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AES and LEED Evidence for Dicarbon Fragments on Ni(110)

The structure of surface carbon intermediates is fundamental to the activity and selectivity of hydrogenation–dehydrogenation catalysis by transition metals. Adsorption and decomposition of hydrocarbons necessarily involves the formation of metal–carbon bonds. Carbonaceous structures (those devoid of carbon-bound hydrogen) presumably exist as one of two extreme forms on metal surfaces: (i) isolated carbon atoms with only carbon–metal bonds, and (ii) carbons characterized by strong carbon–carbon bonds with weaker interactions with the metal. In the extreme, the former can be considered as a surface carbide chemilayer, and the latter as a graphite residue. In view of the low heats of formation of bulk carbides of the Group VIII metals, it seems reasonable to suppose that carbonaceous residues on these metals may be characterized by strong carbon–carbon bonds relative to the metal–carbon absorption bonds. Using AES and LEED, we have studied surface carbon formed by the adsorption and decomposition of ethylene on Ni(110). As will be discussed below, careful AES intensity measurements of the carbon coverage following ethylene exposure at 600 K indicated one carbon atom was present per nickel surface atom. However, the two-dimensional unit cell observed by LEED contained two nickel surface atoms and, therefore, two carbon atoms. These observations suggest that the surface carbide chemilayer formed below 600 K may remain associated as adsorbed dicarbon species.

Ethylene adsorption at room temperature produced a broad hydrogen flash desorption peak with a maximum rate at 375 K and a shoulder at 450 K. All of the hydrogen desorbed before the sample temperature reached 500 K. No additional hydrogen desorbed upon heating from 500 to above 700 K. Figure 1 shows the flash desorption of H_2 following C_2H_4 adsorption at 300 (curve a) and 250 K (curve b). Also included in Figure 1 is the H_2 flash peak observed following H_2 adsorption at 275 K (curve c). As reported in the literature, the evolution of H_2 following room temperature C_2H_4 adsorption showed peaks at 360 and 400 K on Ni(111) (*1*) and at 365 and 390 K on Ni(100) (*2*), with all the H_2 desorbing below 525 K when the sample was flashed at 3 to 8 K/s. This agrees well with our results on Ni(110) and indicates that ethylene adsorbed at 500 K and above immediately decomposes into bound carbon and gaseous H_2.

The Auger spectrum of the Ni(110) surface observed following ethylene decomposition below 600 K was characteristic carbidic carbon. The presence of Auger peaks at 258 and 249 eV in the fine structure just below the strong 270-eV carbon KVV Auger transition was characteristic of a metal carbide surface layer (*3*). However the similarity of the carbidic AES fine structure to that of other metal carbides cannot be used as evidence that the C–C bond was broken. It is clear that the carbidic fine structure differs from the carbon AES fine structure of graphite and implies that metal valence electrons are involved in the carbon Auger de-excitation transi-

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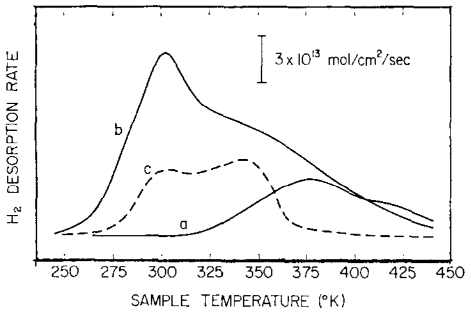

FIG. 1. H_2 flash desorption following C_2H_4 adsorption at (a) 300 and (b) 250 K and (c) H_2 Adsorption at 275 K on Ni(110).

tion. At 600 K or below further ethylene exposure did not increase the carbon Auger signal strength.

The carbide surface formed by cracking ethylene at 525 K exhibited a (2 × 1) LEED pattern. The half-order spacing in the [10] direction, i.e., the close-packed direction in the real lattice, indicated that the surface structure was periodic along the (110) furrows with twice the substrate lattice spacing. The (2 × 1) spots were intense, and the contrast was good, suggesting that the (2 × 1) carbide surface was well ordered, although the pattern was not as sharp as the clean (1 × 1) pattern. Previously, Ertl (*4*) reported (2 × 1) LEED patterns on Ni(110) following ethylene adsorption at room temperature and heating to 550 K. Pitkethly (*5*) also observed (2 × 1) patterns following acetylene adsorption and decomposition.

