontal, those at higher temperature more vertical.

It is interesting to compare the peak energies for the more horizontal adsorbates with those for the more vertical. No significant energy shift in the σ*CC peak is evident, although this might have been expected particularly for ethylidyne (curve b) since the C-C bond is in this case a single σ bond. Note that the π*CM peak has higher energy for the more vertical adsorbates than for the horizontal. We believe this is because the adsorbate-metal bond is indeed stronger for the vertical adsorbates than for the horizontal adsorbates. We have reported a more detailed interpretation of these curves elsewhere [8].

2. **CEELS above 450K**

Above 450K, SIMS data reveal that all H and O has left the surface, leaving only C on the surface [2]. Recent calculations utilizing effective medium theory (EMT) [1] suggest however that further molecular orientation changes occur. In the EMT approach, the atom positions are determined by the electron density, each atom seeking its own unique optimum density. These calculations conclude that at intermediate coverage, the C-C interaction drives atoms closer to Ni, but in a graphite layer, the C-C interaction drives them away from the surface. They conclude then that the carbidic to graphite evolution is clearly discontinuous, so that a nucleation step must be involved. The calculations also suggest that a horizontal C₂ species on a Ni(111) surface is not stable at high temperature, but that a vertical (i.e. perpendicular) C₂ species may be stable on the Ni surface [1]. However, this vertical C₂ is too close to the surface to serve as a nucleation site for graphite formation by itself. Only a C₃ species moves sufficiently far from the metal surface to serve as a graphite nucleation site. Darling et al. [1] then postulate that a vertical C₂
species may either "tip over" to form a C\textsubscript{3} species, which moves away from the surface and forms a graphite nucleation site, or a graphitic layer forms on top of a carbidic layer (i.e. the outer C of the vertical C\textsubscript{2} may become part of the graphite layer, and the inner C may ultimately undergo dissolution into the bulk). In either case, a vertical C\textsubscript{2} serves as the precursor to a nucleation site.

Recently Caputi et al. [5] reported AES and CEELS data for carbon on Ni(100) in the region 520-770 K. Core-level and valence band XPS data have also been reported [5]. A detailed interpretation of the AES and XPS data has revealed extensive C-C bonding on the surface, in what was previously believed to be carbidic (i.e. only C-M bonding) in character [9]. At higher temperatures, just prior to the formation of graphite around 620 K, the amount of C-C bonding appears to decrease. However, no meaningful interpretation of the CEELS data has been reported.

In NEXAFS, the dipole selection rule (i.e. s \rightarrow p only) is appropriate. By CEELS, we mean the use of small electron energies (500-1000 eV) and the measurement of back scattered electrons which have suffered large momentum transfer, in which case the validity of the dipole selection rule is not expected. Thus optically forbidden monopole transitions should be evident. Nevertheless, CEELS data can still be utilized to obtain some of the same information obtainable from NEXAFS data.

We utilize equations derived by Cheung [10] for determining the angular dependence of CEELS data for graphite, which has the \( \sigma \) orbital parallel to the surface (i.e. \( \alpha = 90^\circ \) and \( \beta = 0^\circ \) as defined above). We obtain:

\[
\{ 1s \rightarrow \pi \} \propto 1.5 \xi \sin^2 \varphi + 3 \nu [\cos^2 \varphi - 0.5 \sin^2 \varphi] \sin^2 \theta \tag{3}
\]

\[
\{ 1s \rightarrow \sigma \} \propto \xi / 3 + \nu [1 - 0.5 \sin^2 \varphi] - \nu [\cos^2 \varphi - 0.5 \sin^2 \varphi] \sin^2 \theta \tag{4}
\]

where \( \varphi \) is the electron acceptance angle and \( \xi \) and \( \nu \) are the magnitude of the monopole and dipole contributions, respectively. We compare these
expressions with those above for NEXAFS. If we assume $\theta = 90^\circ$ (i.e. that electrons are counted at all acceptance angles; this mimics the NEXAFS data which utilizes the total electron yield or the Auger yield, which is equivalent to all acceptance angles), we obtain

$$\{1s \rightarrow \pi\} \propto 1.5 \nu \cos^2 \theta$$  \hspace{1cm} (5)

$$\{1s \rightarrow \sigma\} \propto \xi/3 + 0.5 \nu + 0.5 \nu \sin^2 \theta$$ \hspace{1cm} (6)