Furthermore, as observed previously, carbon deposited at temperatures above 650 K formed a surface layer of graphite over the Ni(110) substrate. The basal plane of graphite was found to be parallel to the nickel surface. Based on the diameter of the LEED rings relative to the dimensions of the (1 × 1) LEED spots of nickel substrate, the calculated graphite lattice spacing was 2.48 ± 0.06 Å. This result was in good agreement with the results of Ertl (*4*) (2.6 ± 0.07 Å) and Pitkethly (*5*) (2.46 Å) and with the lattice dimension of crystalline graphite (2.46 Å). Apparently, the carbon atoms formed bonds only within the graphite layer. This assumption seems reasonable since the AES fine structure of the "graphite" overlayer was in good agreement with published AES spectra of crystalline graphite (*6*).

The chemical inactivity of the graphitic surface for further ethylene decomposition, hydrogen adsorption (*7*), and decomposition of formic acid (*8*) indicated that the surface was blanketed by a layer of graphite. This graphite-"saturated" surface was typically produced by 500-Langmuir ethylene exposure at 700 K, although the carbon AES peak-to-peak height did not increase after 300-Langmuir exposure (*7*). Apparently, ethylene rapidly decomposed until the growing layer of carbon inhibited further decomposition into multiple layers of elemental carbon. In comparison with the clean and carbide surfaces, no more than 10% of this surface decomposed formic acid or adsorbed hydrogen. Based on this chemical evidence, we estimate that the

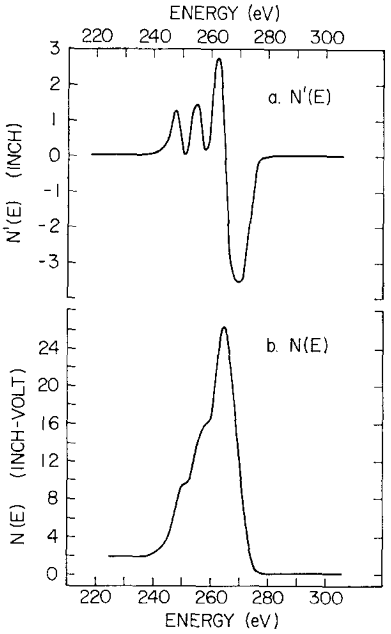

FIG. 2. Carbon AES for saturated (2 × 1)-C Ni(110). (a) $dN(E)/dE$, (b) $N(E)$.

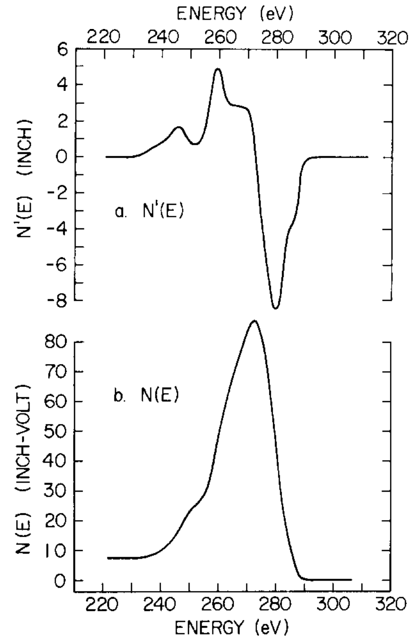

FIG. 3. Carbon AES for saturated graphitic Ni(110). (a) $dN(E)/dE$, (b) $N(E)/dE$.

carbon coverage of the graphite-"saturated" surface was $3.6 \pm 0.2 \times 10^{15}$ atoms/cm^2. For comparison, the carbon density in the basal plane of graphite is 3.82 atoms/cm^2.