These expressions have similar $\sin^2 \theta$ and $\cos^2 \theta$ dependences to those above for NEXAFS as expected. Now if we assume $\theta = 16.5^\circ$ (i.e. the appropriate acceptance angle for a cylindrical mirror analyzer and a 500 eV excitation beam as indicated by Cheung [10]), we obtain the expressions

$$\{1s \rightarrow \pi\} \propto 0.12 \nu + 2.64 \nu \sin^2 \theta$$ \hspace{1cm} (7)

$$\{1s \rightarrow \sigma\} \propto \xi/3 + 0.08 \nu + 0.88 \nu \cos^2 \theta.$$ \hspace{1cm} (8)

Notice the switch in $\cos^2 \theta / \sin^2 \theta$ dependence between eqs. 5, 6 and 7, 8. Eqs. 7 and 8, appropriate for this case, is also different from that for NEXAFS, eqs. 1 and 2. Furthermore, Cheung [10] found empirically for graphite with a 500 eV excitation beam that $\xi/\nu$ is about 8. Thus in CEELS for $\theta = 90^\circ$ (i.e. electron beam perpendicular to surface, which is generally the case for the data discussed in this work) the $\pi$ and $\sigma$ contributions have nearly equal intensity (eqs. 7 and 8 above both give 2.75$\nu$. If the C-C bond is vertical to the surface, we expect a corresponding reversal in the dipole intensity dependencies giving $\{1s \rightarrow \pi\} = 0.08 \nu$ and $\{1s \rightarrow \sigma\} = 5.42 \nu$. In summary, the CEELS data should give about equal $\sigma$ and $\pi$ area intensities for parallel C-C orientation, and be dominated by $\sigma$ intensity for perpendicular C-C orientation.

Figs. 2b and c compare -$d^2N(E)/dE^2$ K edge CEELS curves for various carbonaceous layers on metals [5,6] along with NEXAFS data for CO/Ni(100) at 670K in 2d [7]. We have also included in Fig. 2a NEXAFS [11] data for
condensed benzene and cyclohexane for comparison to show the presence of similar \( \sigma \) and \( \pi \) C-C features in these molecules and the absence of the C-H features for the carbonaceous layers as expected. All of the carbonaceous layers were prepared by exposure of the Ni surfaces to CO at around 500K, and then heating. The dashed curve in 2b was reported by Rosei et al [6] for a Ni(111) surface upon heating to 500K with an estimated coverage of about 0.3 ML (this is a very crude estimate). The solid curves in b (at 520K) and c (at 620K) were reported by Caputi et al [5]. Although they do not estimate the C coverage, it is believed to be greater than or equal to 1 ML. The NEXAFS curve in (d) was reported by Stohr and Jaeger [7] with incident angle \( \Theta = 20^\circ \). Thus it emphasizes vertical \( \sigma \) bonds. The latter curve corresponds to less than 0.5 ML of "carbidic" C on the surface. The K binding energy is about 282.9 eV for a carbidic layer on Ni(100) [12]. We have deconvoluted the Caputi data by a 2 eV Gaussian line shape to regain better resolution since it was taken with a large 6 \( V_{\text{pp}} \) modulation voltage.