The relative amount of surface carbon in the graphite-saturated surface and the (2 × 1) carbide layer was estimated from the relative intensities of the 270-eV carbon AES peak on the two surfaces. The intensity of the Auger current is commonly taken to be proportional to the peak-to-peak height of the derivative of the energy distribution, $dN(E)/dE$. However, this procedure is quantitatively correct only if the fine structure of the Auger peaks remains unchanged. The surface concentration is actually proportional to the double integral of $dN(E)/dE$ with respect to energy (*9*). In order to calculate the relative carbon coverages, the baselines of the carbon $dN(E)/dE$ Auger peaks were drawn so that a smooth secondary background curve was created between 200 and 320 eV, tangentially intercepting the AES spectra at these points. Integration of the $dN(E)/dE$ curve after subtracting the background yielded the $N(E)$ carbon AES curves for the graphite and (2 × 1)-C structures. Figures 2 and 3 show the $dN(E)/dE$ and $N(E)$ curves for the (2 × 1)-C and graphitic surfaces, respectively, after removing the curves $dN(E)/dE$ baseline. For both $N(E)$ distribution curves, a step increase in baseline is present at about 10% of the maximum in $N(E)$. The magnitude of the step increase was very sensitive to the choice of $dN(E)/dE$ baseline. Graphical integration under the $N(E)$ curves, i.e., double integration under the original Auger spectra, provided total carbon Auger current with approximately ±10% accuracy due to uncertainty in the $dN(E)/dE$ baseline. The double integral value for graphitic carbon was 4.0 ± 0.8 times the double integral of the carbide Auger spectrum. The peak-to-peak height ratio was 2.5 ± 0.5. The uncertainty was due primarily to the day-to-day reproducibility of the AES spectra of the saturated carbide and graphitic surfaces. Correspondingly, the coverage of the (2 × 1)-C and (4 × 5)-C structures was $9.4 \pm 2.5 \times 10^{14}$ atoms/cm^2, nearly a monolayer. This coverage was in apparent contradiction with the (2 × 1)-C LEED pattern. The unit cell of the two-dimensional lattice yielding the (2 × 1)-C pattern corresponds to twice the [10] Ni(110) (the close-packed) lattice spacing. Pitkethly (*5*) suggested that the (2 × 1)-C structure was formed by carbon atoms located in the (110) furrows with twice the Ni(110) close-packed spacing in the [10] direction. This structure gives 5.67×10^{14} atoms/cm^2 or half-monolayer coverage for the carbide layer.

Before continuing to a discussion of possible (2 × 1)-C structures with full monolayer carbon coverage, it is necessary to consider the possibility that some graphite patches were formed on the carbide-saturated surfaces. If only 10% of the sample surface area was covered by graphite and the remainder was covered by (2 × 1)-C with half-monolayer coverage density, the apparent carbon coverage would be 9×10^{14} atoms/cm², as observed. Stable carbide layers with (4 × 5)-C LEED patterns (*4, 5*) were produced at 575–600 K (*7, 8*), temperatures some 50–75 K higher than required for formation of the (2 × 1)-C layer. No difference in the fine structure or Auger current of the carbon AES curves was observed for the (4 × 5)-C and (2 × 1)-C surfaces, despite the difference in temperature of deposition. If graphite had, indeed, contributed 30–40% to the Auger current of the 525 K (2 × 1)-C surface, then one might expect that the (4 × 5) carbide layers formed at 60 K would be completely converted into the graphitic form. This was clearly not the case, although the formation of a small amount of graphite on the (4 × 5)-C surface at 600 K cannot be ruled out. We conclude that graphite formation did not contribute significantly to the calculated carbon coverage in the (2 × 1)-C structure.

Since the (2 × 1)-C surface corresponded to full monolayer coverage, the (2 × 1) lattice necessarily contained two carbon atoms per unit (2 × 1) cell. Also, since the ethylene striking the surface was completely dehydrogenated during deposition, either adsorbed C_2 species or dissociated carbon atoms may have formed. Single carbon atoms should prefer those sites where the most Ni–C bonds could be formed. Figure 2 shows two likely binding sites for C atoms on the (110) surface. It should be noted that carbon atoms in hexagonal close-packed bulk Ni_3C (*10*) are located at interstitial sites similar to the octahedral interstitial positions in face-centered cubic nickel. Full monolayer coverage with C atoms located over the octahedral sites, the A sites in Fig. 4, would have produced a (1 × 1) LEED pattern, and if every second A site along the furrow was occupied by a single carbon atom, then the (2 × 1) carbide layer would show half-monolayer coverage. Possibly, carbon atoms were alternately bound to tetrahedral sites, the B_1 and B_2 sites in Fig. 2. A (2 × 1) LEED pattern would then form a full monolayer coverage. It seems equally likely, however, that the strong carbon–carbon bond remained unbroken during deposition, and a bridging C_2 pair was adsorbed at (2 × 1) sites, as the dissociation energy of diatomic C_2 is 145 ± 5 kcal/mol (*11*).

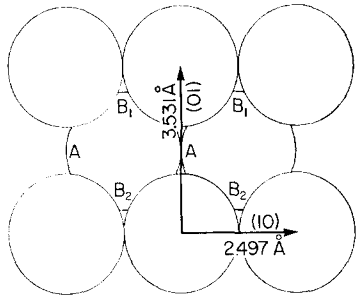

FIG. 4. Proposed carbide sites on Ni(110).

The open (110) nickel surface can accommodate a double-bonded C_2 pair. Two carbon atoms with an ordinary C–C bond length of 1.33 Å, when placed horizontally over B_1 and B_2 sites, form Ni–C bonds with a bond length of 1.67 Å when the two carbon atoms were placed in the plane of the (110) lattice points. The 1.67 Å bond length lies between 1.8 Å, the Ni–C bond length of Ni_3C, and 1.54 Å, the ordinary paraffinic C–C bond length. The (2 × 1) LEED pattern could be produced at full coverage if C_2 pairs occupied every other B_1 and B_2 site. Alternatively, we may visualize C_2 adsorbing vertically over every other A site (see Fig. 4). Bonding in this configuration is similar to that expected for CO adsorption in a (2 × 1) structure on Ni(110) (*12–14*). Recent angular resolved UPS studies on nickel (*15–18*) and other Group VIII transition metals (*17–20*) have produced strong evidence that adsorbed carbon monoxide is bonded with the C–O axis perpendicular to the metal surface.

Of the several UPS studies of ethylene adsorption on nickel reported in the literature, none has examined the transition from chemisorbed ethylene to a carbidic chemilayer. From a UPS study of ethylene and acetylene adsorption on Ni(111), Demuth and Eastman (*21*) concluded that chemisorbed C_2H_4 was dehydrogenated above 230 K into chemisorbed C_2H_2. The spectra of chemisorbed C_2H_2 on Ni(111) apparently was stable to 470 K, above which further dehydrogenation was noted. Page *et al.* (*22*) have presented some evidence for the decomposition of chemisorbed C_2H_4 at high coverages on polycrystalline nickel at room temperature. Page and Williams (*23*) have reported UPS results for ethylene decomposition on Ni(110) at 870 K. Ethylene decomposed at this temperature into a carbonaceous structure with UPS spectra closely related to the UPS spectra of vacuum-cleaned pyrolytic graphite.

Additional UPS studies of ethylene adsorption and decomposition on Ni(110) might confirm or disprove the existence of nondissociated C_2 pairs. Surface carbon could be deposited by decomposition of methane or by disproportionation of CO. One could compare the UPS spectra of "carbidic" layers formed by ethylene or acetylene and methane or CO to distinguish two forms of binding. A UPS study by Plummer *et al.* (*24*) has shown that the C–C bond of chemisorbed ethylene remained unbroken at 600 K on W(110), where complete dehydrogenation occurs. The C–C bonds finally were broken at 1500 K, forming a carbidic surface layer. A similar study on Ni(110) should prove interesting.

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