The deconvolved Caputi data on Ni(100) and the Rosei data on Ni(111) at 500 K are quite similar as expected. They very clearly reveal the characteristic \( \pi^* \text{CC} \) and \( \sigma^* \text{CC} \) peaks at 285 eV and 293 eV respectively as seen in the NEXAFS data (Figs. 1 and 2a). Since C-M bonds do not produce peaks in this energy range [8], this clearly indicates the presence of C-C bonding on the surface, consistent with the AES and XPS data [9] as indicated above. The similar area intensities of the \( \pi^* \text{CC} \) and \( \sigma^* \text{CC} \) peaks clearly indicate that the C-C bonds lie flat on the surface. We would assume that these C-C bonds primarily exist as \( C_n \) (n = 2,3 etc, with n = 2 favored) species on the surface.

The Caputi data at 620K (curve c) reveal dramatic differences from that at 520K. Now the \( \sigma^* \text{CC} \) feature dominates with the \( \pi^* \text{CC} \) feature nearly
missing. This strongly indicates that the C-C bonds now stand perpendicular to the surface. We believe the $\sigma^*_{CC}$ feature now arises from $C_2$ species standing erect on the surface.

NEXAFS data for CO/Ni(100) at 300 K [7] (not shown) clearly show the $\pi^*$ and $\sigma^*$ CO bond features. Heating to 670K breaks all C-O bonds, leaving only atomic C on the surface. Notice that in Fig. 2d, no evidence exist for either C-O or C-C bonds. The features at 284 and 288 eV are attributed [8] to nonbonding $p_z$ orbitals (C dangling bonds pointed away from the Ni surface [8.12]) and $\sigma^*_C$ orbitals bonding the atomic C to the surface. Evidence for these same features also exists in the deconvolved 620K data of Caputi (curve 2c). Comparison with theoretical density-of-state calculations confirms these assignments [8.13].

In summary, our interpretation of the spectroscopic results are consistent with our previous interpretations of the AES and XPS data [9], and with Darling's EMT theoretical results as discussed above [1]. First, the CEELS data do indeed verify that significant horizontal C-C bonding exists on the surface below 600K. We anticipate that this is in the form of $C_n$. Around 620K, some vertical $C_2$ is formed along with considerable $C_1$ (i.e. atomic C). However, the CEELS and NEXAFS data also suggest that vertical $C_2$ is formed only at higher coverages (it is clearly present in the Caputi data [coverage about 1 ML] but absent in Stohr and Jaeger's NEXAFS data [coverage < 0.5 ML]). At higher coverages, we envisage that some of the $C_2$ are forced to flip up to make room for the neighboring horizontal $C_2$'s to dissociate. These vertical $C_2$'s may then serve as the precursor for the nucleation of graphite, since it would explain the lack of graphite formation from $C_2H_4/Ni(100)$ (i.e. at low carbon coverages). Further exposure to $C_2H_2$ at higher temperatures (i.e. producing higher C coverages) does lead to graphite formation on Ni(100)
Thus we provide the first experimental evidence for vertical C$_2$ as a precursor for graphite nucleation and corroborate the theoretical EMT [1] results.

REFERENCES

FIGURE CAPTIONS

Fig. 1  C K NEXAFS data for $\text{C}_2\text{H}_4/\text{Pt}(111)$ at a) 90 K and b) 300 K [3] and for $\text{C}_2\text{H}_4/\text{Ni}(100)$ at c) 130 K and d) 180 K [4]. The Pt data [3] were shifted down by 1.5 eV for better alignment with the Ni data [4] and other NEXAFS data [11]. This shift may arise from energy calibration errors or represent a C K binding energy shift on Pt.

Fig. 2  a) C K NEXAFS data for condensed benzene and cyclohexane [11], b) $-d^2N(E)/dE^2$ C K edge CEELS data for CO/Ni(100) at 500K (dotted line) [5] and CO/Ni(111) at 520K (solid line [6]), c) CEELS data for CO/Ni(100) at 620K [5], and d) NEXAFS data for CO/Ni(100) at 670K, but at low coverage [7].
Adsorbed ethylene

Fig. 1
Fig. 2
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